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Research Article

Selective Hydrogenation of Dodecanoic Acid to Dodecane-1-ol Catalyzed by Supported Bimetallic Ni-Sn Alloy

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Abstract

Selective hydrogenation of dodecanoic acid over supported bimetallic Ni-Sn alloy catalysts into dodecane-1-ol is demonstrated. Bimetallic nickel-tin supported on titanium oxide (Ni-Sn(*1.5*)/TiO_2) and gamma-alumina (Ni-Sn(*1.5*)/γ-Al_2O_3); *1.5* = Ni/Sn molar ratio) were synthesized via hydrothermal method in a sealed-Teflon autoclave reactor at 150 °C for 24 h, then followed by reducing with hydrogen gas at 400 °C for 1.5 h. The synthesized catalysts were characterized by means of XRD, IC-AES, N_2-adsorption (BET method), H_2-chemisorption, and NH_3-TPD. Bimetallic Ni-Sn(*1.5*)/TiO_2 catalyst was found to be effective for hydrogenation of dodecanoic acid (>99 % conversion) to dodecane-1-ol (93% yield) at 160 °C, 30 bar H_2, and 20 h and the highest dodecane-1-ol (97 % yield) was obtained at initial pressure of H_2, 50 bar. An increase of reaction temperature slightly enhanced the degree of hydrodeoxygenation of dodecanoic acid to produce dodecane over both Ni-Sn(*1.5*)/TiO_2 and Ni-Sn(*1.5*)/γ-Al_2O_3 catalysts. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Bimetallic Nickel-Tin Alloy Catalyst; Dodecane; Dodecanoic Acid; Dodecane-1-ol; Hydrogenation

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1. Introduction

The development of oleochemical products including surfactants, lubricants, plasticizers, coatings, and polymers has been made possible by remarkable advances made in organic synthesis, catalysis, and biotechnology [1]. Fatty alcohol is one of the important basic oleochemicals which could be produced by hydrogenation of fatty acids or its esters by using heterogeneous catalysts (e.g. bimetallic copper chromite), but the reaction requires harsh temperature (e.g., up to 300 °C) and pressure (e.g., up to 300 bar of H_2) in the presence of copper-chromite catalysts, which are potentially harmful for the environ-

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ment [2,3]. In this regard, the development of catalysts to produce fatty alcohols under milder conditions has been long-standing industrial target.

Many previous attempts on the reduction of the reaction pressures (down to 20 bar H_2) have been achieved with high conversion and selectivities by replacing Cu or Cr with noble metals such as Ru, Rh, Re, Pd, or Pt [4]. For example, the hydrogenation of carboxylic acids to alcohols using a Pt/TiO_2 catalyst as reported recently by Hardacre et al. at only 130 °C, 20 bar H_2 and gave over 80 % conversion (with 90 % selectivity) after 12 h [5]. Although these results are remarkable, it would be desirable to replace the expensive noble metals with more abundant and economic catalysts still capable of working at low H_2 pressures and moderate reaction temperatures. The commercial Ni-based catalysts such as: RANEY Ni/Kieselgur, or Ni/Al_2O_3 had been applied for fatty acids or fatty ester hydrogenation with high activity. However, the important drawbacks of these catalysts are low selectivity to desired products (i.e., produced the mixture of *cis*- and *trans*-product) and easily deactivated due to carbon deposited on the metal surface [6].

Interactions between metals in bimetallic catalysts can modify their surfaces, which can be beneficial for the conversion and upgrading of highly complex biomass derived compounds [7-9]. In previously published studies, several bimetallic alloy transition metal catalysts (e.g. Pd-M (M = Cu, Co, Ni) [10], Pd-Nb_2O_5 [11], Ru-Sn [12] Rh-Sn [13], and Ru-Ge-B [14] have shown superior performance for the selective hydrogenation of fatty acids compared with their single metal counterpart. Huang *et al.* [10] reported the catalytic performances of supported bimetallic Pd-M (M = Cu, Co, Ni) catalysts in hydrogenation of methyl palmitic in n-heptane solvent at 270 ^{o}C, H_2 55 bar within 7 h. Among these bimetallic catalysts, Pd-Cu/diatomite with loading amount of 1 % (Pd/Cu = 3) displayed the highest catalytic performances in hydrogenation of palmitic acid (99 % conversion) giving 1-hexadecanol (83 % yield) [10]. On the other hand, by using Pd/Nb_2O_5/SiO_2 catalyst, a significant improvement of 1-hexadecanol yield was achieved (c.a. 97 % yield) from palmitic acid in cyclohexane at 180 ^{o}C, H_2 25 bar, within 24 h of reaction time [11].

In previous reports, bimetallic Ru-based catalysts have also demonstrated high activity in hydrogenation of methyl oleate at relatively high temperature and H_2 pressure (ca. 270 ^{o}C and 44 bar, respectively) within 7 h. However, the conversion of methyl oleate and selectivity of oleyl alcohol were only 80 % and 70 %, respectively. The addition of electropositive atom of Sn and B to Ru enhanced the dispersion of Ru and improved the electron density of Ru. The change of electron density Ru enhanced the affinity of Ru towards C=O bond of fatty acids which facilitated the reaction hydrogenation [12,13]. Similar results have been also reported on the hydrogenation of dodecanoic acid and palmitic acid at 300 ^{o}C, 60 bar H_2, within 4 h over Ru-Sn/Al_2O_3 and Rh-Sn/Al_2O_3 catalysts and produced lauryl alcohol and hexadecane-1-ol, respectively. On the other hand, Ru-Ge-B/Al_2O_3 catalyst gave only 20 % of oleyl alcohol with conversion of methyl oleic, ca. 80 % [14].

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 [15] and, *second*, from Raney Ni-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) [16]. We have also recently reported the catalytic performance of the Ni-Sn alloy during hydrogenation of biomass-derived levulinic acid in water to γ-valerolactone (GVL) [17]. Over bulk Ni-Sn alloy catalysts, a relatively high reaction temperature (150 ^{o}C, 40 bar H_2, 6 h) was applied to achieve both a high conversion and GVL yield (99 %) [18]. Alternatively, a GVL yield of >99 % was obtained over Ni-Sn(*x*)/AlOH catalysts at a lower reaction temperature (120 ^{o}C) compared to the bulk catalysts [19].

In this present report, we continue our extend investigation of the hydrogenation of dodecanoic acid over supported bimetallic Ni-Sn alloy catalysts to the corresponding of lauryl alcohol. Bimetallic Ni-Sn alloy was supported on two types of supports c.a. titanium oxide (TiO_2) and gamma-alumina (γ-Al_2O_3). Monometallic nickel supported on TiO_2 (Ni/TiO_2) and γ-Al_2O_3 (Ni/(γ-Al_2O_3) catalysts were also evaluate for comparison.

2. Materials and Methods

2.1 Materials

Sodium hydroxide (NaOH) (97 %), nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$, 99.9%), tin(II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$, 99.9%,), aluminium hydroxide, and TiO_2 (mixture of rutile and anatase; S_{BET} = 50 m^2g^{-1}) were purchased and used as received from WAKO Pure Chemical Industries, Ltd. unless otherwise stated. The γ-Al_2O_3 (S_{BET} = 100 m^2g^{-1}) were purchased from Japan Aerosil Co. All organic chemical compounds were purified using standard procedures prior to use.

2.2 Catalyst preparation

2.2.1 Synthesis of Ni-Sn(1.5)/TiO_2

A typical procedure of the synthesis of titanium oxide supported Ni-Sn (*1.5* is feeding ratio) alloy catalyst is described as follows [15]: $NiCl_2 \cdot 6H_2O$ (7.2 mmol) was dissolved in deionized water (denoted as solution A), and $SnCl_2 \cdot 2H_2O$ (4.8 mmol) was dissolved in ethanol/2-methoxy ethanol (2:1) (denoted as solution B) at room temperature. A one-gram titanium oxide (TiO_2), solutions A, and B were mixed at room temperature; the temperature was subsequently raised to 50 °C and the mixture was stirred for 12 h. The pH of the mixture was adjusted to 12 through the dropwise addition of an aqueous solution of NaOH (3.1 M). The mixture was then placed into a sealed-Teflon autoclave for the hydrothermal reaction at 150 °C for 24 h. The resulting black precipitate was filtered, washed with distilled water, and then dried under vacuum overnight. Prior to the catalytic reaction, the obtained black powder was treated under hydrogen at 400 °C for 1.5 h.

2.2.2 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^{-1} (α1 = 0.154057 nm, $a2$ = 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 Brunauer-Emmett-Teller surface area (S_{BET}) and pore volume (V_p) were measured using N_2 physisorption at -196 °C on a Belsorp Max (BEL Japan). The samples were degassed at 200 °C 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 [20].

The H_2 uptake was determined through irreversible H_2 chemisorption. After the catalyst was heated at 100 °C under vacuum for 30 min, it was then heated at 400 °C 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 0 °C, and the H_2 uptake was calculated according to a method described in the literature [21,22].

The NH_3-TPD was carried out on a Belsorp Max (BEL Japan). The samples were degassed at elevated temperature of 100-200 °C for 2 h to remove physisorbed gases prior to the measurement. The temperature was then kept at 200 °C for 2 h while flushed with He gas. NH_3 gas (balanced NH_3, 80 % ,and He, 20 %) was introduced at 100 °C for 30 min, then evacuated by helium gas to remove the physisorbed also for 30 min. Finally, temperature programmed desorption was carried out at temperature of 100-800 °C and the desorbed NH_3 was monitored by TCD.

2.3 Catalytic reaction

Typical catalytic reaction procedure as follows. Catalyst (0.05 g), dodecanoic acid (1.8 mmol), internal standar of 1,6-hexanediol (0.03 mmol) and *iso*-PrOH (5 mL) as solvent were placed into a glass reaction tube, which fitted inside a stainless-steel reactor. The reactor was flushed with H_2 for ~30 times. Finally, after H_2 was introduced into the reactor with an initial H_2 pressure of 30 bar at room temperature, the temperature of the reactor was increased to 160 °C. After 6 h of the reaction, both heating and stirring were stopped, the autoclave was removed from the hot plate and then cooled in ice-cold water. Once cooled, the contents of the autoclave were transferred into sample bin then centrifuged (~4000 rpm for 10 min) and ready for GC-FID analysis. The Ni-Sn(*1.5*)/TiO_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.

2.4 Product analysis

Gas chromatography analysis of the reactant (dodecanoic acid) and products was performed on a Perkin Elmer Autosystem XL with a flame ionization detector with an InertCap 225 (i.d. 0.25 mm, length 30 m, d.f. 0.25 mm) capillary column of GL Science Inc. Tokyo Japan. The products were confirmed by a comparison of their GC retention time, mass spectra with those of authentic samples. Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and an RT-βDEXsm capillary column.

The amount of remained reactant and products were determined from GC data using internal standard of 1,6-hexanediol that was introduced to the reactor before reaction run. Calibration curve was performed using known concentrations of internal standard, reactants and products in order to determine the correct response factors. The conversion of dodecanoic acid, yield, and selectivity of the products were calculated according to the following equations:

$$Conversion = \frac{F_0 - F_t}{F_0} x100\% \quad (1)$$

$$Yield = \frac{mol\ product}{F_0} x100\% \quad (2)$$

$$Selectivity = \frac{mol\ product}{total\ mol\ products} x100\% \quad (3)$$

where F_0 is the introduced mol reactant (dodecanoic acid), 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.

3. Results and Discussion

3.1 Catalyst characterization

The chemical compositions, BET specific surface area (S_{BET}), and total pore volume (V_p) for γ-Al_2O_3 or TiO_2 supported Ni-Sn(*1.5*) catalysts after H_2 treatment at 400 °C for 1.5 h are summarized in Table 1. Based on the ICP-AES analyses, the compositions of the supported Ni-Sn alloy were approximately equivalent to the feeding ratios of each precursor and were reflected in the composition of each Ni-Sn alloy phase. The total loading amount of Ni-Sn was 2.3~2.4 mmol.g^{-1} for all of the supported Ni-Sn(*1.5*) samples (the composition (mol%) of Ni and Sn are listed in Table 1). The S_{BET} and total pore volume (V_p) of each supported Ni-Sn(*1.5*) alloy samples were also summarized in Table 1. It is found that the S_{BET} and V_p of Ni-Sn(*1.5*)/γ-Al_2O_3 were 94 m^{2}g^{-1} and 0.39 cm^{3}g^{-1}, respectively (entry 1), while for Ni-Sn(*1.5*)/TiO_2 were 52 m^{2}g^{-1} and 0.17 cm^{3}g^{-1} (entry 2). It can be observed that S_{BET} and total pore volume of TiO_2 supported catalyst lower than that of γ-Al_2O_3 supported catalysts. It was reported that metal species lead more dispersible on support with lower porosity (e.g. TiO_2) due to strong interaction between metal and support which will prevent metal aggregation or sintering during thermal treatment [15,23].

The H_2 uptake for Ni-Sn(*1.5*)/TiO_2 and Ni-Sn(*1.5*)/γ-Al_2O_3 samples were 9.0 and 13.0 μmolg^{-1}, respectively and the average Ni-Sn alloy crystallite sizes derived from Scherrer equation of Ni_3Sn_2 (101) phase at 2θ = 30.8° were 16 nm and 6 nm, respectively. The H_2 uptake supported Ni-Sn alloy in this work was much lower than that of the Raney Ni or supported Ni on aluminium hydroxide, suggesting that the presence of second metal of Sn reduced significantly the accessibility of hydrogen on the surface of Ni metal. Consequently, the catalytic reaction may be effectively proceeded at high pressure of H_2 as its have been reported previously [15-19],

The XRD patterns of Ni-Sn(*1.5*)/γ-Al_2O_3 alloy catalyst after H_2 treatment at 400 °C for 1.5 h are shown in Figure 1. It can be observed easily that Ni_3Sn_2 species as major alloy phase was formed on γ-Al_2O_3 with sharped peaks with very similar patterns to the JCPDS card standard of Ni_3Sn_2 of 6-414 [24]. On the other hand, the XRD patterns Ni-Sn(*1.5*)/TiO_2 exhibited broadened peaks at 2θ = 30.8°, 42.5°, and 44.2°, which correspond to the Ni_3Sn_2 (101),

Table 1. Chemical composition, BET surface area (S_{BET}), and total pore volume (V_p) for Ni-Sn(*1.5*)/γ-Al_2O_3 and Ni-Sn(*1.5*)/TiO_2 catalysts after H_2 treatment at 400 °C for 1.5 h.

Entry	Catalyst^a	Comp.^{b} (mol%)	S_{BET}^{c} (m^2 g^{-1})	V_p^{c} (cm^3 g^{-1})
1	Ni-Sn(*1.5*)/γ-Al_2O_3	$Ni_{60.2}Sn_{39.8}$	94	0.39
2	Ni-Sn(*1.5*)/TiO_2	$Ni_{60.4}Sn_{39.6}$	52	0.17

^{a}The value between the parenthesis is Ni/Sn molar ratio. ^{b}Molar composition of Ni or Sn, determined by ICP-AES. ^{c}Determined by N_2 adsorption at -196 °C. 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.

Ni_3Sn_2 (102), and Ni_3Sn_2 (110) diffraction peaks, respectively (Figure 2). These results suggest that the higher dispersions of Ni-Sn alloy on the TiO_2 were formed as roughly depicted in the average Ni_3Sn_2 (101) crystallite sizes, which were 6 nm (Table 2). In conclusion, the XRD analysis and H_2 measurement results confirm that Ni-Sn alloy phases were also formed on the supports and that their characteristics were consistent with the results observed for the bulk material as reported previously [15].

The results of ammonia-temperature programmed desorption (NH_3-TPD) measurements of the synthesized catalysts are summarized in Table 3 and the NH_3-TPD profiles are shown in Figure 3 and Figure 4. It can be observed that Ni-Sn(*1.5*)/γ-Al_2O_3 alloy catalyst consisted of three different peak positions of 178, 510, and 607 °C with acidic amount of 0.23, 0.03, and 0.09 mmol.g^{-1}, respectively (Figure 3 and Table 3, entry 1) with total number of acid sites = 0.35 mmol.g^{-1}. Therefore, it can be concluded that Ni-Sn(*1.5*)/γ-Al_2O_3 catalyst has mainly weak acid sites. On the other hand, Ni-Sn(*1.5*)/TiO_2 displayed the peak position at 611 °C with total number of acidic sites = 0.29 mmol.g^{-1} that can be attributed to the strong acid sites (Figure 4 and Table 3, entry 2) [25, 26].

3.2 Hydrogenation of dodecanoic acid

3.2.1 Screening of catalysts

Results of selective hydrogenation of dodecanoic acid over supported bimetallic Ni-Sn(*1.5*) catalysts are summarized in Table 4 and the reaction pathways are shown in

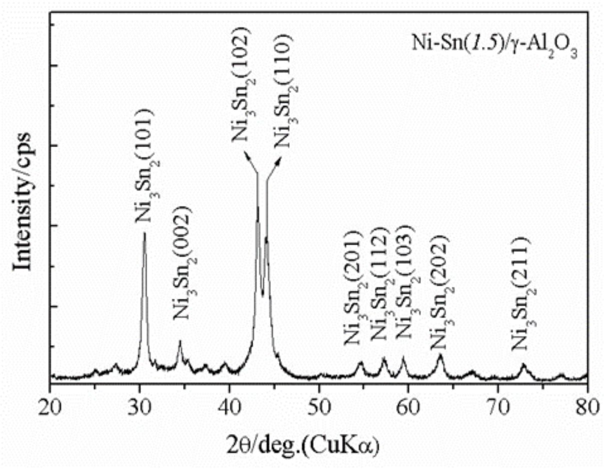


Figure 1. XRD patterns of bimetallic Ni-Sn (*1.5*) supported on g-Al_2O_3 after H_2 treatment at 400 °C for 1.5 h

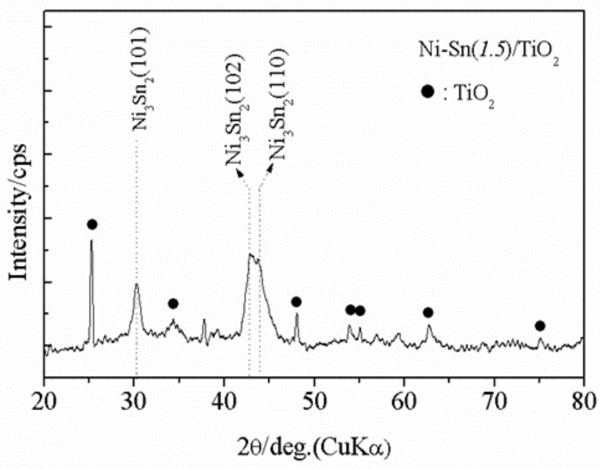


Figure 2. XRD patterns of bimetallic Ni-Sn(*1.5*) alloy supported on TiO_2 after H_2 treatment at 400 °C for 1.5 h

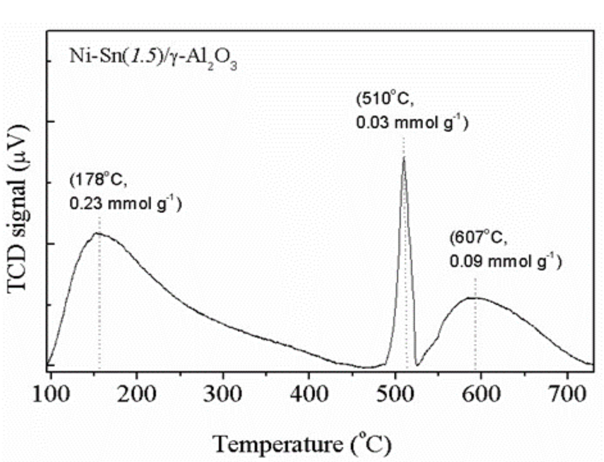


Figure 3. NH_3-TPD spectra of Ni-Sn(*1.5*)/γ-Al_2O_3 catalyst after H_2 treatment at 400 °C for 1.5 h

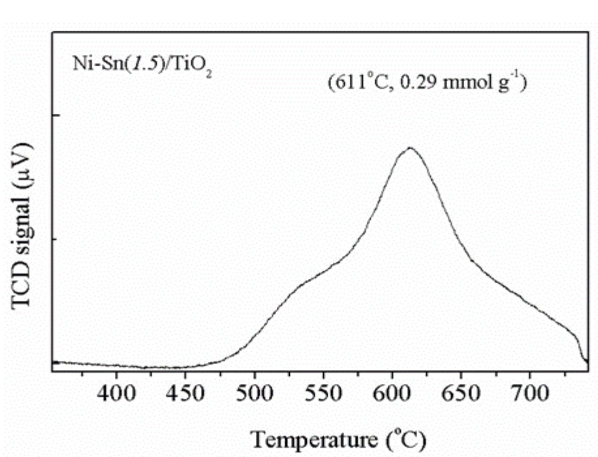


Figure 4. NH_3-TPD spectra of Ni-Sn(*1.5*)/TiO_2 catalyst after H_2 treatment at 400 °C for 1.5 h

Scheme 1. It can be observed that by using the Ni-Sn(*1.5*)/γ-Al_2O_3 catalysts, the conversion of dodecanoic acid was 59 % with dodecane-1-ol yield was 40 % while dodecane-1,1-diol and dodecane yields were 1 % and 4 %, respectively (entry 1). The conversion of dodecanoic acid reached 89 % when the reaction time was extended to 16 h and yielded 57 % and 4 % of dodecane-1-ol and dodecane, respectively (entry 2). Interestingly, Ni-Sn(*1.5*)/TiO_2 catalyst displayed a high conversion of dodecanoic acid (*c.a.* 85 %) and high yield of dodecane-1-ol (*c.a.* 80 %) (entry 3). The yield of dodecane-1-ol increased significantly to 90 % (with 97 % conversion) without significant formation of by-product when the reaction time was extended to 16 h (entry 4). It can be observed that Ni-Sn(1.5)/TiO_2 catalyst showed higher catalytic performance than that of Ni-Sn(*1.5*)/γ-Al_2O_3. The high conversion of dodecanoic acid and the high yield of dodecan-1-ol over Ni-Sn(*1.5*)/TiO_2 can be attributed to the relatively high dispersion of Ni-Sn alloy on TiO_2 giving rise to active sites with a significantly higher catalytic activity. Alternatively, the high conversion and selectivity may be a result of the strong interactions between the active metals and TiO_2 generating significant interactions between C=O groups and Ni-TiO_x sites and leading to high selectivity to dodecane-1-ol [27].

The results of re-usability test confirmed that Ni-Sn(*1.5*)/TiO_2 catalyst was re-usable and the activity and selectivity of the catalyst can be restored to the initial after reducing with H_2

Table 2. H_2 chemisorption and average crystallite sizes of Ni_3Sn_2 alloy phase for Ni-Sn(*1.5*)/γ-Al_2O_3 and Ni-Sn(*1.5*)/TiO_2 catalysts after H_2 treatment at 400 °C for 1.5 h

Entry	Catalyst^a	H_2 uptake^b (mmol g^{-1})	D^c(nm)
1	Ni-Sn(1.5)/γ-Al_2O_3	9.1	16
2	Ni-Sn(1.5)/TiO_2	13.0	6

^{a}The value between the parenthesis is Ni/Sn molar ratio. ^{b}Based on total H_2 uptake at 0 °C (noted after corrected for physical and chemical adsorption. ^{c}The average crystallite sizes of Ni_3Sn_2(101) alloy phase at 2θ = 30.8° was derived from Scherrer equation.

Table 3. NH_3-TPD results for Ni-Sn(*1.5*) alloy supported on γ-Al_2O_3 and TiO_2 catalysts after H_2 treatment at 400 °C for 1.5 h

Entry	Catalyst^a	NH_3-TPD data^b	
		Peak postion (°C)	Acidic amount^c (mmol.g^{-1})
1	Ni-Sn(*1.5*)/γ-Al_2O_3	178 (weak)	0.23
		510 (medium)	0.03
		607 (strong)	0.09
2	Ni-Sn(*1.5*)/TiO_2	611 (strong)	0.29

^{a}The value in the parenthesis is Ni/Sn molar ratio. ^{b}Ammonia-temperature programmed desorption (NH_3-TPD). ^{c}Acidic amount (mmol.g^{-1}) was derived from NH_3-TPD spectra.

Table 4. Results of dodecanoic acid hydrogenation/hydrodeoxygenation over supported Ni-based catalysts

Entry	Catalyst^a	LA of Ni^b (mmol g^{-1})	Conversion^c (%)	Yield^c(%)			
				(1)	(2)	(3)	Others^d
1	Ni-Sn(*1.5*)/γ-Al_2O_3	2.4	59	40	1	4	14
2^e	Ni-Sn(*1.5*)/γ-Al_2O_3	2.4	89	57	0	4	28
3	Ni-Sn(*1.5*)/TiO_2	2.5	85	80	0	3	2
4^e	Ni-Sn(*1.5*)/TiO_2	2.5	97	90	0	6	1
5^f	Ni-Sn(*1.5*)/TiO_2	2.5	85	83	0	1	1
6^g	Ni-Sn(*1.5*)/TiO_2	2.5	11	0	0	0	10
7	Ni/γ-Al_2O_3	2.7	55	23	0	7	25
8	Ni/TiO_2	2.6	41	39	0	2	0
9	Sn/γ-Al_2O_3	3.7	0	0	0	0	0
10^h	Ni-Sn(*1.5*)/γ-Al_2O_3	2.4	>99	85	0	9	6

Reaction conditions: Catalyst, 0.065 g; dodecanoic acid, 3.2 mmol; *iso*-PrOH, 5 mL, 160 °C; H_2 pressure 30 bar, reaction time is 6 h. ^{a}The value in the parenthesis is Ni/Sn molar ratio. ^{b}Loading amount of Ni metal, determined by ICP-AES. ^{c}Conversion and selectivity of the main products were determined by GC using an internal standard technique. Product *(1)* = dodecane-1-ol, *(2)* dodecane-1,1-diol, and *(3)* dodecane. ^{d}Other products were mainly C_{11} hydrocarbon including undecane ($C_{11}H_{24}$), undecene ($C_{11}H_{22}$), and trace amount of cracking product like 1-pentylbenzene was identified by using GC-MS analysis. ^{e}Reaction time was 16 h. ^{f}Re-usability test (second reaction run) after the recovered Ni-Sn(*1.5*)/TiO_2 was re-activated by reducing with H_2 at 400 °C for 1.5 h. ^{g} The catalytic reaction in absence of H_2 gas. ^{h}Reaction temperature was 180 °C, reaction time 6 h.

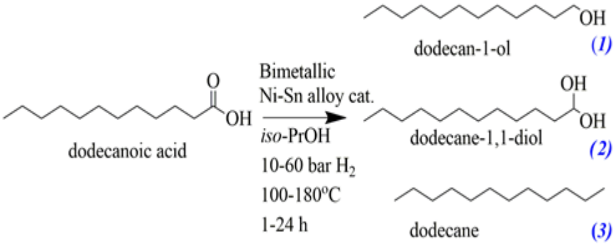
(85 % conversion and 83 % yield, entry 5). Catalytic reaction over Ni-Sn(*1.5*)/TiO_2 catalyst in absence of H_2 gas gave dodecanoic acid conversion of 11 % without the formation of hydrogenated products (entry 6). Compared to the supported bimetallic catalysts, monometallic Ni/γ-Al_2O_3 and Ni/TiO_2 catalysts exhibited lower activity under the same reaction conditions (entries 7 and 8). Moreover, Sn/AlOH was not active as catalysts and did not produce the hydrogenated products under the same conditions (entry 9). In addition, Ni-Sn(*1.5*)/γ-Al_2O_3 catalyst produced dodecane-1-ol (85 %), dodecane (9%), and other products (6 %) when the reaction temperature was 180 °C within 6 h (entry 10).

3.2.2 Profile of reaction kinetics

Kinetics of the hydrogenation of dodecanoic acid over bimetallic Ni-Sn(*1.5*)/TiO_2 and Ni-Sn(*1.5*)/γ-Al_2O_3 catalysts are shown in Figure 5. When Ni-Sn(*1.5*)/γ-Al_2O_3 catalyst was used, dodecanoic acid was slowly increased at the initial reaction time to achieve a 93 % yield after 24 h. 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^{n+}) from metallic tin (Sn^0), as reported by Sordelli *et al.* (Rh-Sn) [28] and Margitfalvi *et al.* (Pt-Sn) [29]. Since the crystallite size or dispersion of Ni-Sn alloy could affect the length of the induction period, the induction period of Ni-Sn(*1.5*)/TiO_2 diminished, and a 100 % dodecanoic acid conversion (~90 % dodecane-1-ol yield) was achieved after 20 h. The excellent catalytic performance of Ni-Sn(*1.5*)/TiO_2 produces a promising candidate suitable for the large-scale production of dodecane-1-ol from the selective hydrogenation of dodecanoic acid.

3.2.3 Effect of reaction temperature

The effect of reaction temperature on the catalytic performance of Ni-Sn(*1.5*)/TiO_2 in dodecanoic acid hydrogenation are also investigated and the results are shown in Figure 6. The conversion of dodecanoic acid gradually increased as the increase of reaction temperature and reached to completed reaction at 180 °C within 6 h with dodecane-1-ol yield of 91 % (entry 4). A small amount of dodecane (4 % yield) and other products (total yield of 12 %) were observed at 100 °C and diminished at higher reaction temperature. These results indicated that further reaction of dodecane-1-ol did not occurred effectively over Ni-Sn(*1.5*)/TiO_2 catalyst.



Scheme 1. Hydrogenation of dodecanoic acid over supported bimetallic Ni-Sn(1.5) alloy catalysts.

3.2.4 Effect of initial pressure of H_2

The effect of the initial H_2 pressure on the dodecanoic acid conversion and product selectivity is shown in Figure 7. The conversion of dodecanoic acid and dodecane-1-ol yield increased, whereas the selectivity of (2), (3), and other products decreased smoothly to almost 0% between 40-60 bar. The highest yield of dodecane-1-ol (97 %) was achieved at initial pressure H_2 of 50-60 bar, suggesting the hydrogenation reaction of dodecanoic acid to dodecane-1-ol over Ni-Sn(*1.5*)/TiO_2 catalyst can be proceed effectively under relatively high pressure of H_2. These results are consistent with the low H_2 uptake of bimetallic Ni-Sn(*1.5*)/TiO_2.

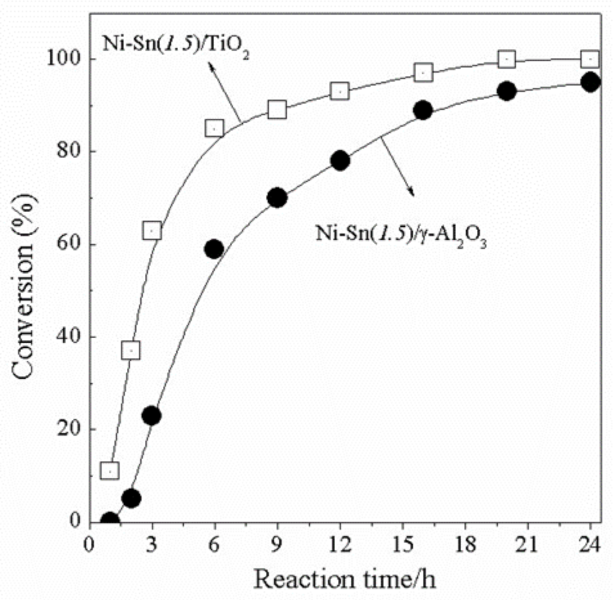


Figure 5. Kinetics of the hydrogenation of dodecanoic acid over bimetallic Ni-Sn(*1.5*)/TiO_2 and Ni-Sn(*1.5*)/γ-Al_2O_3 catalysts. Reaction conditions: Catalyst, 0.065 g; dodecanoic acid, 3.2 mmol; *iso*-PrOH, 5 mL, 160 °C; H_2 pressure 30 bar, reaction time is 1-24 h

4. Conclusion

Selective hydrogenation of dodecanoic acid into dodecane-1-ol over supported bimetallic Ni-Sn alloy catalysts is demonstrated. Bimetallic Ni-Sn(*1.5*)/TiO_2 catalyst was found to be effective for hydrogenation of dodecanoic acid (>99 % conversion) to dodecane-1-ol (93 % yield) at 160 ^oC, 30 bar H_2, and 20 h and the highest dodecane-1-ol (97 % yield) was obtained at initial pressure of H_2 50 bar. An increase of reaction temperature slightly enhanced the degree of hydrodeoxygenation of dodecanoic acid to produce dodecane over both Ni-Sn(*1.5*)/TiO_2 and Ni-Sn(*1.5*)/γ-Al_2O_3 catalysts.

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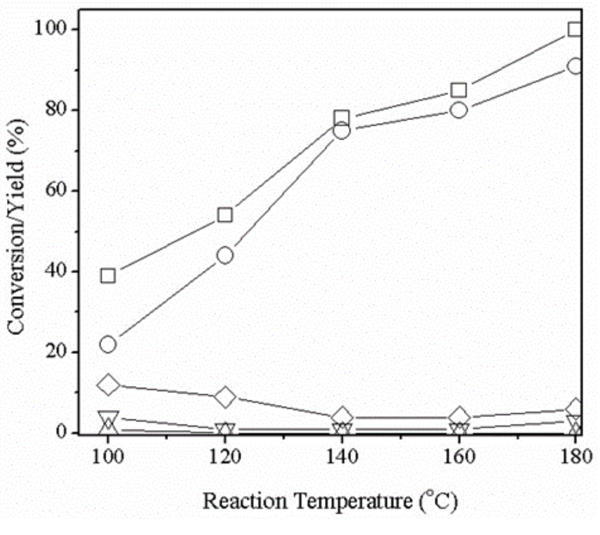

Figure 6. Results of dodecanoic acid hydrogenation over Ni-Sn(*1.5*)/TiO_2 at different reaction temperature. *Reaction conditions:* Catalyst, 0.065 g; dodecanoic acid, 3.2 mmol; *iso*-PrOH, 5 mL; reaction temperature, 100-180 ^oC; H_2 pressure 30 bar; reaction time is 6 h. (□) Conversion of dodecanoin acid. (○) Yield of dodecane-1-ol. (△) Yield of dodecane-1,1-diol, and (▽) Yield of dodecane. (◇) Other products.

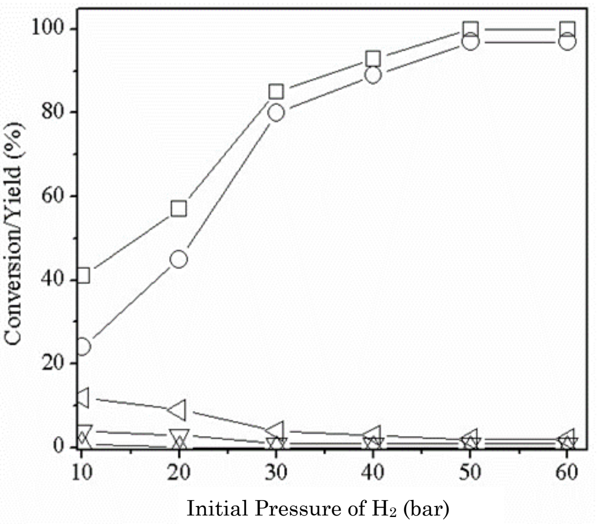

Figure 7. Results of dodecanoic acid hydrogenation over Ni-Sn(*1.5*)/TiO_2 at different initial pressure of H_2. *Reaction conditions:* Catalyst, 0.065 g; dodecanoic acid, 3.2 mmol; *iso*-PrOH, 5 mL, 160 ^oC; H_2 pressure 10-50 bar; reaction time is 6 h. (□) Conversion of dodecanoin acid. (○) Yield of dodecane-1-ol. (△) Yield of dodecane-1,1-diol, and (▽) Yield of dodecane. (◇) Other products.

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