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Selective Hydrogenation of Stearic Acid to 1-Octadecanol Using Bimetallic Palladium-Tin Supported on Carbon Catalysts at Mild Reaction Conditions

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Abstract

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Bimetallic palladium-tin catalysts supported on microporous carbon (denoted as Pd-Sn(x)/C, loading amount of Pd = 5 wt% and $x = \text{Pd/Sn}$ molar ratio; *c.a.* 3.0; 1.5; and 1.0) showed high selectivity in the hydrogenation of stearic acid towards 1-octadecanol (stearyl alcohol) under mild reaction conditions. Pd-Sn(x)/C catalysts were synthesized via the hydrothermal method at temperature of 150 °C for 24 h, and reduced with H₂ at 44 °C for 3 h. Pd-Sn(1.5)/C catalyst exhibited the highest yield of stearyl alcohol (1-octadecanol) (up to 73.2%) at 100% conversion of stearic acid at temperature 240 °C, initial H₂ pressure of 3.0 MPa, reaction time of 13 h, and in 2-propanol/water solvent. The high selectivity of alcohols over Pd-Sn(1.5)/C catalyst can be attributed to the formation of bimetallic Pd-Sn alloy phases (*e.g.* Pd₃Sn and Pd₃Sn₂) as obviously depicted by XRD analysis. The presence of co-promotor Sn and the formation of bimetallic may play a pivotal role in the high selectivity of 1-octadecanol.

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Keywords: hydrogenation; stearic acid; 1-octadecanol; bimetallic Pd-Sn catalyst

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1. Introduction

Fatty alcohols are non-ionic surfactants widely used as lubricants, emulsifiers, polymers, oil additives, emollients and thickeners in

alimentary, cosmetic industries, and intermediate of biofuel synthesis [1]. Fatty alcohols can be produced from the catalytic hydrogenation of fatty acids using both heterogeneous and homogeneous catalysts is the important step in the transformation of biobased resources [2–7]. Commercially, the production of fatty alcohols involves methanolysis of triglycerides or fatty

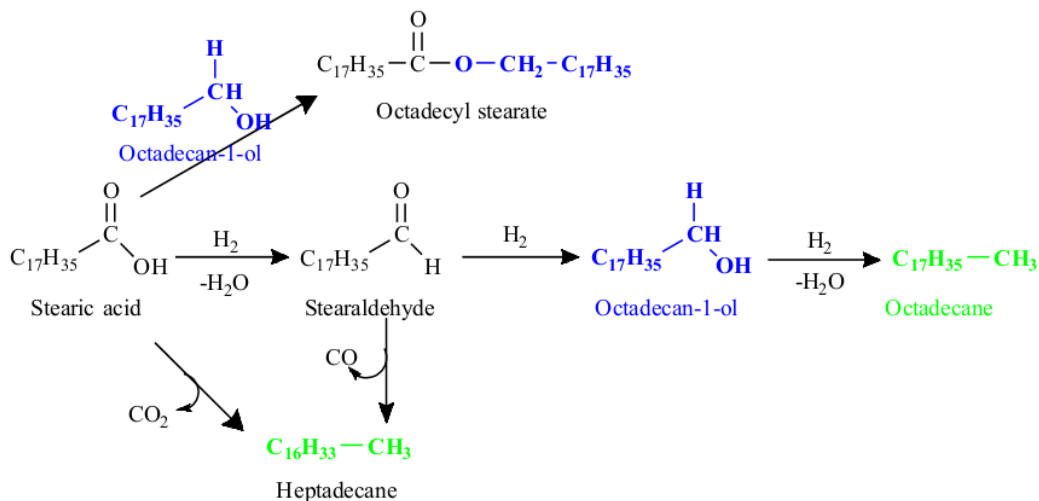
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acids, followed by hydrogenolysis using copper chromite catalysts at temperatures ranging from 200 to 400 °C and H₂ pressures of 20–50 MPa [8–10]. In this regard, the development of catalysts to produce fatty alcohols under milder conditions has been a long-standing industrial target. Moreover, chromium catalysts are not environmentally friendly; therefore, the development of chromium-free catalysts is highly desired in order to reduce the environmental pollution.

Since the catalytic conversion of biomass-derived fatty acids involved the decarbonylation, decarboxylation, and deoxygenation/hydrogenation reactions, the yield of desired products may be depended on the catalyst types or/and the reaction conditions [9,11–13]. Noble platinum metal group (PGM), such as Ru, Rh, Pd catalysts, were reported to be active in the selective hydrogenation of fatty acids, however the selectivity towards desired product of fatty alcohols was in wide range of moderate to high [14]. To enhance the selectivity of PGM metal catalysts, the modification of those metals is necessary; *i.e.* the addition of more electropositive metals (*e.g.* Sn and In) [15,16] or oxophilic metal oxides, such as MoO_x and ReO_x [17], or the use of oxide supports that strongly interact with the active metals (*e.g.* TiO₂ and Nb₂O₅) [18,19]. Many kinds of Ru-based catalysts have been studied [20–23], from which bimetallic supported Ru₃Sn₇ nanocluster catalyst showed the highest selectivity towards fatty alcohols (240 °C, 4.0 MPa H₂, and 120 min) in coconut oil hydrogenation

[24]. A maximum yield of fatty alcohol was 98.6%, which obtained using Ru₃Sn₇ nanocluster containing trace amount of SnO species [25,26]. Pt/TiO₂ catalyst was reported to be effective for carboxylic acids hydrogenation, and enhanced hydrogenation activity could be achieved after modified catalyst with Re without the alcohol selectivity loss [27]. Tomishige and co-workers reported that a moderate conversion of stearic acid (79%) to stearyl alcohol with selectivity up to 90% at mild reaction conditions (2.0 MPa, 130 °C) was achieved by using oxometallic rhenium oxide-platinum supported on titanium oxide (Pt-Re/TiO₂) catalyst [28,29]. The presence ReO_x species in ReO_x-Pd/SiO₂ greatly improved the hydrogenation rate of stearic acid conversion to high selectivity of 1-octadecanol. The high catalytic activity of ReO_x-Pd/SiO₂ could be attributed to the presence of the intermediate oxidation state of Reⁿ⁺ such as Re³⁺ and/or Re⁴⁺ that can play a crucial role on the formation of the catalytically active site [29]. Moreover, Murzin *et al.* [30] reported that 4wt%ReO_x/TiO₂ catalyst showed high conversion of stearic acid to high yield of 1-octadecanol (>93%) at 200 °C and 4.0 MPa H₂. They reported that a high yield of 1-octadecanol was attributed to a long adsorption of the acid compared to alcohol on the catalyst, which inhibits further alcohol transformation to alkanes [30]. However, the use of noble metal-based catalysts and low substrate loading is not economic and less viability in the upgrading of biomass-derived platform industry. Therefore,



Scheme 1. Conceived reaction routes for the catalytic transformation of stearic acid to stearyl alcohol (1-octadecanol) using heterogeneous catalysts.

alternative economical and eco-friendly heterogeneous catalysts that would ensure the preferred hydrogenation of the carboxylic acids (fatty acid) to fatty alcohols are highly desired (Scheme 1).

Palladium catalysts were disclosed in the patent and journal literatures as being capable of hydrogenating of carbonyl compounds to alcohols and high overall activity in the deoxygenating carboxylic acid to alkanes under hydrothermal atmosphere [31,32]. Commercial 5 wt% Pd/C catalyst has been studied extensively for deoxygenation of fatty acid to alkanes at temperature of 160–230 °C both in presence or in absence of hydrogen [33–37]. Moreover, bimetallic unlike tin modified-Ru or rhenium oxide modified-Pt catalysts, the utilization of bimetallic palladium-tin (Pd–Sn) catalysts for the hydrogenation of carboxylic acid to alcohols are rarely investigated. Ru–Sn catalyst have showed to be superior heterogeneous catalysts for the selective synthesis of fatty alcohols from fatty acids [5,38]. The obtained yield of GVL over bimetallic Ru–Fe/TiO₂ was 52.4% that much higher than that of monometallic counterpart Ru/TiO₂ (22.7%) [39]. In this regard, Damayanti et al. reported the use of bimetallic Pd–Fe/TiO₂ catalyst for the hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL) at 170 °C, 3.0 MPa H₂ for 7 h. Bimetallic Ni–Sn(1.5)/TiO₂ catalyst showed high yield of lauryl alcohol at (97%) at >99% conversion of lauric acid at 160 °C, 3.0 MPa H₂ for 20 h [40]. Additionally, in our recent published work, we reported that the promotion effect of Cu in bimetallic Pd–Cu/C catalyst greatly increased the affinity of Pd–Cu toward hydrogenation of carbonyl group of unsaturated compounds, leading to high selectivity of unsaturated alcohols [41].

In this paper, we report the selective hydrogenation of stearic acid to 1-octadecanol (stearyl alcohol) using supported bimetallic palladium-tin on microporous carbon (denoted as Pd–Sn(x)/C, loading amount of Pd is 5 %wt and $x = \text{Pd/Sn}$ molar ratio; *c.a.* 3.0; 1.5; and 1.0) catalysts under moderate reaction conditions. Pd–Sn(x)/C catalyst has been synthesized via the hydrothermal method at temperature of 150 °C for 24 h, and reduced with H₂ at 400 °C for 3 h. Pd–Sn(1.5)/C catalyst exhibited the highest yield of 1-octadecanol (121%) at 100% stearic acid conversion at 240 °C, 3.0 MPa H₂, in 2-propanol/H₂O and after 13 h. The effect of reaction temperature, initial H₂ pressure, and reaction time on the conversion and product distribution is discussed systematically.

2. Materials and Methods

2.1 Materials

Palladium (II) acetate (Pd(CH₃COO)₂; 98%) and tin (II) chloride dihydrate (SnCl₂·2H₂O; 99%) were purchased from WAKO Pure Chemical Industries, Ltd), active carbon ($S_{\text{BET}} = 815 \text{ m}^2/\text{g}$), Y-Zeolit, HZSM-5 Si/Al 85 ($S_{\text{BET}} = 417 \text{ m}^2/\text{g}$; $V_p = 0.225 \text{ cm}^3/\text{g}$; pore diameter = 3.64 nm), Nb₂O₅ dan TiO₂ anatase were purchased and used as received from WAKO Pure Chemical Industries, Ltd. γ -Al₂O₃ ($S_{\text{BET}} = 100 \text{ m}^2/\text{g}$) was purchased from Japan Aerosil Co. Commercial 5 wt% Pd/C, Ethanol (96.0%; Merck Millipore), ethylene glycol (EG) (99.5%; Merck Millipore), NaBH₄ (95.0%; Tokyo Chemical Industry(TCI)), NaOH (99.0%; Merck Millipore), Stearic acid (98%; TCI), 1-octadecanol (98%; TCI), heptadecane (99%; TCI), dodecane (99%, TCI) were purchased from Tokyo Chemical Industries Co. (TCI) and used as received.

2.2 Methods

2.2.1 Catalyst preparation

A typical procedure of the synthesis of supported bimetallic Pd–Sn(1.5)/C (Pd = 5 wt% and Pd/Sn feeding molar ratio of 1.5) catalyst is described as follows [42]: Pd(CH₃COO)₂ (0.4613 mmol) was dissolved in deionised water (denoted as solution A), and SnCl₂·2H₂O (0.2947 mmol) was dissolved in ethanol/ethylene glycol (20: 10 v/v ml) (denoted as solution B) at room temperature. Solutions A and B, and 1.0 g of support (microporous C; $S_{\text{BET}} = 815 \text{ m}^2.\text{g}^{-1}$) were mixed at room temperature; the temperature was subsequently raised to 50 °C and the mixture was gently 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 or 6.0 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 reduced with hydrogen (H₂) gas at 400 °C for 3 h [43]. For comparison and study of support effects, Pd–Sn(1.5) supported on various support materials such as Nb₂O₅, TiO₂, γ -Al₂O₃, and typical Y-zeolite and HZSM-5 were also prepared using the same procedure.

2.2.2 Characterizations

The prepared catalysts were characterized by powder X-ray diffraction on a RIGAKU MINIFLEX 600 instrument using monochromatic CuK α radiation ($\lambda = 0.15418$ nm). It was operated at 40 kV and 20 mA with a step width of 0.02° and a scan speed of 5° min^{-1} . The mean crystallite size of Ni was calculated from the full width at half maximum (FWHM) of the Pd(111) diffraction peak according to the Scherrer's equation.

Nitrogen adsorption isotherms at -196°C were measured using a μ sorp 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 specific surface area by means of the BET equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.995. The Barrett–Joyner–Halenda (BJH) and Horvath–Kawazoe (HK) approaches were used to calculate total pore volume and pore size distribution from desorption data [44].

The ammonia-temperature programmed-desorption (NH_3 -TPD) was carried out on a Bel-sorp 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 373 K 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 – 900°C and the desorbed NH_3 was monitored by TCD.

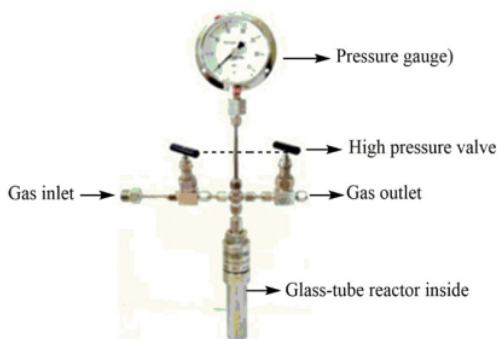


Figure 1. Typical batch system reactor of TAI-ATSU techno with glass-fitted inside (volume: 30 mL, max. 35 MPa, 300°C).

The active surface areas were determined by H_2 chemisorption. After the catalyst was heated at 120°C under vacuum for 30 min, it was heated at 400°C under H_2 for 30 min and under vacuum for 30 min, followed by evacuation to room temperature for 30 min. The adsorption of H_2 was conducted at 0°C . The active surface area was calculated from the volume of H_2 desorbed by assuming an H/Pd stoichiometry of one, respectively and the number of Pd atom for the (111) plane is 1.5×10^{15} per cm^2 Pd based on an equal distribution of the three lowest index planes of Pd [45].

The interaction of reactant and product adsorbed on the surface of catalyst post the reaction was monitored by attenuated total reflection-infrared (ATR-IR) using Bruker Diamond at wavenumber of 400 – 4000 cm^{-1} .

2.2.3 Catalytic reactions testing

A typical procedure for hydrogenation of stearic acid is described as follows: catalyst Pd–Sn(1.5)/C (0.05 g), stearic acid (0.2844 g; 1.0 mmol), 2-propanol: H_2O (5 ml; 4.0: 1.0 v/v) as solvent were placed into a glass reaction tube, which fitted inside a stainless steel reactor (Figure 1). After H_2 was introduced into the reactor with an initial H_2 pressure of 3.0 MPa at room temperature, the temperature of the reactor was increased to 240°C using electric furnace, 800 rpm. After 7 h, the reactor was cooled to room temperature, internal standard of dodecane was added and the conversion of stearic acid and the yield of 1-octadecanol were determined by GC analysis. The Pd–Sn(1.5)/C catalyst was easily separated using either simple centrifugation or filtration.

2.2.4 Product Analysis

GC analysis of the reactant (stearic acid) and products (1-octadecanol, ester, and heptadecane) was performed on a Perkin Elmer Auto System XL equipped with a flame ionization detector and a Thermo Scientific capillary column (id = 0.25 mm; length = 15 m; and od = $0.25 \mu\text{m}$). It was operated under following conditions: injector and detector temperatures (250°C); air flow (450 mL/min); H_2 flow (45 mL/min); N_2 flow (14 mL/min); and split ratio of 50:1. Temperature column has set gradually into two steps (first: 100 – 220°C (ramping of 20°C/min) and second: 220 – 300°C (ramping of 18°C/min). Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and an RT- β DEXm capillary column. The products were confirmed

by a comparison of their GC retention time, mass spectra with those of authentic samples. The conversion, yield and selectivity of the products were calculated according to the following equations:

$$\text{Conversion} = \frac{F_0 - F_t}{F_0} \times 100\% \quad (1)$$

$$\text{Yield} = \frac{\text{mol product}}{\Delta F} \times 100\% \quad (2)$$

$$\text{Selectivity} = \frac{\text{mol product}}{\text{total mol product}} \times 100\% \quad (3)$$

where, F_0 is the introduced mol reactant (stearic 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.

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3. Results and Discussion

3.1 Catalyst characterization

The N_2 -adsorption/desorption of microporous carbon (C) support and the synthe-

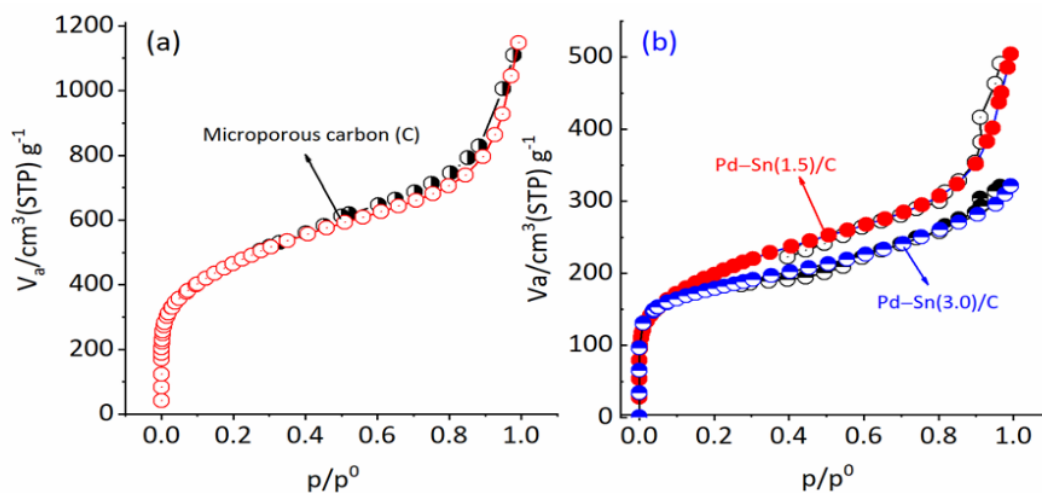


Figure 2. N_2 -adsorption/desorption profiles of (a) microporous carbon (C) and (b) the synthesized Pd-Sn(3.0)/C and Pd-Sn(1.5)/C catalysts after reduction with H_2 at 400 °C for 3 h.

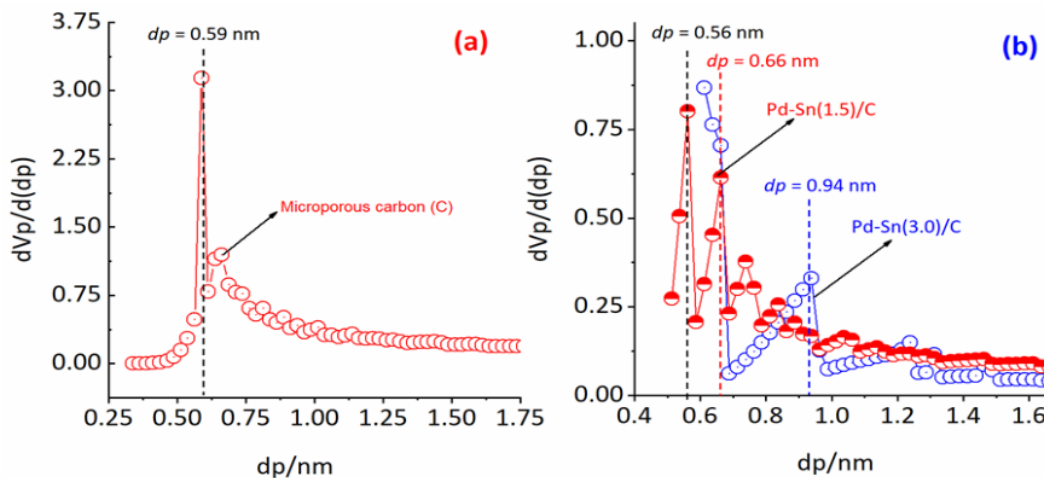


Figure 3. Pore distribution of (a) microporous carbon (C) and (b) the synthesized bimetallic Pd-Sn(3.0)/C and Pd-Sn(1.5)/C catalysts after reduction with H_2 at 400 °C catalysts using HK approach.

sized bimetallic Pd-Sn(3.0)/C and Pd-Sn(1.5)/C catalysts was performed and the profiles are shown in Figure 2. The hysteresis loop of adsorption/desorption of both the synthesized Pd-Sn(3.0)/C and Pd-Sn(1.5)/C samples show a very similar to that of former microporous carbon support, suggesting that there is no significant change of the pore structure of catalyst support during the introducing Pd and Sn metals or thermal activation using N₂ or H₂ at 400 °C. It has been reported that carbon support has high thermal and chemical stability at the range of 300–500 °C under H₂ or N₂ atmosphere [31,46].

To determine the pore size distribution of microporous carbon C support and the synthesized catalysts, the plot of volume of adsorbed-N₂ versus pore distribution using Horvath-Kawazoe (HK) approach were performed as

shown in Figure 3. As expected, the microporous carbon (C) support shows the microstructure of carbon with narrow pore size distribution of 0.59–0.66 nm (Figure 3a). After introduction of Pd-Sn, the shift of pore size distribution at ≥ 0.66 nm for after reduction with H₂ at 400 °C and recovered samples are clearly observed (Figure 3b). However, there is no clear evidence for the shift of pore size distribution towards small pore sizes or big pore sizes after introducing the Pd-Sn species or thermal activation using N₂ or H₂ at 400 °C.

To confirm the importance of catalyst acidity, ammonia-temperature programmed desorption (NH₃-TPD) was performed (Figure 4) and the results are summarized in Table 1. Microporous carbon and commercial 5wt% Pd/C have total acidity of 0.019 mmol.g⁻¹ and 0.103 mmol.g⁻¹, respectively which mainly consisted

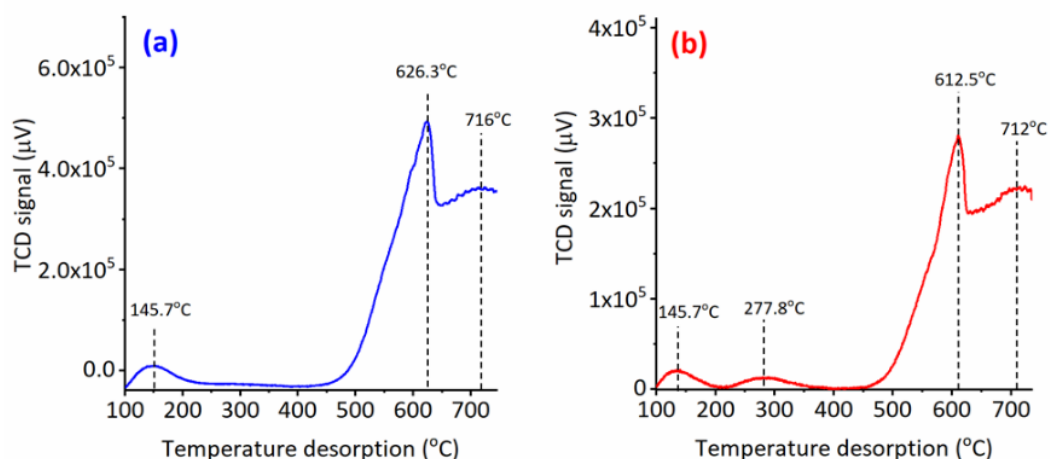


Figure 4. Typical ammonia-temperature programmed desorption (NH₃-TPD) profiles of the synthesized (a) Pd-Sn(3.0)/C and (b) Pd-Sn(1.5)/C catalysts after reduction with H₂ at 400 °C.

Table 1. Physicochemical properties of the synthesized supported bimetallic Pd-Sn(1.5)/C catalysts.

| Entry | Catalysts ^a | LA ^a (mmol.g ⁻¹) | | S _{BET} ^b (m ² .g ⁻¹) | Pore vol. ^b (cm ³ .g ⁻¹) | PSD ^b (nm) | H ₂ uptake ^c (mmol.g ⁻¹) | Total acid sites ^d (mmol.g ⁻¹) | D ^e (nm) |
|----------------|------------------------|--|-------|---|---|--------------------------|---|--|------------------------|
| | | Pd | Sn | | | | | | |
| 1 | Micro. carbon (C) | - | - | 815 | 1.762 | 0.59 | NA | 0.019 ^f | NA |
| 2 | 5wt% Pd/C | 0.498 | - | 936 | 0.431 | 0.98 | 25.3 | 0.103 | NA |
| 3 | Pd-Sn(3.0)/C | 0.458 | 0.154 | 637 | 0.49 | 0.94 | 26.7 | 0.338 | 8.1 |
| 4 | Pd-Sn(1.5)/C | 0.461 | 0.295 | 719 | 0.769 | 0.66 | 19.2 | 0.418 | 9.9 |
| 5 ^g | Pd-Sn(1.5)/C rec. | 0.461 | 0.295 | 677 | 0.551 | 0.56 | - | - | - |

^aValues in the parentheses are the Pd/Sn molar ratios determined by ICP-OES; LA = loading amount. ^bDetermined by N₂ adsorption at -196 °C; pore sizes distribution (PSD) was calculated by using Horvath-Kawazoe's approach. ^cBased upon the total H₂ uptake at 0 °C (after corrections for physical and chemical adsorption). ^dTotal acid sites were derived from NH₃-TPD data. ^eAverage Pd(111) or Pd-Sn crystallite sizes were calculated according to the Scherrer equation. ^fMicroporous carbon was calcined at 573 °C for 4 h under N₂ atmosphere [47]. ^gRecovered Pd-Sn(1.5)/C after the first reaction run. NA = not available.

of weak acidity (entries 1 and 2). After introducing Sn loading amount of 0.0154 mmol.g⁻¹ and 0.295 mmol.g⁻¹, the total acidity of Pd-Sn(3.0)/C (Figure 4a) and Pd-Sn(1.5)/C

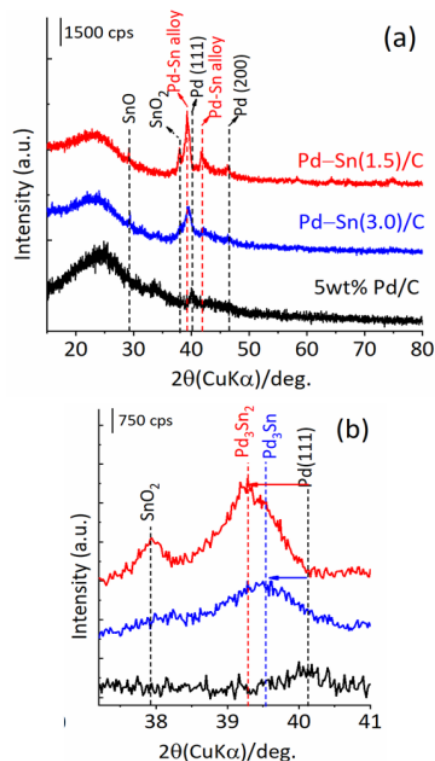


Figure 5. (a) XRD patterns of commercial 5 wt% Pd/C and the synthesized bimetallic Pd-Sn(3.0)/C and Pd-Sn(1.5)/C after reduction with H₂ at 400 °C for 3 h. (b) Selected diffraction peaks (2θ = 37–41°) of each samples.

(Figure 4b) remarkable increased to 0.338 mmol.g⁻¹ and 0.418 mmol.g⁻¹, respectively (entries 3-4). There was a significant different in the total acidity of Pd-Sn/C with different Sn loading amounts, suggesting that the effect of total acidity may be played important role during the selective hydrogenation of stearic acid to 1-octadecanol (stearyl alcohol) under the current operating conditions.

Figure 5 shows the XRD pattern of commercial 5wt% Pd/C, pre-reduced bimetallic Pd-Sn(3.0)/C and Pd-Sn(1.5)/C catalysts. The commercial 5wt% Pd/C exhibited a typical diffraction peak of metallic Pd(111) at 2θ = 40.18° (Figure 5(a)). In the case of Pd-Sn(3.0)/C catalyst, the typical diffraction peaks at 2θ = 29.4°, 39.5°, 42.1°, and 46.5° were clearly observed, which can be attributed to the tin oxide (SnO) and metallic Pd(111) and Pd(200) phases (JCPDS#05-0681), respectively [48]. A significant shifting the diffraction at 2θ = 40.2° of former Pd/C toward lower angle in Pd-Sn(3.0)/C (2θ = 39.5°) can be suggested due to the modified surface structure of Pd(111) in the presence of Sn promoter either to form surface bimetallic or alloy Pd-Sn (Figure 5b) [49,50]. Further increasing the Sn loading amount (Sn = 0.295 mmol) to form Pd-Sn(1.5)/C catalyst, two diffraction peaks of Pd-Sn alloy at 2θ = 39.3° and 41.8° which assigned as Pd-Sn alloy phases are intensified. By using the Scherrer's equation, the average crystallite sizes of Pd(111) in Pd-Sn(3.0)/C and Pd-Sn(1.5)/C were 8.1 nm and 9.9 nm (Table 1), respectively at around of the overlapped diffraction peaks of Pd(111) and Pd-Sn alloy phase (Figure 5a-b). A small new peak was also observed at 2θ = 37.9°, which can be associated to SnO₂ species (JCPD#29-1484) both in the in Pd-Sn(3.0)/C and Pd-Sn(1.5)/C samples (Figure 5a).

Table 2. Results of solvent screening for hydrogenation of stearic acid using bimetallic Pd-Sn(1.5)/C catalyst.

| Entry | Solvent | Conversion ^a (%) | Yield ^b (%) | | |
|-------|---|-----------------------------|------------------------|-------|---------------------|
| | | | 1-Octadecanol | Ester | Others ^c |
| 1 | Methanol | 56.3 | 1.7 | 50.6 | 4 |
| 2 | Ethanol | 67.4 | 3.2 | 59 | 5.2 |
| 3 | 2-Propanol | 87.2 | 9.1 | 53 | 25.1 |
| 4 | H ₂ O | 17 | 7.1 | <0.1 | 9.9 |
| 5 | 1,4-Dioxane | 21.7 | 11.5 | <0.1 | 10.2 |
| 6 | Ethanol/H ₂ O (1:5: 0.5 v/v) | 89 | 13.7 | 61.3 | 14 |
| 7 | 1,4-Dioxane/H ₂ O (4.5: 0.5 v/v) | 49.2 | 21.2 | <0.1 | 28 |
| 8 | 2-Propanol/H ₂ O (4.5: 0.5 v/v) | 84.3 | 32.2 | 32.1 | 20 |

Reaction conditions: catalyst (0.05 g); stearic acid (0.344 g; 1.0 mmol); solvent (5.0 ml); temperature 240 °C; initial H₂ pressure (3.0 MPa); reaction time (7 h). ^aConversion was determined by GC using an internal standard technique. ^bYields were determined by GC using a GC area ratio according to GC-MS data. ^cOthers are included hydrocarbon and small part of unidentified products based on the GC-MS analyses data.

3.2 Catalytic Reaction Testing

3.2.1 Screening of solvent

In the first set experiment of catalytic reactions, the effect of solvent used on the conversion and yield in the hydrogenation of stearic acid over Pd-Sn(1.5)/C catalyst was studied and the results are summarized in Table 2. In alcoholic solvents (*e.g.* methanol, ethanol, and 2-propanol), as expected, the conversion of stearic acid was around 56–87% with very low yield of 1-octadecanol (1.7–9.1%), whereas the yield of stearic ester was obtained (entries 1-3). By using protic polar solvent (H₂O) or aprotic polar solvent (1,4-dioxane), the yields of 1-octadecanol were 7.1% and 11.5%, respectively (entries 4 and 5). The utilization of 1,4-dioxane solvent seems to be promising as indicated by relatively higher yield of 1-octadecanol than the others, however, 1,4-dioxane is relatively more expensive and somehow less environmentally friendly than that of alcoholic or water solvent.

Therefore, the mixture of H₂O and alcoholic as well as 1,4-dioxane solvents were examined for the hydrogenation of stearic acid to 1-octadecanol under the same reaction conditions. In 2-propanol/H₂O (4.5:0.5 v/v) and 1,4-dioxane/H₂O (4.5:0.5 v/v) solvents, the yield of 1-octadecanol slightly increased to 13.7% and 21.3%, respectively (entries 6 and 7). The highest yield of 1-octadecanol (32.2%) was obtained in 2-propanol/H₂O (4.5:0.5 v/v) solvent at 84.3% conversion (entry 8), therefore, the mixture 2-propanol/H₂O will be applied as a solvent for further catalytic reaction using various cata-

lysts (screening of catalyst) and optimization of reaction parameters such as temperature, initial H₂ pressure, time profiles, and reusability test.

3.2.2 Screening of catalyst

The catalytic reaction of stearic acid using various palladium-based catalysts were performed and the results are summarized in Table 3. By using a commercial Pd/C (Pd = 5 wt%) catalyst, a 79.3% conversion of stearic acid was obtained and produced only 7.1% yield of 1-octadecanol with side-products of ester (16.5%) and others mainly consisted of C₁₇–C₁₈ aliphatic hydrocarbon (55.7%) (entry 1). A remarkably high yield of C₁₇–C₁₈ aliphatic hydrocarbon was obtained, suggesting the deoxygenation (decarbonylation or decarboxylation) reaction of stearic acid under current operating reaction was occurred predominantly. Lamb *et al.* suggested that liquid deoxygenation of C₁₈ free fatty acid primarily occurred in the presence of a 5wt% Pd/C catalyst, led to high yield of heptadecane [37].

After introducing Sn = 0.1542 mmol to form Pd-Sn(3.0)/C (3.0 is Pd/Sn molar ratio; Pd is 5wt%; Sn = 0.1542 mmol) catalyst, stearic acid conversion slightly increased to 87.0% and the yield of 1-octadecanol remarkably increased to 27.4% (approximately 4-fold to Pd/C catalyst). However, yield of isopropyl stearate is remained high (29.3%), while other product reduced significantly to 30.3% (entry 2). A remarkable increase the yield of of

Table 3. Results of catalyst screening for hydrogenation of stearic acid to 1-octadecanol.

| Entry | Catalyst ^a | Conversion ^b (%) | Yield ^c (%) | | |
|----------------|---|-----------------------------|------------------------|--------------------|---------------------|
| | | | 1-Octadecanol | Isopropyl stearate | Others ^d |
| 1 | Pd/C ^e | 79.3 | 7.1 | 16.5 | 55.7 |
| 2 | Pd-Sn(3.0)/C | 87 | 27.4 | 29.3 | 30.3 |
| 3 | Pd-Sn(1.5)/C | 89.3 | 56.2 | 23.1 | 10 |
| 4 | Pd-Sn(1.0)/C | 63.8 | 28.2 | 25.6 | 10 |
| 5 ^f | Pd-Sn(1.5)/C | 73.5 | 49.7 | 17.4 | 6.4 |
| 6 | Pd-Sn(1.5)/TiO ₂ | 77.9 | 32.8 | 32.2 | 2.9 |
| 7 | Pd-Sn(1.5)/Nb ₂ O ₅ | 79.2 | 23.4 | 52.4 | 3.4 |
| 8 | Pd-Sn(1.5)/g-Al ₂ O ₃ | 84.4 | 32.5 | 45.3 | 6.6 |
| 9 | Pd-Sn(1.5)/Y-Zeolite | 46 | 11.7 | 29 | 5.3 |
| 10 | Pd-Sn(1.5)/HZSM-5 | 71.7 | 6.5 | 59.4 | 5.8 |

^aThe value in the parenthesis is Pd/Sn molar ratio; determined by ICP-OES. Reaction conditions: catalyst (0.05 g); stearic acid (0.2844 g; 1.0 mmol); solvent 2-propanol/H₂O; 5.0 ml; 4.0: 1.0 v/v; temperature 240 °C; initial H₂ pressure (3.0 MPa); reaction time (7 h). ^bConversion was determined by GC using an internal standard technique. ^cYields were determined by GC using GC area ratio according to GC-MS data. ^dOthers are included hydrocarbon and small part unidentified products using GC or GC-MS analyses. ^eCommercially available 5 wt% Pd/C. ^fReusability test of Pd-Sn(1.5)/C catalyst; recovered catalyst was reused directly without any further thermal treatment.

1-octadecanol of 56.2% (approximately 8-fold compared to Pd/C catalyst) at stearic acid conversion of 89.3% was obtained over Pd-Sn(1.5)/C catalyst (loading amount of Sn was 0.2947 mmol; Pd/Sn = 1.5), while the yield of ester and others significantly diminished to 23.1% and 10%, respectively (entry 3). The high yield of 1-octadecanol obtained over Pd-Sn(1.5)/C catalyst can be associated with the presence of bimetallic Pd-Sn alloy phases as depicted by XRD patterns (Figure 5). We believe that our Pd-Sn catalyst systems have a similar catalytic behaviour to that of Ru-Sn systems as had been reported by Desphande *et al.* [25,26]. They concluded that the highest activity and selectivity are attributed to Ru⁰ sites interacting with Sn²⁺ or Sn⁴⁺ Lewis acid sites via oxygen, wherein the Lewis acid preferentially activates C=O of the ester, facilitating hydrogen transfer from adjacent Ru-H sites. Most recently, Luo *et al.* suggested that two types of sites: (a) Ru⁰ interacting with Sn²⁺ or Sn⁴⁺ via the oxygen; (b) nanocluster Ru₃Sn₇ alloy, wherein ruthenium as well as tin is present in zero oxidation state (this may be present in small quantities on the surface) [24]. Moreover, further increasing the loading amount of Sn to 0.4613 mmol (Pd-Sn(1.0)/C), stearic acid conversion significantly decreased to 63.8% as well as the yield of 1-octadecanol (28.2%) (entry 4). The reusability test of Pd-Sn(1.5)/C catalyst was also performed and the results are also shown in Table 3, entry 5.

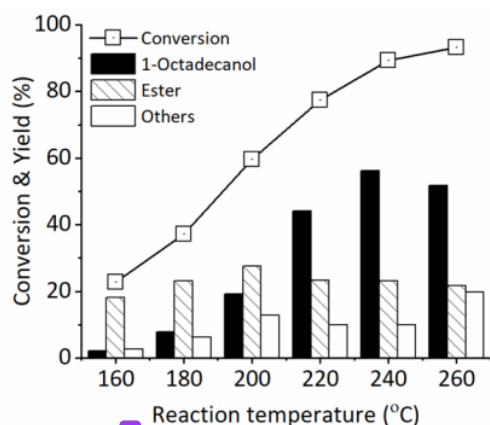


Figure 6. Effect of reaction temperature on conversion and yield in the hydrogenation of stearic acid using Pd-Sn(1.5)/C catalyst. Reaction conditions: catalyst (0.05 g); stearic acid (0.2844 g; 1.0 mmol); solvent (2-propanol/H₂O (5.0 ml; 4.0: 1.0 v/v); initial H₂ pressure (3.0 MPa); reaction time (7 h).

The conversion of stearic acid slightly decreased to 73.5% as well as the yield of 1-octadecanol (49.7%), isopropyl stearate (17.4%), and others (6.4%) (entry 5). Results of N₂-adsorption-desorption of the recovered Pd-Sn(1.5)/C showed that the S_{BET}, pore volume, and pore size distribution (PSD) slightly decreased, indicating the hydrothermal reaction conditions may affect the structure of catalyst (Table 1, entry 5).

To complete the catalyst screening tests, various supported Pd-Sn catalysts were synthesized and applied for the same catalytic reaction. TiO₂-, Nb₂O₅-, and γ-Al₂O₃-supported Pd-Sn catalysts demonstrated similar catalytic activity (78–84% conversion of stearic acid) and produced 23–32% yield of 1-octadecanol under the same reaction conditions (entries 6–8). The supported bimetallic nanoparticles could be synergistically catalyzed the hydrogenation of fatty acid to alcohols as reported by Slowing *et al.* [51], who applied copper oxide-iron oxide on mesoporous silica for stearic acid hydrogenation under moderate conditions. They claimed that in situ reduction of copper oxide to its metallic form thereby activates hydrogen, which can be spilled over to the iron oxide where stearic acid binds and are selectively reduced to 1-octadecanol [51]. Further optimization of reaction parameters using those catalysts are under investigation and will be reported in the upcoming manuscript. Moreover, Pd-Sn supported on zeolite matrixes, such as Y-zeolite and HZSM-5 catalysts, were also examined for the hydrogenation of stearic acid under the same reaction conditions. However, the results are unsatisfactory in terms of stearic acid conversion and yield of 1-octadecanol (entries 9–10). Therefore, it can be concluded that Pd-Sn(1.5)/C is the best catalyst for stearic acid hydrogenation and it will be examined for further evaluation of reaction parameters.

3.2.3 Effect of reaction temperature

The effect of reaction temperature on conversion and yield in the hydrogenation of stearic acid using Pd-Sn(1.5)/C catalyst was examined at the range of 160–260 °C and the results are shown in Figure 6. The reaction temperature notably affected the catalytic activity and product distribution. Stearic acid conversion was only 22.6% at 160 °C, yielding approximately 2.1% 1-octadecanol, 18.1% ester (isopropyl stearate) and other side-products were mainly C₃₆ compounds. Remarkably, both

the conversion of stearic acid (89.3%) and yield of 1-octadecanol (56.2%) immensely increased when the reaction temperature was increased to 240 °C. Further increasing the reaction temperature to 260 °C led to a 93.2% conversion of stearic acid, while the yield of 1-octadecanol slightly decreased to 51.7%. It should be noted that the yield of ester (isopropyl stearate) gradually increased as the reaction temperature increased to 200 °C, then decreased smoothly at reaction temperature over 220 °C. On the other hand, other products significantly increased at 260 °C, which can be rationalized due to the further hydrogenation reaction of formed ester to 1-octadecanol or dehydration-hydrogenation of 1-octadecanol to hydrocarbon (*e.g.*, octadecane). Further reactions would be occurred at high reaction temperature indicated by Wang *et al.*, who reported the hydrogenation of stearic acid to 1-octadecanol using bimetallic Ni-Fe alloy 250–270 °C [52]. Therefore, we concluded that the optimized reaction temperature for the hydrogenation of stearic acid using Pd-Sn(1.5)/C catalyst is 240 °C, which it will be used for evaluation of initial H₂ pressure and time profiles.

3.3.4 Effect of initial H₂ pressure

The effect of initial H₂ pressure on the conversion and yield in the hydrogenation of stearic acid using Pd-Sn(1.5)/C catalyst at 240 °C for 7 h was investigated and the results are

shown in Figure 7. The conversion of stearic acid increased slowly when the initial H₂ pressure increased up to 3.0 MPa, yielding the highest 1-octadecanol (56.2%) at 89.3% stearic acid conversion. When the initial H₂ pressure was furtherly increased to 4.0 MPa, stearic acid conversion was 90.3% and yielded 52.7% 1-octadecanol. It should be noted that the increase of initial H₂ pressure greatly affected to the decrease of intermediate ester product, leading to high yield of 1-octadecanol (Figure 7(a)). Therefore, it can be concluded that the optimized initial H₂ pressure would be 3.0 MPa. Turn over frequency (TOF) value was used to evaluate the intrinsic activity of Pd-Sn(1.5)/C catalyst with keeping the conversion of stearic acid lower than 20%. A linear relationship between ln (TOF) and ln initial H₂ pressure could be obtained, and the slope represented the reaction order with respect to hydrogen pressure (Figure 7(b)). The reaction order to hydrogen over Pd-Sn(1.5)/C catalyst was calculated to be 0.479, indicated that high accessibility of hydrogen and promoted the reaction rate of stearic conversion.

3.4.5 Time profiles

The kinetic study of stearic acid hydrogenation was carried out using Pd-Sn(1.5)/C catalyst at 240 °C, 3.0 MPa of H₂, in 2-propanol/H₂O solvent to understand the

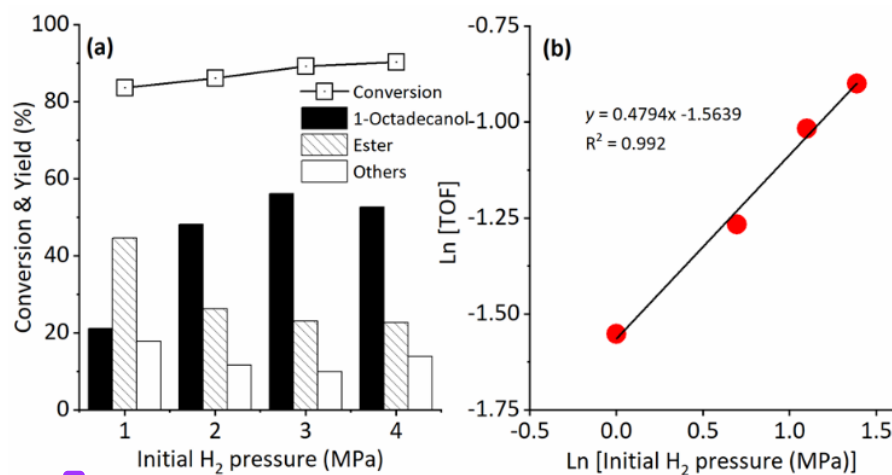


Figure 7. (a) Effect of initial H₂ pressure on conversion and yield in the hydrogenation of stearic acid using Pd-Sn(1.5)/C catalyst. Reaction conditions: catalyst (0.05 g); stearic acid (0.2844 g; 1.0 mm⁶); solvent (2-propanol/H₂O (5.0 mL; 4.0:1.0 v/v); reaction temperature (240 °C); reaction time (7 h). (b) the effect of initial H₂ pressure on the rate of reaction on Pd-Sn(1.5)/C catalyst at low level stearic conversion (~20%).

conversion of stearic acid and the evolution of product formation and the results are shown in Figure 8.

Stearic acid conversion was elevated smoothly and achieved 100% conversion when the reaction time was 13 h, yielding 73.2% 1-octadecanol, 15.3% ester (isopropyl stearat), and 11.5% others. The yield of isopropyl stearat slightly increased to 23.1% at a reaction time of 7 h, suggesting that the formation of isopropyl stearat was one of important intermediate then followed by its hydrogenation to form 1-octadecanol. To confirm this suggestion, the catalytic reaction of typical methyl stearate was performed under the same reaction conditions. A 65.4% conversion of methyl stearate and 37.6% yield of 1-octadecanol were obtained at 240 °C, 3.0 MPa H₂ and after 7 h.

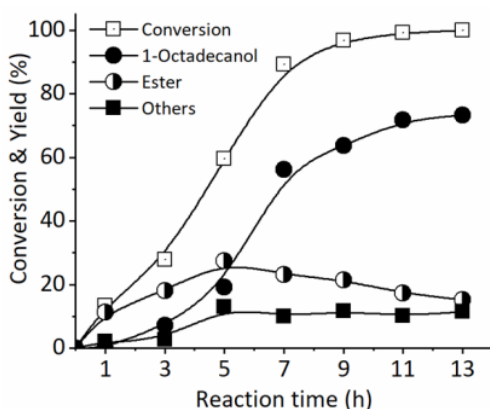


Figure 8. Time profiles of stearic acid hydrogenation using Pd-Sn(1.5)/C catalyst. Reaction conditions: catalyst (0.05 g); stearic acid (0.2844 g; 1.0 mmol); solvent (2-propanol/H₂O (5.0 mL; 4.0:1.0 v/v); reaction temperature (240 °C); initial H₂ pressure (3.0 MPa).

3.4.6 Catalytic reaction of various fatty acids

To gain the catalyst effectivity on the hydrogenation of carboxylic acids, the catalytic reactions of various fatty acids, esters and typical dicarboxylic acid (e.g., levulinic acid) were carried and the results are summarized in Table 4.

Oleic acid was converted to oleyl alcohol (48.2%), ester (14.5%) and others (20.3%) in the presence of Pd-Sn(1.5)/C catalyst (entry 1). The hydrogenation of methyl stearate yielded 63.2% stearyl alcohol (1-octadecanol) at 97% conversion of methyl stearate (entry 2). The conversion of methyl stearate is much higher than that of stearic acid under the same reaction conditions as mentioned above (Table 3, entry 3), suggesting the synthesis of fatty alcohols is more preferable from ester than that of its fatty acids [38]. Hydrogenation of palmitic acid gave 79.2% yield of 1-hexadecanol at 98.7% conversion (entry 3). When lauric acid and methyl laurate were used as substrate, the conversion were 100% and the high lauryl alcohol yields of 96–98% were obtained (entries 4-5), which are in good agreement with the previous results using Ni-Sn(1.5) alloy catalyst [40]. The hydrogenation of typical cellulosic biomass-derived levulinic acid yielded 99% of γ -valerolactone(GVL) without the formation of the side products (entry 6). This result indicates that the catalytic performances of bimetallic Pd-Sn alloy better than bimetallic Pd-Fe catalysts toward hydrogenation LA to GVL as reported by Damayanti *et al.* [39]. Moreover, the catalytic reaction of 1-octadecanol gave 24.7% yield of hydrocarbon (C18) and small amount of unidentified product under the same reaction conditions (entry 7). This result suggests that the further reaction of the formed alcohol to another side product was occurred during the hydrogenation

Table 4. Results of the hydrogenation of various fatty acid using Pd-Sn(1.5)/C catalyst.

| Entry | Substrate | Conversion ^a (%) | Yield ^b (%) | | |
|-------|-----------------|-----------------------------|------------------------|-------|---------------------|
| | | | Alcohol | Ester | Others ^c |
| 1 | Oleic acid | 83 | 48.2 | 14.5 | 20.3 |
| 2 | Methyl stearate | 97 | 69.2 | 0 | 27.8 |
| 3 | Palmitic acid | 98.7 | 79.2 | 9.5 | 10 |
| 4 | Lauric acid | 100 | 96 | 0 | 4 |
| 5 | Methyl laurate | 100 | 98.2 | 0 | 1.8 |
| 6 | Levulinic acid | 100 | 99 | <0.1 | <0.1 |
| 7 | 1-octadecanol | 24.7 | - | - | 24.7 |

Reaction conditions: catalyst (0.05 g); substrate (0.2844 g; 1.0 mmol); solvent (2-propanol/H₂O; 5.0 mL; 4.0:1.0 v/v); temperature 240 °C; initial H₂ pressure (3.0 MPa); reaction time (7 h). ^aConversion was determined by GC using an internal standard technique. ^bYields were determined by GC using GC area ratio according to GC-MS data. ^cOthers are included aliphatic hydrocarbon or unidentified products using GC or GC-MS analyses.

of stearic acid as indicated by the amount of others. To confirm this suggestion, ATR-IR analysis of the recovered catalyst was carried out and the results are shown in Figure 9. Two absorption peaks at wavenumber (ν) 1067 cm^{-1}

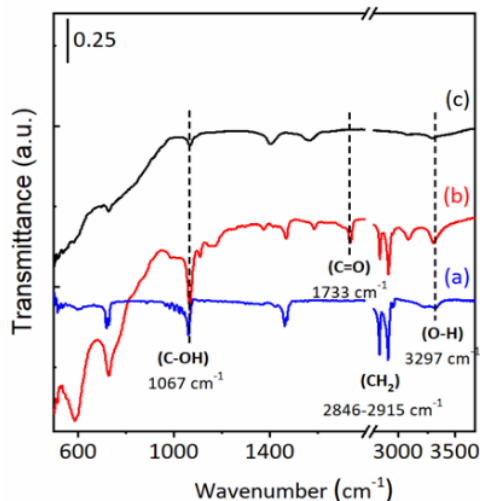
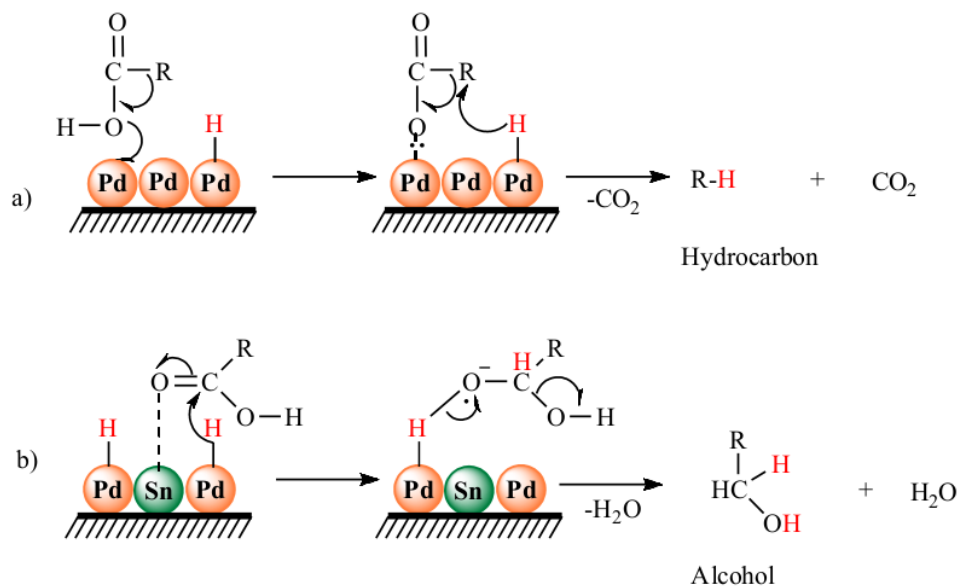


Figure 9. ATR-IR spectra of fresh and recovered catalysts and its possible interaction between Pd-Sn(1.5)/C catalyst and molecular reactant of stearic acid. (a) 1-octadecanol; (b) wetted recovered catalyst; (c) dried recovered catalyst.

and 3297 cm^{-1} that can be assigned as C–O and O–H stretchings, respectively. The presence of sharp peak at $2846\text{--}2915\text{ cm}^{-1}$ which can be assigned as --CH_2 was also clearly observed. A small peak at 1733 cm^{-1} was observed at Figure 9b, which can be attributed as the C=O functional group of remained stearic acid reactant. Additionally, the absorption peaks at around 1480 cm^{-1} and 720 cm^{-1} can be attributed as the $\text{sp}^3\text{ C-H}$ and $\text{sp}^2\text{ C-H}$ bends, respectively.

The profiles of reaction products obtained over Pd/C catalyst significantly shifted toward 1-octadecanol (stearyl alcohol) after the introduction of Sn to form bimetallic Pd–Sn(x)/C catalysts as already described above. The results of substrate scope, evaluation of reaction parameters, and ATR-IR analysis are obviously good agreement with the reaction products. Therefore, the possible reaction mechanism of stearic acid hydrogenation is proposed as shown in Scheme 2. It has been reported that the decarboxylation reaction of stearic acid was favorable occurred than that of hydrogenation in the presence of Pd/C catalyst and produced hydrocarbon (Scheme 2(a)). Our results are in good agreement with the previous reports [13,34]. On the other hand, the high selectivity of alcohol over Pd–Sn(x)/C catalysts may be due to the increased oxyphilicity of the surface associated with the Sn cations which interact with the lone electron pair of carbonyl group



Scheme 2. Possible reaction mechanism for the hydrogenation of stearic acid using a) supported monometallic Pd/C and b) supported bimetallic supported Pd–Sn catalysts.

oxygen, as depicted in Scheme 27). Takeda *et al.* suggested that Pd plays in a promoting the reduction and dispersion of Re species, and strengthening the interaction of stearic acid with the catalyst surface, while 7e presence of partially reduced Re promoted the heterolytic dissociation of H_2 then finally enhanced the hydrogenation of stearic acid to stearyl alcohol [29]. Desphande also suggested that the interaction of the substrate with tin on the catalyst surface favours the formation of carbanion and aldehyde as the intermediate then rapidly hydrogenate to alcohol [25]. Similarly, Pallassana *et al.* [53] and Olcay *et al.* [54] have reported that carboxylic acid was adsorbed on the surface of Pd^0 and Re^0 , and the activated heterolytically hydrogen as hydride species will attacks the adsorbed carboxylic acids and the hydrogenolysis of C-OH proceeds to give the adsorbed aldehyde which easily hydrogenate to alcohol.

4. Conclusions

We described the selective hydrogenation of stearic acid to corresponding alcohol using Pd-based catalysts under mild reaction conditions. Bimetallic palladium-tin catalysts supported on microporous carbon (denoted as Pd-Sn(x)/C, loading amount of Pd = 5 wt% and $x = Pd/Sn$ molar ratio; *c.a.*, 3.0; 1.5; and 1.0) showed high selectivity in the hydrogenation of stearic acid towards 1-octadecanol (stearyl alcohol). Pd-Sn(1.5)/C catalyst exhibited the highest yield of stearyl alcohol (1-octadecanol) (up to 73.2%) at 100% conversion of stearic acid at temperature 240 °C, initial H_2 pressure of 3.0 MPa, a reaction time of 13 h, and in 2-propanol/water solvent. The high selectivity of alcohols over Pd-Sn(1.5)/C catalyst can be attributed to the formation of bimetallic Pd-Sn alloy phases (*e.g.*, Pd_3Sn and Pd_3Sn_2) as obviously depicted by XRD analysis. The presence of co-promotor Sn and the formation of bimetallic may play a pivotal role in the high selectivity of 1-octadecanol.

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