Research Paper

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

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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 $InCl_2 \cdot H_2O$ solution in an ethanol/H_2O mixture at 423 K for 2 h, followed by reduction with H_2 at 573–873 K for 1.5 h. The formation of Ni-In alloy phases such as Ni_3In_2, Ni_3In, Ni_2In, and NiIn in Ni-In(*2.0*)/AA was clearly observed after reduction with H_2 at 873 K for 1.5 h. Ni-In(*2.0*)/AA contained a Ni_2In 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.

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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, solvents, 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].Autor name:

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] Pd-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., $NiCl_2$ or $NiCl_2 \cdot 4H_2O$) 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 Ni_3Sn_2 alloy dispersed on TiO_2 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-

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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 [12]. 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 (50%wt Ni and 50%wt Al) was purchased from Kanto Chemical Co., Inc.). NaOH, $InCl_3 \cdot 4H_2O$ and $SnCl_2 \cdot 2H_2O$ were purchased from WAKO Pure 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 CuKα radiation (λ = 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} (α1 = 0.154057 nm, α2 = 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 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 [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–17 B equipped with a thermal conductivity detector and an RT-βDEXsm 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:

$$Conversion : \frac{introduced\ mol\ reactant(F_0) - remained\ mol\ reactan(F_t)}{introduced\ mol\ reactant(F_0)} x100\%$$