

Novel preparation method of bimetallic Ni-In alloy catalysts supported on amorphous alumina for the highly selective hydrogenation of furfural

by Maria Dewi Astuti .

Submission date: 14-Sep-2021 03:53PM (UTC+0700)

Submission ID: 1648150872

File name: 2018_Molecular_Catalysis_2018_445_52-60.pdf (1.57M)

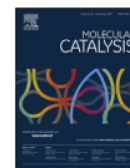
Word count: 7697

Character count: 37183



ELSEVIER

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Research Paper

Novel preparation method of bimetallic Ni-In alloy catalysts supported on amorphous alumina for the highly selective hydrogenation of furfural



Rodiansono^{a,*}, Maria Dewi Astuti^a, Dwi Rasy Mujiyanti^a, Uripto Trisno Santoso^a, Shogo Shimazu^{b,*}

^a Department of Chemistry, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru 70714, Indonesia

^b Graduate School of Engineering, Chiba University, 1-33 Yayoi, Inage, Chiba, 263-8522, Japan

ARTICLE INFO

11

Article history:

Received 11 July 2017

Received in revised form 31 October 2017

Accepted 2 November 2017

Keywords:

4 bimetallic Ni-In alloy catalyst

Selective hydrogenation

Biomass-derived furfural

Furfuryl alcohol

ABSTRACT

A novel preparation method for bimetallic nickel-indium alloy catalysts supported on amorphous alumina (Ni-In(x)/AA; x = Ni/In molar ratio) catalysts has been developed and evaluated for the highly selective hydrogenation of biomass-derived furfural. Ni-In(x)/AA catalysts were obtained via the hydrothermal treatment of Raney[®] nickel supported on aluminium hydroxide (R-Ni/AlOH) and an InCl₃·H₂O solution in an ethanol/H₂O mixture at 423 K for 2 h, followed by reduction with H₂ at 573–873 K for 1.5 h. The formation of Ni alloy phases such as Ni₃In₂, Ni₃In, Ni₂In, and NiIn in Ni-In(2.0)/AA was clearly observed after reduction with H₂ at 873 K for 1.5 h. In(2.0)/AA contained a Ni₂In alloy as the major phase, which exhibited the best catalytic performance for the selective hydrogenation of furfural into furfuryl alcohol and was stable for at least five consecutive reaction runs.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Biomass feedstock valorizations are currently being explored by using heterogeneous catalysts to produce bio-based platform chemicals, fuels, and various commodity products. Furfural (F) is one of the most promising biorefinery platform molecules because it can be transformed into a wide range of value-added derivative molecules, which can be used as plasticizers, pigments, agrochemicals, monomers in the production of resins (e.g., furfuryl alcohol (FA) and tetrahydrofurfuryl alcohol (THFA)) and gasoline blends (e.g., methyl furan (MF) or terminal diols (e.g., pentanediol (PD)) [1–3]. F could be produced effectively from C-5 sugars in hemicellulosic biomasses, such as xylan, arabinose and C-6 sugars in form of glucose or fructose via acidic hydrolysis [4–6].

Interactions between metals in bimetallic catalysts can modify their surfaces, which can be beneficial for the conversion and upgrading of highly complex biomass fractions [7–9]. Copper chromite was the first industrial bimetallic catalyst for the hydrogenation of F under harsh reaction conditions (473–573 K, 20–30 MPa) with maximum FA yields of ca. 70% [10]. In previ-

ously published studies, several bimetallic alloy transition metal catalysts (e.g., Ni-Sn [11–13], Ni-Fe [14,15], Ni-In [16], Cu [17], and Pt-Zn [18]) have shown superior performance for the selective hydrogenation of F compared with their single metal counterpart. Delbecq et al. have suggested that an increase in the charge density of Pt metals by the addition of hyperelectronic metals or the formation of a metal alloy could enhance the affinity towards the C=O bond rather than towards the C=C bond to form unsaturated alcohols in the hydrogenation of α,β -unsaturated aldehydes [19,20]. Moreover, unlike tin alloyed with Pt, the utilization of Ni-Sn alloy-based catalysts for the selective hydrogenation of unsaturated carbonyl compounds has been rarely investigated to date [21].

In our previous investigations, we have reported the synthesis of both bulk and supported bimetallic Ni-Sn alloy catalysts from two types nickel precursors: first, from nickel salt (e.g., NiCl₂ or NiCl₂·4H₂O) produced from both bulk and supported Ni-Sn alloys [11] and, second, from Raney[®] nickel supported on aluminium hydroxide (R-Ni/AlOH), which produced a nickel-tin alloy supported on aluminium hydroxide (Ni-Sn(x)/AlOH; x = Ni/Sn molar ratio) [12,13]. The catalysts showed high activity and selectivity during hydrogenation of F to FA [11–13], and the catalyst that consisted of the Ni₃Sn₂ alloy dispersed on TiO₂ allowed a remarkable reduction in the reaction temperature from 453 K to 383 K [11]. We have also recently reported the catalytic performance of the Ni-

* Corresponding authors.

E-mail addresses: rodiansono@unlam.ac.id (Rodiansono), shimazu@faculty.chiba-u.jp (S. Shimazu).

<https://doi.org/10.1016/j.mcat.2017.11.004>

2468–8231/© 2017 Elsevier B.V. All rights reserved.

Sn alloy during hydrogenation of biomass-derived levulinic acid in water to γ -valerolactone (GVL) [22,23]. Over bulk Ni-Sn alloy catalysts, a relatively high reaction temperature (433 K, 4.0 MPa H_2 , 6 h) was applied to achieve both a high conversion and GVL yield (99%) [22]. Alternatively, a GVL yield of >99% was obtained over Ni-Sn(x)/AlOH catalysts at a lower reaction temperature (393 K) compared to the bulk catalysts [23]. We found that the selectivity of Ni could be controlled precisely by changing the Ni/Sn ratio in a Ni-Sn alloy or of the dispersion of the Ni-Sn alloy on an appropriate support that might play a key role in chemoselectivity enhancement.

Herein, we report our extended investigation on a facile and novel preparation method for nanosized bimetallic nickel-indium alloy catalysts supported on amorphous alumina (denoted Ni-In(x)/AA; x is Ni/In molar ratio and AA is amorphous alumina). Ni-In(x)/AA catalysts were synthesized via a very similar synthetic procedure to Ni-Sn(x)/AlOH, which has been reported elsewhere [64]. The effects of the loading amount of In and thermal treatment on the activity and selectivity of Ni-In(x)/AA catalysts during the hydrogenation of furfural to furfuryl alcohol were studied systematically.

2. Experimental

2.1. Reagents

Raney Ni-Al alloy (50wt Ni and 50wt Al) was purchased from Kanto Chemical Co., Inc.). NaOH, $InCl_3 \cdot 4H_2O$ and $SnCl_2 \cdot 2H_2O$ were purchased from WAKO Chemical Industries, Ltd., and $GaCl_3$, $AgNO_3$, $NbCl_5$, and $ZrCl_4$ were purchased from Sigma-Aldrich, Co., and used as received. Furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, ethanol, and isopropanol were purchased from Tokyo Chemical Industries (TCI) Ltd. and purified using standard procedures prior to use.

2.2. Catalyst synthesis

2.2.1. Synthesis of R-Ni/AlOH

A typical procedure for the synthesis of the Raney nickel supported on aluminium hydroxide catalyst (denoted as R-Ni/AlOH) is described as follows [12,24]: Raney Ni-Al alloy powder (2.0 g) was slowly added to a dilute aqueous solution of NaOH (0.31 M, 16 mL) at room temperature. The temperature was raised to 363 K, and 4 mL of 3.1 M NaOH solution was subsequently added and stirred for 30 min. The mixture was then 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 the filtrate was neutralized and then stored in water. Finally, the catalyst was dried under vacuum prior to use.

2.2.2. Synthesis of Ni-In/AlOH

A typical procedure for the synthesis of the nickel-indium alloy supported on aluminium hydroxide (denoted as Ni-In(2.0)/AlOH, 2.0 is Ni/In molar ratio) consisted of first mixing R-Ni/AlOH at room temperature in an ethanol/ H_2O solution (~25 mL) that contained 4.5 mmol $InCl_3 \cdot 4H_2O$ and then stirring for 2 h. 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 and ethanol, and dried under vacuum overnight. The Ni-In(x)/AlOH samples were reduced by hydrogen (H_2) at 673 K for 1.5 h, which produced Ni-In(x)/AA, where AA is amorphous alumina. The Ni-In(2.0)/AlOH sample was reduced by hydrogen (H_2) at 573–873 K for 1.5 h in order to investigate the effect of temperature reduction on the formation of the Ni-In alloy in Ni-In(2.0)/AA.

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 then 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 the H_2 uptake was calculated according to a method described in the literature [26,27].

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were recorded on a Mac Science M18XHF instrument using monochromatic $CuK\alpha$ radiation ($\lambda = 0.15418$ nm). The XRD equipment operated at 40 kV and 200 mA with a step width of 0.02° and a scan speed of 4° min^{-1} ($2\theta = 0.154057$ nm, $\alpha_2 = 0.154433$ nm). Inductively coupled plasma (ICP) 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 measurements. The amount of nitrogen adsorbed on 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 [25]. SEM images of the synthesized catalysts were taken on a JEOL JSM-610 microscope after the samples were coated using a JEOL JTC-1600 autofine coater. TEM images were recorded on a JEOL JEM1400 microscope. Raman spectra were collected on a JASCO NRS-2100 laser-Raman spectrophotometer with an Ar beam lamp at excitations of 488 nm and 514.5 nm.

2.4. Typical procedure for the selective hydrogenation of furfural

The catalyst (50 mg), furfural (1.1 mmol), and isopropanol (3 mL) as the solvent were placed into a glass reaction tube, which fit inside a stainless steel reactor. After H_2 was introduced into the reactor at an initial H_2 pressure of 3.0 MPa at room temperature, the temperature of the reactor was increased to 383–453 K. After 75 min, the conversion of furfural (F) and the yields of furfuryl alcohol (FA) and tetrahydrofurfuryl alcohol (THFA) were determined using GC analysis. The used Ni-In(2.0)/AA 773 K/ H_2 catalyst was easily separated using either simple centrifugation (4000 rpm for 10 min) or filtration, then finally dried overnight under vacuum at room temperature prior to re-usability testing.

2.5. Product analysis

GC analysis of the reactant (F) and products (FA and THFA) was performed on a Shimadzu GC-8A with a flame ionization detector equipped with a silicone OV-101 packed column (length (m) = 3.0; inner diameter (mm) = 2.0; methylsilicone from Sigma-Aldrich Co. Ltd.). Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and an RT- β DEXsm capillary column. 1H and ^{13}C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; the samples for NMR analysis were dissolved in chloroform- d_1 with TMS as the internal standard. The products were confirmed by a comparison of their GC retention time, mass, 1H and ^{13}C NMR spectra with those of authentic samples.

The conversion of furfural, yield, and selectivity of the products were calculated according to the following equations:

$$\text{Conversion} = \frac{\text{introduced mol reactant}(F_0) - \text{remained mol reactant}(F_1)}{\text{introduced mol reactant}(F_0)} \times 100\%$$

$$\text{Yield} : \frac{\text{mol product}}{\text{consumed mol reactant} (\Delta F)} \times 100\%$$

$$\text{Selectivity} : \frac{\text{mol product}}{\text{total mol products}} \times 100\%$$

where F_0 is the introduced mol reactant (furfural, F), F_t is the remaining mol reactant, and ΔF is the consumed mol reactant (introduced mol reactant- remained mol reactant), which are all obtained from GC analysis using an internal standard technique.

31

3. Results and discussion

3.1. Catalyst characterization

A series of bimetallic alloys (Ni-In(x)/AA, [3] Ni/In molar ratio) prepared via hydrothermal treatment of a mixture of Raney® nickel supported on aluminium hydroxide (R-Ni/AlOH) [12,24] and $\text{InCl}_2 \cdot \text{H}_2\text{O}$ solution in ethanol/ H_2O at 423 K for 2 h, produced the *as-prepared* Ni-In(x)/AlOH. After reduction of the *as-prepared* Ni-In(x)/AlOH with H_2 treatment at 573–873 K for 1.5 h, Ni-In(x)/AA, $x = \text{Ni/In}$ molar ratio and AA = amorphous alumina were produced. The physicochemical properties of the synthesized Ni-In(x)/AA catalysts are summarized in Table 1.

Based on the ICP-AES results, the loading amounts of In were 1.4, 2.3, 4.5, 6.2, and 9.4 mmol g^{-1} , which was reflected by the Ni/In molar ratios of 5.1, 3.1, 2.0, 1.1, and 0.8, respectively. The results also indicate that S_{BET} increased gradually, while the H_2 uptake decreased with an increase in the loading amount of In. The S_{BET} values of the Ni-In(x)/AA samples were higher than those of the *as-prepared* samples (Ni-In(x)/AlOH) because of thermal treatment or the formation of amorphous alumina. In the Ni-In(2.0)/AA sample, the H_2 uptake was 75 $\mu\text{mol g}^{-1}$ (entry 4), which is comparable to the previous results of the H_2 uptake of Ni-Sn(1.4)/AlOH [12]. An increase in the loading amount of In reduced the surface activity of Ni, as also indicated by the H_2 uptake in samples with Ni/In ratios of 1.1–0.8 (entries 5–7) and bulk Ni-In(2.0) (entry 8).

51

The average crystallite sizes of the Ni(111) species or bimetallic Ni-In before and after H_2 treatment were calculated by using the Scherrer equation using the diffraction peak at $2\theta = 44.4^\circ$ and the results are also summarized in Table 1. The findings indicate that the average crystallite sizes of Ni(111) or bimetallic Ni-In are larger than that of the *as-prepared* sample due to thermal treatment under hydrogen atmosphere. Compared with the bulk Ni-In(2.0) catalyst with average crystallite sizes of bimetallic Ni-In of 39.8 nm (entry 8), the crystallite sizes in Ni-In(x)/AA catalysts are much smaller. The crystallite sizes of Ni or the Ni-In alloy in Ni-In(x)/AA are also consistent with the H_2 uptake. These results suggest that the dispersion of active metal on amorphous alumina may influence the catalytic activity.

The XRD patterns of R-Ni/AlOH and the *as-prepared* Ni-In(x)/AlOH with different Ni/In molar ratios are shown in Fig. 1. R-Ni/AlOH showed sharp diffraction peaks at $2\theta = 44.3^\circ$, 51.5° , and 76.3° , which correspond to the Ni(111), Ni(200), and Ni(220) species, respectively (Fig. 1a). Sharp diffraction peaks were also observed at $2\theta = 18.3^\circ$, 27.8° , and 40.5° , which represent bayerite, and at $2\theta = 18.7^\circ$, 20.4° , 36.7° , 37.8° , 53.2° , 63.9° , and 70.7° , which correspond to gibbsite (Fig. 1a–f). In contrast, the XRD patterns of the *as-prepared* Ni-In(x)/AlOH exhibited broadened peaks at $2\theta = 44.4^\circ$ due to the formation of bimetallic Ni-In, i.e., Ni_2In and Ni_3In_2 (Fig. 1b–f). The formation of bimetallic Ni_2In_3 (#JCPDS-36-1147) at $2\theta = 31.9^\circ$ and indium oxides such as In_2O_3 (#JCPDS-06-416) at $2\theta = 22.4^\circ$, 39.4° , 51.0° , and 57.6° were also observed (Figure d–f) [24,28].

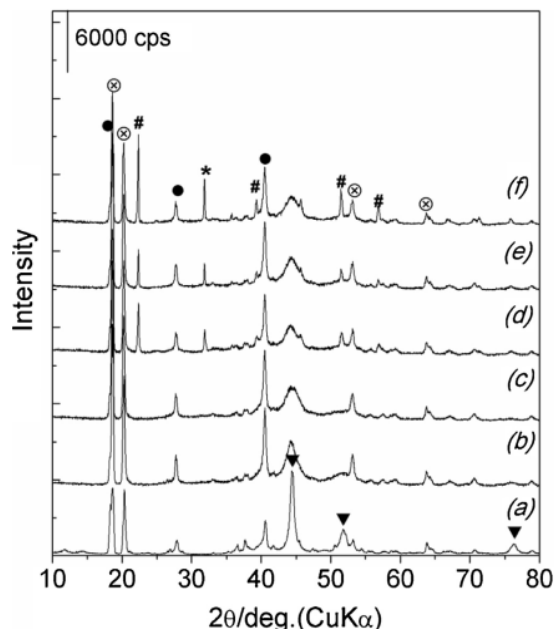


Fig. 1. XRD patterns of (a) R-Ni/AlOH and the *as-prepared* Ni-In(x)/AlOH ($x = \text{Ni/In}$ molar ratio) at different Ni/In molar ratios of (b) 5.1, (c) 3.1, (d) 2.0, (e) 1.1, and (f) 0.8. (●) bayerite; (⊙) gibbsite; (#) In(OH)_3 ; (▼) Ni(O) ; (*) Ni_2In_3 .

59

To confirm the formation of the bimetallic Ni-In alloy, the *as-prepared* Ni-In(x)/AlOH samples were reduced with H_2 at 673 K for 1.5 h and resulted in the bimetallic Ni-In alloy supported on amorphous alumina (denoted as Ni-In(x)/AA) and the XRD patterns are shown in Fig. 2.

The results indicate that controlled thermal treatment under H_2 transformed the remaining aluminium hydroxides (both bayerite and gibbsite phases) into amorphous alumina, which were not detectable using XRD analysis. The diffraction peak at $2\theta = 44.4^\circ$ that is recognized as an identical peak of the Ni(111) species became broadened and overlapped with the bimetallic Ni-In alloy phases with an increase in the loading amount of In (Fig. 2a–e). A shoulder peak at $2\theta = 43.2^\circ$ was also observed for a Ni/In ratio of 0.8 (where the amount of Ni \gg In) that can be attributed to the formation of the bimetallic Ni_3In species (#JCPDS-21-404) (Fig. 2e). Additionally, the broadened peak of the Ni(111) species both in the *as-prepared* and H_2 -treated samples suggest the formation of a bimetallic Ni-In alloy that might have selectively occurred on the surface of Ni(111) rather than on the surface of Ni(200) or Ni(220) [29–31].

The low-frequency Raman spectrum of the *as-prepared* Ni-In(2.0)/AlOH resembles Ni-Sn(1.4)/AlOH, as has been previously reported [23]. It is found that the low-frequency Raman spectrum showed a 530 cm^{-1} band, which can be attributed to the $\gamma(\text{OH})$ vibrational mode and Al-O-Al deformation, whereas the 315 cm^{-1} band is ascribed to Al-O-Al stretching vibrations of gibbsite or bayerite (Fig. 3). Alternatively, the bands of Al-O-Al deformation and Al-O-Al stretching vibrations disappeared after H_2 treatment at 673 K for 1.5 h (Fig. 3b) due to the formation of amorphous alumina [32–34], which had been not detected by XRD [12,13]. Scanning electron microscopy (SEM) images, EDS spectra and TEM images of both Ni-In(3,1)/AA and Ni-In(2.0)/AA are shown in Figs. S1, S2, and S3 (see ESI), respectively.

Table 1
Physicochemical properties of the synthesized bimetallic Ni–In alloy catalysts supported on amorphous alumina (Ni–In(*x*)/AA, *x* = Ni/In molar ratio).

Entry	Catalysts ^a	Ni ^a	In ^a	H ₂ uptake ^b /	S _{BET} ^c /	D ^d /nm
		(mmol ⁻¹)	(mmol ⁻¹)	μmol g ⁻¹	m ² g ⁻¹	
1	Raney Ni	4.0	0	121	70	8.6
2	R-Ni/AlOH	3.5	0	104	150	9.0
3	Ni–In(5.1)/AA	7.1	1.4	84	128(101)	8.0(5.2)
4	Ni–In(3.1)/AA	7.2	2.3	71	120(90)	7.0(3.8)
5	Ni–In(2.0)/AA	8.8	4.5	75	154(98)	3.8(2.9)
6	Ni–In(1.1)/AA	7.0	6.2	76	161(75)	6.6(3.9)
7	Ni–In(0.8)/AA	7.2	9.4	48	157(72)	5.2(3.4)
8 ^e	Bulk Ni–In(2.0)	4.1	2.0	29	43	39.8

^a Values between parentheses are the Ni/In molar ratios determined by ICP-AES.

^b Based upon the total H₂ uptake at 273 K (after corrections for physical and chemical adsorption).

^c Specific surface area of BET (S_{BET}) of samples after H₂ treatment at 673 K for 1.5 h, determined by N₂ adsorption at 77 K; values between parentheses are the S_{BET} values of the as-prepared samples.

^d Average Ni(111) or Ni–In crystallite sizes were calculated according to the Scherrer equation; values between parentheses are the crystallite sizes of Ni(111) or Ni–In of the as-prepared catalysts.

^e Bulk Ni–In(2.0) catalysts were synthesized via the hydrothermal treatment of a mixture of NiCl₂ and InCl₃·4H₂O solutions at 423 K for 24 h, followed by H₂ treatment at 673 K for 1.5 h.

3.2. Catalytic reactions: furfural hydrogenation

3.2.1. Selection of the second metals

At the first stage, the catalytic performances of various transition metal modified-R-Ni/AlOH such as Sn, In, Ga, Ag, Nb, and Zr, were first evaluated by the selective hydrogenation of the typical unsaturated aldehyde furfural (F) to furfuryl alcohol (FA), which is a promising chemical intermediate for the synthesis of biosourced products widely used in polymer industry. Conventional Raney nickel (Raney Ni) and Raney nickel supported on aluminium hydroxide (R-Ni/AlOH) catalysts were also synthesized and evaluated using the same reaction conditions as catalyst references. The detailed information for these catalysts is summarized in Table S1 in the ESI. The XRD patterns of as-prepared R-Ni/AlOH are shown in Fig. S4 in the ESI. The results of the catalytic hydrogenation of F are summarized in Table 2, and the reaction pathways are shown in Scheme 1.

Conventional Raney Ni exhibited a 99.6% conversion of F and FA and THFA yields of 48% and 51%, respectively (entry 1). As expected, by using the R-Ni/AlOH catalyst, F converted completely to produce a 99% yield of THFA (entry 2). Interestingly, the addition of Sn or In shifted the product selectivity to FA with yields of 91% and 40%, respectively (entries 3 and 4). In tin-alloyed Ni-based (Ni–Sn) catalysts, the catalytic performances have been reported previously [11–13,22,23]. Alternatively, the presence of Ga, Ag, and Nb significantly reduced the activity of R-Ni/AlOH (entries 5, 6, and 7), while Zr did not affect the activity or selectivity of the former catalyst (entry 8). Therefore, in the present report, we focused on catalytic performance studies of indium-alloyed Ni catalysts on F hydrogenation including the effect of loading amount, H₂ treatment, time profiles, and catalyst reusability.

3.2.2. Effect of In loading amount

The results for the selective hydrogenation of F using the as-prepared supported bimetallic Ni–In(*x*)/AlOH catalysts are summarized in Table 3.

It can be observed that after introducing 1.4 mmol InCl₃·4H₂O to R-Ni/AlOH, the conversion of F drastically decreased to 47% and yielded 40% FA (entry 1). By increasing the loading amount of In to 9.4 mmol g⁻¹, the FA yield was almost constant (entries 7 and 8, 51% and 39%, respectively). The prolonged reaction time of 180 min over Ni–In(2.0)/AlOH produced a marked increase in the FA yield from 55% to 92% (entries 3 and 4, respectively). In contrast, the yield of tetrahydrofurfuryl alcohol (THFA) decreased to 4% (entry 4). The FA yield decreased when initial H₂ pressure of 2.0 MPa was applied (entry 5, 40%). The F conversion and FA yield drastically

decreased without the presence of H₂ (entry 6). The R-Ni–In/SiO₂ catalyst (loading amount of In, 2.7 mmol g⁻¹) produced a 43% conversion and a 39% yield of FA (entry 9). Moreover, the In/AlOH, In₂O₃, and InCl₃·4H₂O catalysts (entries 10–12) and the absence of a catalyst (entry 13) did not produce hydrogenated products of F under the same conditions. In addition, screening tests using solvents (e.g., methanol, ethanol, toluene, 1-propanol, and H₂O) other than isopropanol (*iso*-PrOH) were also performed, and the results were inferior to the results with *iso*-PrOH, as reported previously [35].

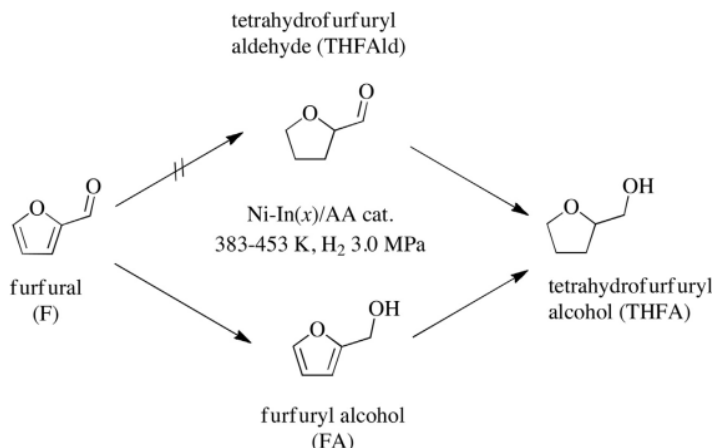
The H₂ treatment of as-prepared Ni–In(*x*)/AlOH at 673 K for 1.5 h resulted in Ni–In(*x*)/AA catalysts (the XRD patterns are shown in Fig. 2). The catalysts were evaluated for the catalytic hydrogenation of biomass-derived furfural to furfuryl alcohol, and the results are summarized in Table 4. Interestingly, over H₂-treated Ni–In(*x*)/AA catalysts, the high conversion of F was achieved and produced a high yield of FA (entries 1–6). In Ni–In(2.0)/AA, F was converted completely into almost a 100% yield of FA. The high yield of FA without the formation of THFA, even though the reaction time was prolonged to 360 min (entry 4), obviously indicated the important role of In in the Ni–In alloy catalyst system. Additionally, over the indium-modified Raney Ni supported on silica (R-Ni–In/SiO₂ 673 K/H₂) catalyst, the conversion of F was 96% with yield of FA that was much lower than that of Ni–In(2.0)/AA under the same reaction conditions (entry 7). The XRD patterns of this catalyst are shown in Fig. S5 in the ESI, and the physicochemical properties are summarized in Table S1 in the ESI. Moreover, by using the bulk Ni–In(2.0) catalyst (XRD patterns are shown in Fig. S6 in the ESI), the conversion of F was only 42% under the same reaction conditions (entry 8).

3.2.3. Effect of thermal treatment on Ni–In(2.0)/AlOH catalysts

Among the synthesized Ni–In(*x*)/AA catalysts, Ni–In(2.0)/AA demonstrated a very high activity and selectivity towards the desired product of FA. Therefore, we investigated the effect of temperature during hydrogen treatment on Ni–In(2.0)/AA at 573–873 K for 1.5 h, and the XRD patterns are shown in Fig. 4. After H₂ treatment at 573 K, the diffraction peaks of the aluminium hydroxides (e.g., bayerite and gibbsite) totally disappeared, and the broadened peaks at 2θ = 42–44.5° were hardly distinguished due to the overlap of the bimetallic alloy Ni–In phases and Ni metal diffraction peaks. Peak formation of NiIn (PDF#07-0178) at 2θ = 30.2° and the remaining In₂O₃ at 2θ = 22.3° and 31.9° was clearly observed (Fig. 4a–b). The increase in temperature from 673 K to 873 K transformed the NiIn alloy species to Ni₂In (PDF #65-3486), Ni₃In (PDF#65-3522)

Table 2Results of the catalytic hydrogenation of biomass-derived furfural over the various *as-prepared* bimetallic Ni-M/AlOH catalysts (M = Sn, In, Ga, Ag, Nb, and Zr).

Entry	Catalyst	M ^a /mmolg ⁻¹	Conversion ^b /%	Yield ^b /%	
				FA	THFA
1	Raney Ni	–	99	48	51
2	R-Ni/AlOH	–	>99	1	99
3	Ni-Sn/AlOH	1.0	95.0	91	3
4	Ni-In/AlOH	1.4	47.0	40	7
5	Ni-Ga/AlOH	1.1	12.8	0	0
6	Ni-Ag/AlOH	1.2	44.9	7	16
7	Ni-Nb/AlOH	1.2	47.3	6	17
8	Ni-Zr/AlOH	1.1	>99	0	96

Reaction conditions: catalyst (50 mg), F (1.1 mmol), iso-PrOH (3 mL), H₂ (3.0 MPa), 453 K, 75 min.^a Loading amount of In was determined by ICP-AES.

74

Scheme 1. Reaction pathways of furfural hydrogenation over bimetallic Ni-In catalysts.**Table 3**Results of the catalytic hydrogenation of biomass-derived furfural over *as prepared* bimetallic Ni-In(x)/AlOH catalysts with various loading amounts of indium (In).

Entry	Catalyst ^a	In ^b /mmolg ⁻¹	Conversion ^c /%	Yield ^c /%	
				FA	THFA
1	Ni-In(5.1)/AlOH	1.4	47	40	7
2	Ni-In(3.1)/AlOH	2.3	53	47	6
3	Ni-In(2.0)/AlOH	4.5	61	55	6
4 ^d	Ni-In(2.0)/AlOH	4.5	96	92	4
5 ^e	Ni-In(2.0)/AlOH	4.5	45	40	5
6 ^f	Ni-In(2.0)/AlOH	4.5	17	5	2
7	Ni-In(1.1)/AlOH	6.2	59	51	8
8	Ni-In(0.8)/AlOH	9.4	42	39	3
9 ^g	R-Ni-In/SiO ₂	2.7	43	39	4
10	In/AlOH	4.5	28	0	0
11	In ₂ O ₃	–	28	6	3
12	InCl ₃ ·4H ₂ O	–	52	3	1
13	Neat (no catalyst)	–	15	0	0

^a Values between parentheses are the Ni/In molar ratio. Reaction conditions: catalyst (50 mg), F (1.1 mmol), iso-PrOH (3 mL), H₂ (3.0 MPa), 453 K, 75 min.^b Loading amount of In was determined by ICP-AES.^c Conversion and yield were determined by GC analysis using an internal standard.^d Reaction time was 180 min.^e Initial pressure of H₂ was 2.0 MPa.^f Reaction occurred in the absence of H₂.^g Precursor of nickel was Raney Ni and supported on SiO₂.

and Ni₂In₃ (PDF # 65–3486) alloy phases (Fig. 4c–e), and the peaks became intensified at a temperature of 873 K (Fig. 4e).

The results of the catalytic hydrogenation of F to FA and THFA over Ni-In(2.0)/AA treated with H₂ at different temperature treatments are summarized in Table 5. For Ni-In(2.0)/AA catalysts at 573 K (entry 1) and 673 K (entry 2), a small amount of THFA prod-

uct was obtained over those catalysts (5% and 1% yield of THFA, respectively). The best catalytic performance was achieved over Ni-In(2.0)/AA 773 K (entry 3) and Ni-In(2.0)/AA 873 K (entry 4). We also intentionally carried out the hydrogenation reaction of FA as substrate over Ni-In(2.0)/AA 773 K under the same reaction conditions, and only 5.2% of FA was converted into THFA with a yield of

Table 4
Results of the catalytic hydrogenation of biomass-derived furfural over bimetallic Ni-In(x)/AA catalysts after H₂ treatment at 673 K for 1.5 h.

Entry	Catalyst ^a	In ^b /mmol ^g -1	Conversion ^c /%	Yield ^d /%	
				FA	THFA
1	Ni-In(5.1)/AA	1.4	98	94	4
2	Ni-In(3.1)/AA	2.3	97	95	2
3	Ni-In(2.0)/AA	4.5	>99	100	0
4 ^d	Ni-In(2.0)/AA	4.5	>99	99	1
5	Ni-In(1.1)/AA	6.2	99	96	3
6	Ni-In(0.8)/AA	9.4	97	93	4
7	RNi-In/SiO ₂	2.7	96	87	9
8 ^e	Bulk Ni-In(2.0)	2.0	42	42	0

^a Values between parentheses are the Ni/In molar ratio. Reaction conditions: catalyst (50 mg), F (1.1 mmol), iso-PrOH (3 mL), H₂ (3.0 MPa), 453 K, 75 min.

^b Loading amount of In was determined by ICP-AES.

^c Conversion and yield were determined by GC analysis using an internal standard.

^d Reaction time was 360 min.

^e Bulk Ni-In(2.0) catalyst was synthesized via hydrothermal treatment of NiCl₂ and InCl₃·4H₂O in an ethanol/H₂O mixture at 423 K for 2 h, subsequently followed by reduction with H₂ at 673 K for 1.5 h. The XRD patterns of the as-prepared and H₂-treated bulk Ni-In(2.0) samples are shown in Fig. S6 in the ESI.

Table 5
Results of furfural hydrogenation over various Ni-In(2.0)/AA catalysts after H₂ treatment at various temperature of 573–873 K for 1.5 h.

Entry	Catalyst	Temp. H ₂ treatment/K	Conversion ^a /%	Yield ^b /%	
				FA	THFA
1	Ni-In(2.0)/AA	573	>99	95.0	5.0
2	Ni-In(2.0)/AA	673	>99	99.0	1.0
3	Ni-In(2.0)/AA	773	>99	99.9	0
4	Ni-In(2.0)/AA	873	>99	99.9	0
5 ^b	Ni-In(2.0)/AA	773	5	–	5.0

^a Reaction conditions: catalyst (50 mg), furfural (1.1 mmol), iso-PrOH (3 mL), H₂ 3.0 MPa, 453 K, 75 min.

^b Conversion and yield were determined by GC analysis using an internal standard.

^c Furfuryl alcohol (FA) was the substrate, and reaction time was 180 min.

5%, even after the reaction time was prolonged to 180 min (entry 5). These results suggest that the addition of 38 μm to R-Ni/AIOH to form the bimetallic Ni-In alloy retards the C=C hydrogenation activity of nickel, and as a result, further hydrogenation of the C=C furan ring in F did not proceed in the presence of the Ni-In(2.0)/AA catalyst.

3.2.4. Effect of temperature

The effect of temperature on the catalytic hydrogenation of F to FA was evaluated over both Ni-In(2.0)/AA 773 K/H₂ and bulk Ni-In(2.0) catalysts, and the results are shown in Fig. 5. Differences in the activity of each catalyst were clearly observed. On the bulk Ni-In(2.0) catalyst, the conversion of F gradually increased as temperature increased, and the highest conversion of F (~76%) was achieved at 453 K at the current reaction conditions. In contrast, F was converted completely at 443 K over the Ni-In(2.0)/AA 773 K/H₂ catalyst. These results are very similar to the bimetallic Ni-Sn alloy catalyst system, in which bulk Ni-Sn catalysts have much lower activity and reactivity during F hydrogenation compared with the supported Ni-Sn catalysts, as reported previously [11].

3.2.5. Effect of initial H₂ pressure

The effect of the initial H₂ pressure on F conversion and product selectivity was evaluated over the Ni-In(2.0)/AA 773 K/H₂ catalyst, and the results are shown in Fig. 6. F conversion and FA selectivity gradually increased as the initial H₂ pressure increased, whereas the THFA selectivity decreased smoothly to almost 0% between 2.5 and 3.0 MPa and then gradually increased between 3.5–4.0 MPa.

3.2.6. Kinetics

The kinetics of F hydrogenation at 453 K on the bulk and supported Ni-In(2.0)/AA 773 K/H₂ alloy catalysts are shown in Fig. 7. When the bulk Ni-In(2.0) catalyst was used, FA was slowly

Table 6

Results of the re-usability tests for the Ni-In(2.0)/AA 773 K/H₂ catalyst in the selective hydrogenation of furfural.

Run ^a	1	2	3	4	5
Conversion (%)	>99	95	93	91	91
Selectivity ^b (%)	100	99	99	99	99

Reaction conditions: F, 1.1 mmol (F/Ni ratio = 15); iso-PrOH (3 mL); H₂, 3.0 MPa, 453 K, 75 min.

^a The recovered catalyst was used without any further treatment.

^b Selectivity to FA was determined by GC analysis using an internal standard technique.

increased to achieve a 75% yield, even after 180 min. Therefore, a similar explanation can be applied to the current results as follows. The induction periods could be associated with the slow formation of oxidic tin (Sn^{ox}) from metallic tin (Sn⁰), as reported by Sordelli et al. (Rh-Sn) [36] and Margitfalvi et al. (Pt-Sn) [37]. Since the crystallite size or dispersion of Ni-In alloy could affect the length of the induction period, the induction period of Ni-In(2.0)/AA diminished, and a 100% F conversion (>99% FA yield) was achieved after 75 min. The excellent catalytic performance of Ni-In(2.0)/AA produces a promising candidate suitable for the large-scale production of FA from the selective hydrogenation of furfural (F).

3.2.7. Re-usability test

A re-usability test was performed on the Ni-In(2.0)/AA 773 K/H₂ catalyst, and the results are summarized in Table 6.

The used Ni-In(2.0)/AA catalyst was easily separated by either simple centrifugation or filtration after the reaction. The activity of the catalyst slightly decreased, while a high selectivity was maintained for at least five consecutive runs. The amount of Ni and In that leached into the reaction solution was 0.7% and 1.4%, respectively, after four runs. The small amount of leached metal is consistent with the XRD patterns of the recovered Ni-In(2.0)/AA 773 K/H₂ cata-

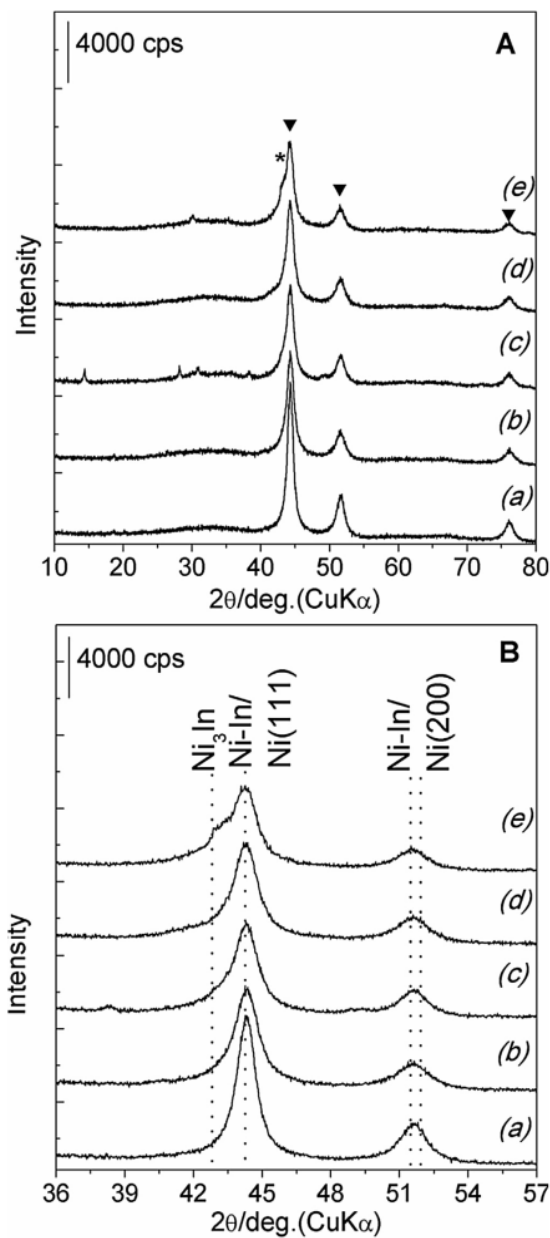


Fig. 2. XRD patterns of the H₂-treated Ni-In(x)/AA at a temperature of 673 K for 1.5 h and selected area at $2\theta = 40\text{--}50^\circ$ for (a) 5.1, (b) 3.1, (c) 2.0, (d) 1.1, and (e) 0.8: (∇) Ni(0); (*) bimetallic Ni₃In (#)CPDS-21-404).

lyst, and no obvious phase separation or agglomeration of the Ni₂In nanoparticles was observed in the used Ni-In(2.0)/AA 773 K/H₂ catalysts, as indicated by the XRD patterns (Fig. S7 in the ESI).

4. Conclusions

A novel preparation method for bimetallic nickel-indium alloy catalysts supported on amorphous alumina (Ni-In(x)/AA; x = Ni/In molar ratio) catalysts has been developed and evaluated for the

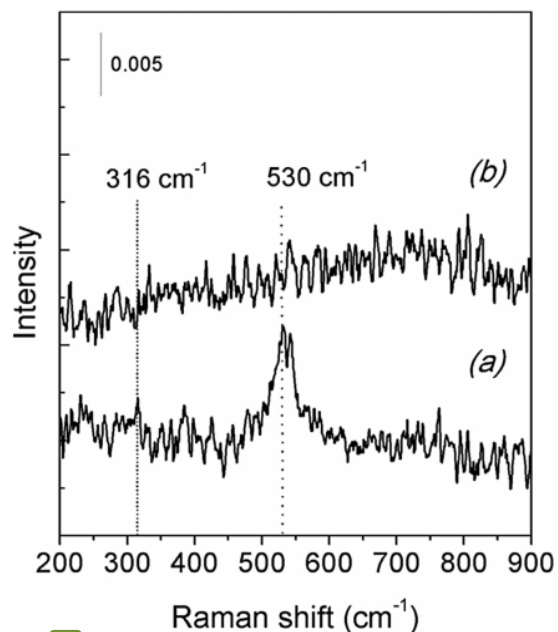


Fig. 3. Raman spectra of (a) the as-prepared Ni-In(2.0)/AlOH and (b) after H₂ treatment at 673 K for 1.5 h (Ni-In(2.0)/AA).

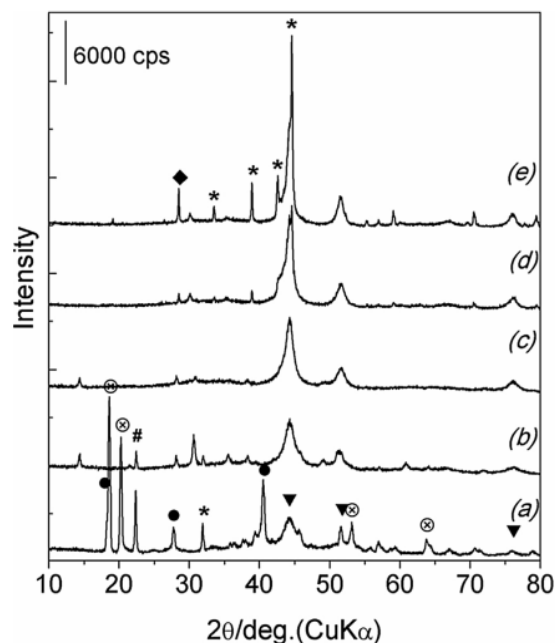
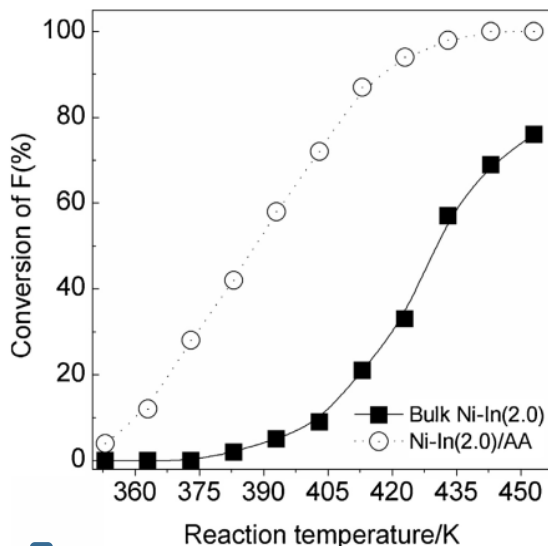
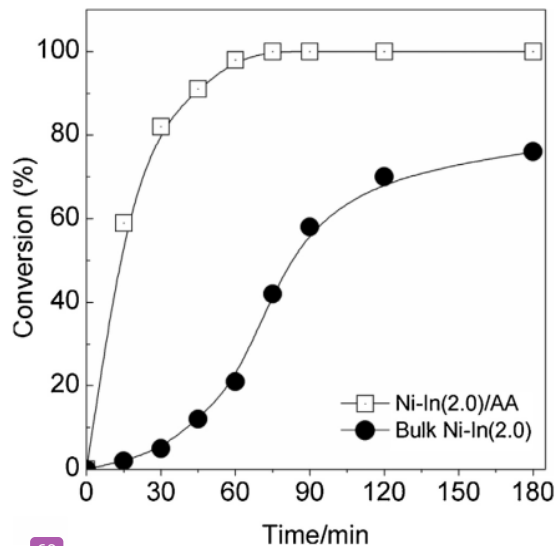


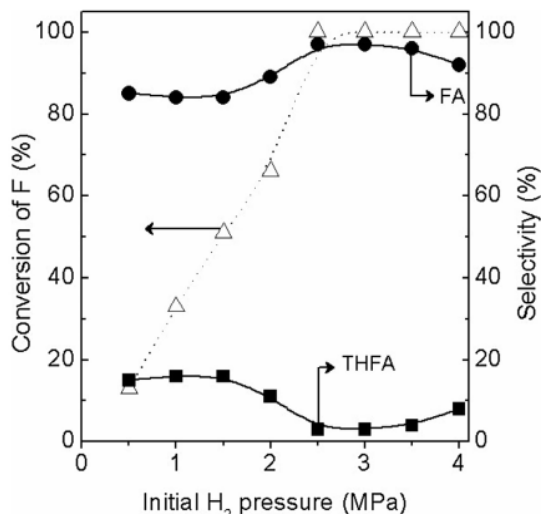
Fig. 4. XRD patterns of (a) as-prepared Ni-In(2.0)/AlOH and H₂ treated (Ni-In(2.0)/AA) at different temperatures of (b) 573, (c) 673, (d) 773, and (e) 873 K for 1.5 h. (●) bayerite; (◻) gibbsite; (#) In(OH)₃; (∇) Ni(0); (*) Ni₃In (#)CPDS-21-404; (◆) Ni₂In₃ (#)CPDS-65-3486).



8 Fig. 5. Effect of reaction temperature on the conversion of furfural (F) over the bulk and supported Ni-In(2.0)/AA 773 K/H₂ alloy catalysts. Reaction conditions: catalyst, 50 mg; F, 1.1 mmol; iso-PrOH, 3 mL; H₂, 3.0 MPa, 75 min.



69 Fig. 7. Kinetics of the hydrogenation of furfural (F) over bimetallic bulk Ni-In(2.0) and Ni-In(2.0)/AA catalysts. Reaction conditions: catalyst, 50 mg; F, 1.1 mmol; iso-PrOH, 3 mL; H₂, 3.0 MPa, 453 K.



41 Fig. 6. Effect of the initial H₂ pressure on the conversion and selectivity in the hydrogenation of furfural (F) over the Ni-In(2.0)/AA 773 K/H₂ alloy catalyst. Reaction conditions: catalyst, 50 mg; F, 1.1 mmol; iso-PrOH, 3 mL; 453 K, 75 min.

highly selective hydrogenation of biomass-derived furfural. The formation of Ni-In alloy phases such as Ni₃In₂, Ni₃In, and Ni₂In in Ni-In(2.0)/AA was clearly observed after H₂ treatment at 873 K for 1.5 h. Ni-Sn(2.0)/AA contained a Ni₂In alloy as the major phase, which exhibited the best catalytic performance for the selective hydrogenation of furfural to furfuryl alcohol exclusively and was stable for at least five consecutive reaction runs.

52 Acknowledgements

This work was financially supported by JSPS-DGHE through the Joint Bilateral Research Project FY 2014–2017, KLN and the Inter-

national Publication Project of DGHE FY 2016 under Grant Number of DIPA-023-04.1.673453/2016, Insentif Riset Nasional (Insinas) FY 2016–2017, and IPTEKS Project FY 2016, Ministry of Research, Technology & Higher Education, Republic of Indonesia.

13 Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.mcat.2017.11.004>.

References

- [1] J. Falbe, H. Bahrmann, W. Lipps, D. Meyer, *Ullmanns Encyclopedia of Industrial Chemistry*, 11, Wiley-VCH Verlag GmbH & Co., 2005, pp. 21.
- [2] J.P. Lange, E. van der Heide, J. van Buijtenen, R. Price, Furfural a promising platform for lignocellulosic biofuels, *ChemSusChem* 5 (2012) 150–166, <http://dx.doi.org/10.1002/cssc.201100648>.
- [3] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M.L. Granados, Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels, *Energy Environ. Sci.* 9 (2016) 1144–1189, <http://dx.doi.org/10.1039/C5EE02666K>.
- [4] P. Gallezot, Conversion of biomass to selected chemical products, *Chem. Soc. Rev.* 41 (2012) 1538–1558, <http://dx.doi.org/10.1039/C1CS15147A>.
- [5] S. Dutta, S. De, B. Saha, Md. I. Alam, Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels, *Catal. Sci. Technol.* 2 (2012) 2025–2036, <http://dx.doi.org/10.1039/c2cy20235b>.
- [6] P.S. Metkar, E.J. Till, D.R. Corbin, C.J. Pereira, K.W. Hutchenson, S.K. Sengupta, Reactive distillation process for the production of furfural using solid acid catalysts, *Green Chem.* 17 (2015) 1453–1466, <http://dx.doi.org/10.1039/C4GC01912A>.
- [7] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Bimetallic catalysts for upgrading of biomass to fuels and chemicals, *Chem. Soc. Rev.* 41 (2012) 8075–8098, <http://dx.doi.org/10.1039/C2CS35188A>.
- [8] J. Pritchard, G.A. Filonenko, R. van Putten, E.J.M. Hensen, E.A. Pidko, Heterogeneous and homogeneous catalysis for the hydrogenation of carboxylic acid derivatives: history, advances and future directions, *Chem. Soc. Rev.* 44 (2015) 3808–3833, <http://dx.doi.org/10.1039/C5CS00038F>.
- [9] M. Besson, P. Gallezot, C. Pine, Conversion of biomass into chemicals over metal catalysts, *Chem. Rev.* 114 (2014) 1827–1870, <http://dx.doi.org/10.1021/cr400226g>.
- [10] J.G.M. Bremner, R.K.F. Keays, The hydrogenation of furfuraldehyde to furfuryl alcohol and sylvan (2-methylfuran), *J. Chem. Soc.* (1947) 1068–1080, <http://dx.doi.org/10.1039/JR9470001068>.
- [11] Rodiansono, S. Khairi, T. Hara, N. Ichikuni, S. Shimazu, Highly efficient and selective hydrogenation of unsaturated carbonyl compounds using Ni-Sn

- alloy catalysts, Catal. Sci. Technol. 2 (2012) 2139–2145, <http://dx.doi.org/10.1039/C2CY20216F>.
- [12] Rodiansono, T. Hara, T. Ichikuni, S. Shimazu, A novel preparation method of Ni-Sn alloy catalysts supported on aluminium hydroxide: application to chemoselective hydrogenation of unsaturated carbonyl compounds, Chem. Lett. 41 (2012) 769–771, <http://dx.doi.org/10.1246/cl.2012.769>.
- [13] Rodiansono, T. Hara, N. Ichikuni, S. Shimazu, Development of nanoporous Ni-Sn alloy and application for chemoselective hydrogenation of furfural to furfuryl alcohol, Bull. Chem. React. Eng. Catal. 9 (1) (2014) 53–59, <http://dx.doi.org/10.9767/bcrec.9.1.5529.53-59>.
- [14] A. Halilu, T.H. Ali, A.Y. Atta, P. Sudarsanam, S.K. Bhargava, S. bee abd hamid, highly selective hydrogenation of biomass-Derived furfural into furfuryl alcohol using a novel magnetic nanoparticles catalyst, Energy Fuels 30 (3) (2016) 2216–2226, <http://dx.doi.org/10.1021/acs.energyfuels.5b02826>.
- [15] W.S. Putro, T. Hara, N. Ichikuni, S. Shimazu, Efficiently recyclable and easily separable Ni-Fe alloy catalysts for chemoselective hydrogenation of biomass-derived furfural, Chem. Lett. 46 (1) (2017) 149–151, <http://dx.doi.org/10.1246/cl.160905>.
- [16] C. Li, Y. Chen, S. Zhang, S. Xu, J. Zhou, F. Wang, M. Wei, D.G. Evans, X. Duan, Ni-In intermetallic nanocrystals as efficient catalysts toward unsaturated aldehydes hydrogenation, Chem. Mater 25 (2013) 3888–3896, <http://dx.doi.org/10.1021/cm4021832>.
- [17] S. Sittitha, W. An, D.E. Resasco, Selective conversion of furfural to methylfuran over silica-supported Ni-Fe bimetallic catalysts, J. Catal. 284 (2011) 90–101, <http://dx.doi.org/10.1016/j.jcat.2011.09.005>.
- [18] D. Shi, J.M. Vohs, Deoxygenation of biomass-Derived oxygenates: reaction of furfural on Zn-Modified Pt(111), ACS Catal. 5 (2015) 2177–2183, <http://dx.doi.org/10.1021/acscatal.5b00038>.
- [19] F. Delbecq, P. Sautet, Competitive CC and CO adsorption of α - β -unsaturated aldehydes on Pt and Pd surfaces in relation with the selectivity of hydrogenation reactions: a theoretical approach, J. Catal. 152 (1995) 217–236, <http://dx.doi.org/10.1006/jcat.1995.1077>.
- [20] F. Delbecq, P. Sautet, Influence of Sn additives on the selectivity of hydrogenation of α - β -unsaturated aldehydes with Pt catalysts: a density functional study of molecular adsorption, J. Catal. 220 (2003) 115–126, [http://dx.doi.org/10.1016/S0021-9517\(03\)002495](http://dx.doi.org/10.1016/S0021-9517(03)002495).
- [21] V. Hlukhyy, F. Raif, P. Clauss, T.F. Fässler, Polar intermetallic compounds as catalysts for hydrogenation reactions: synthesis, structures, bonding, and catalytic properties of $\text{Ca}_{1-x}\text{Sr}_x\text{Ni}_4\text{Sn}_2$ ($x=0, 0.5, 1, 0$) and catalytic properties of Ni_3Sn and Ni_3Sn_2 , Chem. Eur J. 14 (2008) 3737–3744, <http://dx.doi.org/10.1002/chem.200701547>.
- [22] Rodiansono, A. Ghofur, M.D. Astuti, K.C. Sembiring, Catalytic hydrogenation of levulinic acid in water into γ -Valerolactone over bulk structure of inexpensive intermetallic Ni-Sn alloy catalysts, Bull. Chem. React. Eng. Catal. 10 (2) (2015) 192–200, <http://dx.doi.org/10.9767/bcrec.10.2.8284.192-200>.
- [23] Rodiansono, M.D. Astuti, T. Hara, N. Ichikuni, S. Shimazu, Efficient hydrogenation of levulinic acid in water using a supported Ni-Sn alloy on aluminium hydroxide catalysts, Catal. Sci. Technol. 6 (2016) 2955–2961, <http://dx.doi.org/10.1039/C5CY01731A>.
- [24] J. Petro, A. Bota, K. Laszlo, H. Beyer, E. Kalman, I. Dódon, A new alumina-supported, not pyrophoric Raney-type Ni catalyst, Appl. Catal. A 190 (2000) 73–86, [http://dx.doi.org/10.1016/S0926-860X\(99\)00267-7](http://dx.doi.org/10.1016/S0926-860X(99)00267-7).
- [25] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density Chapter 8, Kluwer Academic Publishers, Netherlands, 2004.
- [26] C.H. Bartholomew, R.B. Pannel, J.L. Butler, Support and crystallite size effects in CO hydrogenation on nickel, J. Catal. 65 (1980) 335–347, [http://dx.doi.org/10.1016/0021-9517\(80\)90311-5](http://dx.doi.org/10.1016/0021-9517(80)90311-5).
- [27] C.H. Bartholomew, R.B. Pannel, The stoichiometry of hydrogen and carbon monoxide chemisorption on alumina- and silica-supported nickel, J. Catal. 65 (1980) 390–401, [http://dx.doi.org/10.1016/0021-9517\(80\)90316-4](http://dx.doi.org/10.1016/0021-9517(80)90316-4).
- [28] Powder Diffraction Files, JCPDS-International Centre for Diffraction Data (ICDD), 1997.
- [29] H.E. Swift, J.E. Bozik, Metallic phases and activities of nickel-tin-silica catalysts: dehydrogenation of cyclohexanone, cyclohexanol, and cyclohexane, J. Catal. 12 (1968) 5–14, [http://dx.doi.org/10.1016/0021-9517\(68\)90067-5](http://dx.doi.org/10.1016/0021-9517(68)90067-5).
- [30] E. Nikolla, J. Schwank, S. Lincic, Promotion of the long-term stability of reforming Ni catalysts by surface alloying, J. Catal. 250 (2007) 85–93, <http://dx.doi.org/10.1016/j.jcat.2007.04.020>.
- [31] R. Sun, M. Zheng, J. Pang, X. Liu, J. Wang, X. Pan, A. Wang, X. Wang, T. Zhang, Selectivity-Switchable conversion of cellulose to glycols over Ni-Sn catalysts, ACS Catal. 6 (2016) 191–201, <http://dx.doi.org/10.1021/acs.catal.5b01807>.
- [32] H.D. Ruan, R.L. Frost, J.T. Klopogge, Comparison of Raman spectra in characterizing gibbsite, bayerite, diasporite and boehmite, J. Raman Spectros. 32 (9) (2001) 745–750, <http://dx.doi.org/10.1002/jrs.736>.
- [33] H.D. Ruan, R.L. Frost, J.T. Klopogge, L. Duong, Far-infrared spectroscopy of alumina phases, Spectrochimica Acta Part A 58 (2002) 265–272, [http://dx.doi.org/10.1016/S1386-1425\(01\)00532-7](http://dx.doi.org/10.1016/S1386-1425(01)00532-7).
- [34] S. Cava, S.M.n-name>J.T. Klopogge, L. Duong, Far-infrared spectroscopy of alumina phases, Spectrochimica Acta Part A 58 (2002) 265–272, [http://dx.doi.org/10.1016/S1386-1425\(01\)00532-7](http://dx.doi.org/10.1016/S1386-1425(01)00532-7).
- [35] S. Cava, S.M. Tebcherani, I.A. Souza, S.A. Pianaro, C.A. Paskocimas, E. Longo, J.A. Varela, Structural characterization of phase transition of Al_2O_3 nanopowders obtained by polymeric precursor method, Mater. Chem. Physics 103 (2007) 394–399, <http://dx.doi.org/10.1016/j.matchemphys.2007.02.046>.
- [36] Rodiansono, M.D. Astuti, U.T. Santoso, S. Shimazu, Hydrogenation of biomass-derived furfural over highly dispersed-Aluminium hydroxide supported Ni-Sn(3.0) alloy catalysts, Procedia Chem. 16 (2015) 531–539, <http://dx.doi.org/10.1016/j.proche.2015.12.089>.
- [37] L. Sordelli, R. Psaro, G. Vlaic, A. Cepparo, S. Recchia, A. Fusi, R. Zannoni, EXAFS studies of supported Rh-Sn catalysts for citral hydrogenation, J. Catal. 182 (1999) 186–198, <http://dx.doi.org/10.1006/jcat.1998.2348>.
- [38] J.L. Margitfalvi, A. Tompos, I. Kolosova, J. Vallyon, Reaction induced selectivity improvement in the hydrogenation of crotonaldehyde over Sn-Pt/SiO₂ catalysts, J. Catal. 174 (1998) 246–249, <http://dx.doi.org/10.1006/jcat.1998.1966>.

Novel preparation method of bimetallic Ni-In alloy catalysts supported on amorphous alumina for the highly selective hydrogenation of furfural

ORIGINALITY REPORT

18%

SIMILARITY INDEX

9%

INTERNET SOURCES

16%

PUBLICATIONS

2%

STUDENT PAPERS

PRIMARY SOURCES

- 1 Takayoshi Hara, Moriaki Hatakeyama, Arum Kim, Nobuyuki Ichikuni, Shogo Shimazu. "Preparation of clay-supported Sn catalysts and application to Baeyer–Villiger oxidation", *Green Chemistry*, 2012
Publication 1%
- 2 Zhu, Ling-Jun, Ping-Jun Guo, Xian-Wen Chu, Shi-Run Yan, Ming-Hua Qiao, Kang-Nian Fan, Xiao-Xin Zhang, and Bao-Ning Zong. "An environmentally benign and catalytically efficient non-pyrophoric Ni catalyst for aqueous-phase reforming of ethylene glycol", *Green Chemistry*, 2008.
Publication 1%
- 3 garuda.ristekdikti.go.id
Internet Source 1%
- 4 fjfsdata01prod.blob.core.windows.net
Internet Source 1%

5

Internet Source

1 %

6

Man Yang, Haifeng Qi, Fei Liu, Yujing Ren et al. "One-Pot Production of Cellulosic Ethanol via Tandem Catalysis over a Multifunctional Mo/Pt/WO_x Catalyst", *Joule*, 2019

Publication

1 %

7

Teng-ge Mi, Yang-wen Wu, Ming-xin Xu, Xinyue Zhou, Bin Hu, Li Zhao, Qiang Lu. "Theoretical insights into the roles of active oxygen species in heterogeneous oxidation of CO over Mn/TiO₂ catalyst", *Applied Catalysis A: General*, 2021

Publication

1 %

8

epdf.tips
Internet Source

1 %

9

Kim, B.J.. "Optimization of the pore structure of nickel/graphite hybrid materials for hydrogen storage", *International Journal of Hydrogen Energy*, 201101

Publication

1 %

10

Takayuki Komatsu, Shin-ichiro Hyodo, Tatsuaki Yashima. "Catalytic Properties of Pt-Ge Intermetallic Compounds in the Hydrogenation of 1,3-Butadiene", *The Journal of Physical Chemistry B*, 1997

Publication

1 %

11 Submitted to Xiamen University <1 %
Student Paper

12 jibwiskatsaca.org <1 %
Internet Source

13 pastureproject.org <1 %
Internet Source

14 Kazuya Yamaguchi, Takeshi Koike, Miyuki Kotani, Mitsunori Matsushita, Satoshi Shinachi, Noritaka Mizuno. "Synthetic Scope and Mechanistic Studies of Ru(OH)_x/Al₂O₃-Catalyzed Heterogeneous Hydrogen-Transfer Reactions", Chemistry - A European Journal, 2005 <1 %
Publication

15 Weiyi Ouyang, Alfonso Yopez, Antonio A. Romero, Rafael Luque. "Towards industrial furfural conversion: Selectivity and stability of palladium and platinum catalysts under continuous flow regime", Catalysis Today, 2018 <1 %
Publication

16 ehp.niehs.nih.gov <1 %
Internet Source

17 research.wsulibs.wsu.edu:8080 <1 %
Internet Source

18 physics.umaine.edu

<1 %

19

"Handbook of Heterogeneous Catalysis",
Wiley, 1997

Publication

<1 %

20

Husni Wahyu Wijaya, Takayoshi Hara,
Nobuyuki Ichikuni, Shogo Shimazu.

"Hydrogenolysis of Tetrahydrofurfuryl Alcohol
to 1,5-Pentanediol over a Nickel-Yttrium Oxide
Catalyst Containing Ruthenium", Chemistry
Letters, 2018

Publication

<1 %

21

Sudarsanam Putla, Mohamad Hassan Amin,
Benjaram M. Reddy, Ayman Nafady, Khalid A.

Al Farhan, Suresh K. Bhargava. " MnO
Nanoparticle-Dispersed CeO Nanocubes: A
Remarkable Heteronanostructured System
with Unusual Structural Characteristics and
Superior Catalytic Performance ", ACS Applied
Materials & Interfaces, 2015

Publication

<1 %

22

cdmf.org.br

Internet Source

<1 %

23

Submitted to Indian Institute of Technology,
Bombay

Student Paper

<1 %

24

Pengfei Guo, Shengyun Liao, Xinli Tong.
"Heterogeneous Nickel Catalysts Derived
from 2D Metal–Organic Frameworks for
Regulating the Selectivity of Furfural
Hydrogenation", ACS Omega, 2019

Publication

<1 %

25

Submitted to Universitas Riau

Student Paper

<1 %

26

Tao Deng, Guofeng Zhao, Ye Liu, Yong Lu.
"Catalytic distillation for one-step cyclohexyl
acetate production and cyclohexene-
cyclohexane separation via esterification of
cyclohexene with acetic acid over
microfibrous-structured Nafion-SiO₂/SS-fiber
packings", Chemical Engineering and
Processing - Process Intensification, 2018

Publication

<1 %

27

Wenbo Zhang, Huiyue Xin, Yaqiong Zhang, Xin
Jin, Peng Wu, Wenhui Xie, Xiaohong Li.
"Bimetallic Pt-Fe catalysts supported on
mesoporous TS-1 microspheres for the liquid-
phase selective hydrogenation of
cinnamaldehyde", Journal of Catalysis, 2021

Publication

<1 %

28

Halilu, Ahmed, Tammar Hussein Ali,
Abdulazeez Yusuf Atta, Putla Sudarsanam,
Suresh K. Bhargava, and Sharifah Bee Abd
Hamid. "Highly Selective Hydrogenation of

<1 %

Biomass- Derived Furfural into Furfuryl Alcohol using a Novel Magnetic Nanoparticles Catalyst", Energy & Fuels, 2016.

Publication

29

Hiroshi Fujiwara. "A Supported Rhodium Hydroxide Catalyst: Preparation, Characterization, and Scope of the Synthesis of Primary Amides from Aldoximes or Aldehydes", Chemistry - An Asian Journal, 09/01/2008

Publication

30

Submitted to Sardar Vallabhbhai National Inst. of Tech.Surat

Student Paper

31

Fang, Huihuang, Jianwei Zheng, Xiaolin Luo, Junmou Du, Alberto Roldan, Stefano Leoni, and Youzhu Yuan. "Product tunable behavior of carbon nanotubes-supported Ni-Fe catalysts for guaiacol hydrodeoxygenation", Applied Catalysis A General, 2017.

Publication

32

Guangyi Li, Ning Li, Mingyuan Zheng, Shanshan Li, Aiqin Wang, Yu Cong, Xiaodong Wang, Tao Zhang. "Industrially scalable and cost-effective synthesis of 1,3-cyclopentanediol with furfuryl alcohol from lignocellulose", Green Chemistry, 2016

Publication

<1 %

<1 %

<1 %

<1 %

33

Bang, Yongju, Joongwon Lee, Seung Ju Han, Jeong Gil Seo, Min Hye Youn, Ji Hwan Song, and In Kyu Song. "Hydrogen production by steam reforming of liquefied natural gas (LNG) over mesoporous nickel–alumina xerogel catalysts prepared by a single-step carbon-templating sol–gel method", *International Journal of Hydrogen Energy*, 2012.

Publication

<1 %

34

H. D. Ruan. "Comparison of Raman spectra in characterizing gibbsite, bayerite, diaspore and boehmite", *Journal of Raman Spectroscopy*, 09/2001

Publication

<1 %

35

Nobutaka Yamanaka, Takayoshi Hara, Nobuyuki Ichikuni, Shogo Shimazu. "Chemoselective hydrogenation of unsaturated nitro compounds to unsaturated amines by Ni-Sn alloy catalysts", *Chemistry Letters*, 2018

Publication

<1 %

36

Raji Vadakkekara, Mousumi Chakraborty, Parimal A. Parikh. "Room temperature benzaldehyde oxidation using air over gold–silver nanoalloy catalysts", *Journal of the Taiwan Institute of Chemical Engineers*, 2015

Publication

<1 %

- 37 lib.dr.iastate.edu Internet Source <1 %
-
- 38 www.thieme-connect.com Internet Source <1 %
-
- 39 Koustuv Ray, Goutam Deo. "A potential descriptor for the CO₂ hydrogenation to CH₄ over Al₂O₃ supported Ni and Ni-based alloy catalysts", *Applied Catalysis B: Environmental*, 2017
Publication <1 %
-
- 40 Lei Ye, Yiwen Han, Jing Feng, Xuebin Lu. "A review about GVL production from lignocellulose: Focusing on the full components utilization", *Industrial Crops and Products*, 2020
Publication <1 %
-
- 41 Wenjing Yang, Haiyang Cheng, Bin Zhang, Yan Li et al. "Hydrogenation of levulinic acid by RuCl(PPh)₃ in supercritical CO₂: the significance of structural changes of Ru complexes via interaction with CO", *Green Chemistry*, 2016
Publication <1 %
-
- 42 Zeyou Pan, Xiangfei Xue, Changsen Zhang, Dengtai Wang, Yunyun Xie, Ruiqin Zhang. "Evaluation of process parameters on high-density polyethylene hydro-liquefaction <1 %

products", Journal of Analytical and Applied Pyrolysis, 2018

Publication

43

sels-group.eu

Internet Source

<1 %

44

Mengqing Sun, Jie Xia, Haifeng Wang, Xiaohui Liu, Qineng Xia, Yanqin Wang. "An efficient NiZrO catalyst for hydrogenation of bio-derived methyl levulinate to γ -valerolactone in water under low hydrogen pressure", Applied Catalysis B: Environmental, 2018

Publication

<1 %

45

Mohammad Ghashghaee, Samahe Sadjadi, Samira Shirvani, Vahid Farzaneh. "A Novel Consecutive Approach for the Preparation of Cu-MgO Catalysts with High Activity for Hydrogenation of Furfural to Furfuryl Alcohol", Catalysis Letters, 2017

Publication

<1 %

46

Paal, Z.. "Preparation, physical characterization and catalytic properties of unsupported Pt-Rh catalyst", Journal of Catalysis, 20070910

Publication

<1 %

47

Xiangfeng Guan, Xiaomei Chen, Guangshe Li, Yipeng Zang, Haifeng Lin, Dong Luo, Liping Li. "Direct synthesis of carbon-coated Li₄Ti₅O₁₂

<1 %

mesoporous nanoparticles for high-rate lithium-ion batteries", RSC Advances, 2013

Publication

48

Xiaofeng Yang, Aiqin Wang, Xiaodong Wang, Tao Zhang, Keli Han, Jun Li. "Combined Experimental and Theoretical Investigation on the Selectivities of Ag, Au, and Pt Catalysts for Hydrogenation of Crotonaldehyde", The Journal of Physical Chemistry C, 2009

Publication

49

Xiaoyu Meng, Yusen Yang, Lifang Chen, Ming Xu, Xin Zhang, Min Wei. "A Control over Hydrogenation Selectivity of Furfural via Tuning Exposed Facet of Ni Catalysts", ACS Catalysis, 2019

Publication

50

Yifeng Zhu, Xiao Kong, Hongyan Zheng, Yulei Zhu. "Strong metal-oxide interactions induce bifunctional and structural effects for Cu catalysts", Molecular Catalysis, 2018

Publication

51

Zhang, Xiuling, Lanbo Di, and Qian Zhou. "Methane conversion under cold plasma over Pd-containing ionic liquids immobilized on γ -Al₂O₃", Journal of Energy Chemistry, 2013.

Publication

52

Zhitong Zhao, Jingyang Jiang, Mingyuan Zheng, Feng Wang. "Advancing development

<1 %

<1 %

<1 %

<1 %

<1 %

of biochemicals through the comprehensive evaluation of bio-ethylene glycol", Chemical Engineering Journal, 2021

Publication

53

orca.cf.ac.uk

Internet Source

<1 %

54

pureadmin.qub.ac.uk

Internet Source

<1 %

55

www.chlorpars.com

Internet Source

<1 %

56

www.investigo.biblioteca.uvigo.es

Internet Source

<1 %

57

www.scribd.com

Internet Source

<1 %

58

Cai-Hong Hao, Xiao-Ning Guo, Yung-Tin Pan, Shuai Chen, Zhi-Feng Jiao, Hong Yang, Xiang-Yun Guo. "Visible-Light-Driven Selective Photocatalytic Hydrogenation of Cinnamaldehyde over Au/SiC Catalysts", Journal of the American Chemical Society, 2016

Publication

<1 %

59

Chen, Yanjun, and Jixiang Chen. "Selective hydrogenation of acetylene on SiO₂ supported Ni-In bimetallic catalysts:

<1 %

Promotional effect of In", Applied Surface Science, 2016.

Publication

60

Fulajtárova, Katarína, Tomáš Soták, Milan Hronec, Ivo Vávra, Edmund Dobročka, and Mária Omastová. "Aqueous phase hydrogenation of furfural to furfuryl alcohol over Pd–Cu catalysts", Applied Catalysis A General, 2015.

Publication

<1 %

61

Gregory S. Hutchings, Wesley Luc, Qi Lu, Yang Zhou, Dionisios G. Vlachos, Feng Jiao. "Nanoporous Cu–Al–Co Alloys for Selective Furfural Hydrodeoxygenation to 2-Methylfuran", Industrial & Engineering Chemistry Research, 2017

Publication

<1 %

62

Jinlian Zhu, Guochuan Yin. "Catalytic Transformation of the Furfural Platform into Bifunctionalized Monomers for Polymer Synthesis", ACS Catalysis, 2021

Publication

<1 %

63

S. Umasankar, P. Santhana Krishnan, G. Sonia Theres, P. Tamizhdurai, K. Shanthi. "Liquid phase hydrogenation of furfural to biofuel over robust NiCu/Laponite catalyst: A study on the role of copper loading", Advanced Powder Technology, 2021

Publication

<1 %

64

Shinya Furukawa, Akira Yokoyama, Takayuki Komatsu. " Efficient Catalytic System for Synthesis of α -Stilbene from Diphenylacetylene Using Rh-Based Intermetallic Compounds ", ACS Catalysis, 2014

Publication

<1 %

65

Tang, Xing, Xianhai Zeng, Zheng Li, Lei Hu, Yong Sun, Shijie Liu, Tingzhou Lei, and Lu Lin. "Production of γ -valerolactone from lignocellulosic biomass for sustainable fuels and chemicals supply", Renewable and Sustainable Energy Reviews, 2014.

Publication

<1 %

66

Xiao Chen, He Cao, Xiaozhen Chen, Yan Du, Ji Qi, Jingjie Luo, Marc Armbrüster, Changhai Liang. "Synthesis of Intermetallic Pt-Based Catalysts by Lithium Naphthalenide-Driven Reduction for Selective Hydrogenation of Cinnamaldehyde", ACS Applied Materials & Interfaces, 2020

Publication

<1 %

67

Yuan, P.. "Investigation on the delaminated-pillared structure of TiO₂-PILC synthesized by TiCl₄ hydrolysis method", Microporous and Mesoporous Materials, 20060728

Publication

<1 %

68

Yuewen Shao, Junzhe Wang, Huining Du, Kai Sun, Zhanming Zhang, Lijun Zhang, Qingyin Li,

<1 %

Shu Zhang, Qing Liu, Xun Hu. "Importance of Magnesium in Cu-Based Catalysts for Selective Conversion of Biomass-Derived Furan Compounds to Diols", ACS Sustainable Chemistry & Engineering, 2020

Publication

69

scholarbank.nus.edu.sg

Internet Source

<1 %

70

www.greenenergypark.co.za

Internet Source

<1 %

71

Nagaraja, B.M.. "Vapor phase selective hydrogenation of furfural to furfuryl alcohol over Cu-MgO coprecipitated catalysts", Journal of Molecular Catalysis. A, Chemical, 20070316

Publication

<1 %

72

Willinton Y. Hernández, Jeroen Lauwaert, Pascal Van Der Voort, An Verberckmoes. "Recent advances on the utilization of layered double hydroxides (LDHs) and related heterogeneous catalysts in a lignocellulosic-feedstock biorefinery scheme", Green Chemistry, 2017

Publication

<1 %

73

Áine O'Driscoll, Teresa Curtin, Willington Y. Hernández, Pascal Van Der Voort, James J. Leahy. "Hydrogenation of Furfural with a Pt-Sn Catalyst: The Suitability to Sustainable

<1 %

Industrial Application", Organic Process Research & Development, 2016

Publication

74

Wang, Shengguang, Vassili Vorotnikov, and
Dionisios G. Vlachos. "Coverage Induced
Conformational Effects on Activity and
Selectivity: Hydrogenation and
Decarbonylation of Furfural on Pd(111)", ACS
Catalysis

Publication

<1 %

Exclude quotes Off

Exclude matches Off

Exclude bibliography On