Catalytic hydrogenation of stearic acid to 1-octadecanol using supported bimetallic Pd–Sn(3.0)/γ-Al2O3 catalyst

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1. Introduction

The depletion of fossil fuel pushed numerous scientists to have great attention to searching for new energy resources and strategies to meet the increasing energy demand. The production of biodiesel has been intensively studied in recent years, in part due to political decisions to increase the use of biofuels, especially biodiesel palm oil-based. For instance, the Indonesian government has set a target energy level mixed with B50 to fossil diesel by 2025 [1]. On the other hand, diesel-like hydrocarbons, consisting of C16 to C18 carbon atoms, provide good fuel properties, such as viscosity, cloud point, and boiling point [2]. Long-chain hydrocarbons can be produced from fatty acids and their derivatives via hydrodetergrent or catalytic hydrodeoxygenation (hydrogenation–dehydration–decarbonylation) [3]. The hydrogenation of fatty acids (e.g., stearic acid) to fatty alcohol using both heterogeneous and homogeneous catalysts is the crucial step in the transformation of biobased resources since fatty alcohol is widely used as the component of cosmetics, food ingredients, surfactant, plasticizer, lubricant, and intermediate of biofuel synthesis [4]. The use of homogeneous catalysts, such as Ru–Triphos complex [5] or iron–base PNP-pincer [6], showed high selectivity towards alcohols from the hydrogenation of carboxylic acids. However, homogeneous catalysts demonstrated much more selective than heterogeneous ones, with several drawbacks such as using expensive organic ligands, lack of reusability, and challenges associated with removing residual heavy metals in the isolated products. However, due to the high cost of the metal ligands used in these catalyst systems and problems associated with recycling the homogeneous catalysts, heterogeneous catalysts have proven to be more attractive choices for industrial applications [7].

Several attempts on the hydrogenation of stearic acid to 1-octadecanol using heterogeneous catalysts have
been reported previously [8]. The hydrogenation of fatty acids over a copper–chromite catalyst is commercially used to hydrogenate fatty acid esters to alcohols under severe conditions (2–50 MPa, 473–673 K) [9, 10, 11]. In addition, the presence of toxic chromium in the copper–chromite catalyst poses an environmental and health hazard. Therefore, the development of catalysts without using Cr and under milder reaction conditions has been attempted. Bimetallic platinum group metal (PGM) based catalysts such as Pt–Re/TiO₂ (2.0 MPa, 403 K) reported 61–90% selectivity to Co–C₆ fatty alcohols at 79–83% conversion [12]. The presence of co–promoter ReOₓ in Pd–ReOₓ/SiO₂, Rh–ReOₓ/SiO₂, and Ir–ReOₓ/SiO₂ catalysts (8.0 MPa, 413 K) enhanced the performance of Pd, Rh, and Ir catalysts to have 94–98% selectivity of 1-octadecanol at 100% conversion [13]. However, noble metal–based catalysts and low substrate loading are not economical and have less viability in upgrading the biomass–derived platform industry. Therefore, alternative economic and eco–friendly heterogeneous catalysts that would ensure the preferred hydrogenation of the carboxylic acids (fatty acid) to fatty alcohol are highly desired.

The electropositive metals such as tin (Sn), indium (In) of iron (Fe) have been widely used as co–promoter for Ru, Pd, or Ni–based bimetallic catalysts. Toba et al. [14] reported that 2wt% Ru–4.7wt% Sn/Al₂O₃ showed high selectivity toward alcohols (89.4%) at 97.3% adipic acid conversion at 513 K and 6.5 MPa of H₂ [14]. Bimetallic Ni–Sn alloy supported on TiO₂ (Ni–Sn(1.5)/TiO₂) catalyst showed a high yield of lauryl alcohol at 97% at >99% conversion of lauric acid at 433 K, 3.0 MPa H₂, for 20 h [15]. Damayanti et al. reported using bimetallic Pd–Fe/TiO₂ catalyst for the hydrogenation of levulinic acid (LA) to γ–valerolactone (GVL) at 443 K, 3.0 MPa H₂ for 7 h. The obtained yield of GVL over Ru–Fe/TiO₂ was 52.4%, much higher than that of Pd/TiO₂ (22.7%) [16]. Most recently, supported bimetallic Pd–Sn(x)/C catalysts demonstrated a high yield of 1-octadecanol (73.3%) at 100% conversion of stearic acid. 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 Pd₅Sn₃) as obviously depicted by XRD analysis [17].

Scheme 1. Conceived reaction routes for the catalytic transformation of stearic acid using heterogeneous catalysts

In this paper, an extended investigation on the gamma–alumina supported bimetallic palladium–tin catalysts (denoted as Pd–Sn(3.0)/γ-Al₂O₃; Pd = 5%wt and Pd/Sn molar ratio is 3.0) for the hydrogenation of stearic acid to 1-octadecanol under mild reaction conditions has been investigated. The current results showed that Pd–Sn(3.0)/γ-Al₂O₃ catalyst showed the highest conversion of stearic acid (99.1%) and 1-octadecanol yield (43.2%), which were higher than that of other supported Pd–Sn catalysts under the applied reaction conditions.

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., Y–Zeolit, HZSM–5 Si/Al 85 (S_BET = 417 m²/g; V_p = 0.2252 cm³/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_BET = 100 m²/g) was purchased from Japan Aerosol Co. 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).

2.2. Catalyst preparation

A typical procedure of the synthesis of supported bimetallic Pd–Sn(3.0)/γ–Al₂O₃ (Pd = 5%wb/b and Pd/Sn feeding molar ratio of 3.0) catalyst is described as follows [15, 17]: Pd(CH₃COO)₂ (0.4613 mmol) was dissolved in deionized water (denoted as solution A), and SnCl₂·2H₂O (0.1537 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 (γ–Al₂O₃) were mixed at room temperature; the temperature was subsequently raised to 323 K, and the mixture was gently stirred for 12 h. The mixture was adjusted to pH 12 by dropwise an aqueous solution of NaOH (3.1 M or 6.0 M) and placed into a sealed–Teflon autoclave for the hydrothermal reaction at 423 K 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 673 K for 3 h [18]. Bimetallic Pd–Sn supported on Y–Zeolite, HZSM–5 Si/Al = 8, Nb₂O₅ dan TiO₂ catalysts were also synthesized using a similar procedure.

2.3. Characterizations

The prepared catalysts were characterized by powder X–ray diffraction on a RIGAKU MINIFLEX 600 instrument using monochromatic CuKα radiation (λ=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. According to Scherrer’s equation, the mean crystal size of Ni was calculated from the full width at half maximum (FWHM) of the Pd(111) diffraction peak.

Nitrogen adsorption isotherms at 77 K were measured by Belsorp Max (BEL Japan). The samples were degassed at 473 K for 2 h to remove physisorbed gases prior to the measurement. The amount of nitrogen adsorbed onto the samples was used to calculate the
specific pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.995. The Barrett–Joyner–Halenda (BJH) approach was used to calculate desorption data’s total pore volume and size distribution [19].

The temperature-programmed desorption of ammonia (NH\textsubscript{3}-TPD) was carried out on a Belsorp Max (BEL Japan). The samples were degassed at an elevated temperature of 373–473 K for 2 h to remove physically adsorbed gases prior to the measurement. The temperature was then kept at 473 K for 2 h while flushed with helium gas. NH\textsubscript{3} gas (80% balanced NH\textsubscript{3} and 20% He) was introduced at 373 K for 30 minutes, then evacuated by helium gas to remove the physically adsorbed for 30 minutes. Finally, temperature-programmed desorption was carried out at 273–1073 K temperatures, and TCD monitored the desorbed NH\textsubscript{3}.

Attenuated total reflection–Fourier transformed infrared (ATR–FTIR) analysis was performed on a Diamond Bruker spectrometer with a resolution of 2 cm\textsuperscript{-1} and a scanning number of 36. A 20 mg sample in powder form was degassed under vacuum (10\textsuperscript{-3} Pa) for 1 h at 423 K in the TAIATSU techno with glass-fitted inside. Then, it was cooled to room temperature, and the initial background spectrum was recorded. After the sample was exposed to pyridine vapor under vacuum for 60 minutes and overnight, followed by removal of the excessive pyridine at 323 K for 0.5 h, then measured by ATR–FTIR.

### 2.4. Catalytic reactions

A typical procedure for hydrogenation of stearic acid was described as follows: catalyst (0.05 g), stearic acid (0.2844 g; 1.0 mmol), 2-propanol:H\textsubscript{2}O (5 mL; 4.0:1.0 v/v) as solvent were placed into a glass reaction tube, which fitted inside a stainless steel reactor. After H\textsubscript{2} was introduced into the reactor with an initial H\textsubscript{2} pressure of 2.0 MPa at room temperature, the reactor’s temperature was increased to 513 K using an electric furnace, 800 rpm. After 13 h, at room temperature, the internal standard of dodecane was added, and the conversion of stearic acid and the yield of 1-octadecanole were determined by GC analysis. The Pd–Sn/γ-Al\textsubscript{2}O\textsubscript{3} catalyst was easily separated using simple centrifugation or filtration.

2.5. Product Analysis

GC analysis of the reactant (stearic acid) and products (1-octadecanol, ester, and heptadecane) was performed on a Perkin Elmer AutoSystem XL equipped with a flame ionization detector and Thermo Scientific (0.25 mm x 15 m x 0.25 μm) capillary column. It was operated under the following conditions: injector and detector temperatures (523 K); airflow (450 mL/min); H\textsubscript{2} flow (45 mL/min); N\textsubscript{2} flow (14 mL/min); and a split ratio of 50:1. The temperature column has been set gradually into two steps (first: 373–493 K (ramping of 20 K/min) and second: 493–573 K (ramping of 18 K/min). Gas chromatography–mass spectrometry (GC–MS) was performed on a Shimadzu GC-17 equipped with a thermal conductivity detector and an RT–βDEXsm capillary column. The products were confirmed by comparing their GC retention time and mass spectra with those of authentic samples.

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

**Conversion:**

\[
\text{Conversion} = \frac{\text{mol reactant} \times 100\%}{\text{mol reactant}}
\]

**Yield:**

\[
\text{Yield} = \frac{\text{mol product} \times 100\%}{\text{mol reactant}}
\]

**Selectivity:**

\[
\text{Selectivity} = \frac{\text{mol product} \times 100\%}{\text{total mol products}}
\]

\(F_0\) is the introduced mol reactant (stearic acid), \(F_x\) 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 a standard internal technique.

### 3. Results and Discussion

#### 3.1. Catalysts characterization

The N\textsubscript{2}–adsorption/desorption and pore distribution (Horvath–Kawazoe (HK) method) of the synthesized bimetallic Pd–Sn(3.0)/γ-Al\textsubscript{2}O\textsubscript{3} catalyst were performed, and the profiles are shown in Figure 2.

The hysteresis loop of adsorption/desorption of the synthesized bimetallic Pd–Sn(3.0)/γ-Al\textsubscript{2}O\textsubscript{3} sample is very similar to that of IV type, which indicates the strong interaction between the molecule adsorbate and catalyst surface. The formation of the hysteresis loop also indicated the condensation of molecule adsorbate during the desorption of N\textsubscript{2} gas [20] (Figure 2(a)). The plot of the volume of adsorbed-N\textsubscript{2} versus pore distribution using the Horvath–Kawazoe (HK) method was performed to determine the pore size distribution of the synthesized catalysts, as shown in Figure 2(b). The pore size distribution was ±0.16 nm after reduction with H\textsubscript{2} at 400°C. However, there is no clear evidence for the change in the pore size distribution towards small pore sizes or big pore sizes after introducing the Pd–Sn species or thermal activation using N\textsubscript{2} or H\textsubscript{2} at 400°C.

![Figure 1. Typical batch system reactor of TAIATSU techno with glass-fitted inside (volume: 30 mL, max. 35 MPa, 300°C)](image-url)
pore–volume, and pore size distributions (entry 1). Pd–Sn(3.0)/γ-Al₂O₃ catalyst has similarity with Pd–Sn(3.0)/C, which has both microstructures on the surface. The differences are Pd–Sn(3.0)/C has a higher surface area than Pd–Sn(3.0)/γ-Al₂O₃ with pore size distribution and pore volume smaller than Pd–Sn(3.0)/γ–Al₂O₃ (entry 2) [17].

To validate the pore structure (micropore and mesopore area) and the possible adsorption of the catalyst sample, the t-plot and α-plot techniques were performed. The results are shown in Figure 3. The frontline of t-plot profiles showed that the sample has mainly micropore structure (≤ 1.0 nm) (Figure 3(a)), whereas the frontline of α-plot profiles showed both the micropore and the mesopore structures (≥ 2.0 nm) (Figure 3(b)). The pore size at ≥ 2.0 nm was observed when the volume of N₂ gas increased up to 200 cm³/g. Therefore, it can be concluded that the synthesized Pd–Sn(3.0)/γ-Al₂O₃ catalyst has both micro and mesopore structures [21].

**Table 1.** Physicochemical properties of supported bimetallic Pd–Sn(3.0)/γ-Al₂O₃ catalyst

| Entry | Surface area (Sm) m²/g | SA(t-plot) m²/g | SA(α-plot) m²/g | Pore size distribution/nm | Pore volume/cm³/g |
|-------|------------------------|----------------|----------------|---------------------------|-----------------|
|       | Micro. | Micro. | Meso. | Meso. | BJH | HK | BET | BJH |
| 1     | 291.83 | 90.8 | 89.2 | 62.4 | 3.4 | 1.21 | 1.16 | 0.55 | 0.53 |
| 2     | 637    | -    | -    | -    | -   | 0.94 | 0.49 | -    | -    |

Table 1 summarized the porosity properties (specific surface area (Sm)), micro and mesopore surface area,
the modified surface structure of Pd(111) in the presence of SnO (JCPDS#04-1070) which can be attributed to the tin oxide (SnO) supported bimetallic Pd–Sn catalyst. The yield of 1-octadecanol was only 6.5% at a conversion of 91.7%, obtained over Pd–Sn(3.0)/HZM–5 catalyst (entries 1–4). The currently obtained yields of 1-octadecanol using Pd–Sn(3.0) supported on various metal oxides and zeolites were much lower than that of supported Pd–Sn(1.5) catalysts under similar reaction conditions as recently reported by Rodiansono et al. [17]. By using Pd–Sn(3.0)/γ–Al2O3 catalyst, a remarkably high yield of 1-octadecanol (22.7%) at 94.7% conversion of stearic acid was achieved (entry 5).

In order to understand the reaction profiles, the hydrogenation of stearic acid in the presence of a Pd–Sn(3.0)/γ–Al2O3 catalyst at different reaction times was carried out. At an earlier reaction time of 1 h, the conversion of stearic acid was only 12.9% without forming a hydrogenated product of 1-octadecanol (entry 6). The yield of 1-octadecanol significantly increased to 12.5% (at 84.4% conversion of stearic acid) when the reaction time of 5 h was applied. Further prolonged reaction time to 13 h, the conversion of stearic acid was nearly 100%, and a maximum yield of 1-octadecanol (43.2%) was obtained (entry 8). To confirm the importance of bimetallic Pd–Sn instead of monometallic Pd catalyst, the catalytic reaction over Pd/γ–Al2O3 gave 81.3% conversion of stearic acid. The products were distributed to 1-octadecanol (21%), ester (isopropyl stearate) (26.5%), and others (52.7%) after 13 h (entry 9). These results suggested that the presence of Sn in Pd–Sn(3.0)/γ–Al2O3 might enhance the selectivity product of 1-octadecanol by inhibiting the decarboxylation reaction compared to the monometallic Pd/γ–Al2O3 catalyst [31, 32].

3.2. Screening of catalyst

The catalytic reaction of stearic acid using various palladium–based catalysts was performed in 2-propanol/H2O (4.0:1.0 v/v) solvent, 513 K, 2.0 MPa H2 for 7 h, and the results are summarized in Table 3. The catalytic conversion of stearic acid using various supported bimetallic Pd–Sn catalysts was investigated, and the results were also shown in Table 3. The conversion of stearic acid was varied at 47–92%, the maximum yield of 1-octadecanol was only 6.5% at a conversion of 91.7%, obtained over Pd–Sn(3.0)/HZM–5 catalyst (entries 1–4). The currently obtained yields of 1-octadecanol using Pd–Sn(3.0) supported on various metal oxides and zeolites were much lower than that of supported Pd–Sn(1.5) catalysts under similar reaction conditions as recently reported by Rodiansono et al. [17]. By using Pd–Sn(3.0)/γ–Al2O3 catalyst, a remarkably high yield of 1-octadecanol (22.7%) at 94.7% conversion of stearic acid was achieved (entry 5).

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The conversion of stearic acid using Ni–FeOₓ and Ru₅Snₓ/SiO₂ catalysts were reported as 75–100%. The 20% and 99% yields were obtained using Ni–FeOₓ and Ru₅Snₓ/SiO₂ catalysts, respectively (entry 10–11). Although both catalysts showed good performance, these catalysts required harsher reaction conditions than the Pd–Sn₃/Al₂O₃ catalyst.

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

| Entry | Catalyst | Reaction time (h) | Conv. (%) | Yield (%) | 1-octadecanol | Ester | Others |
|-------|----------|------------------|-----------|-----------|----------------|-------|---------|
| 1     | Pd–Sn(3.0)/NbₓOᵧ | 7                | 79.2      | 3.4       | 72.4           | 3.4   |         |
| 2     | Pd–Sn(3.0)/TiₓOᵧ | 7                | 47.9      | 2.8       | 42.2           | 2.9   |         |
| 3     | Pd–Sn(3.0)/YₓZeolite | 7              | 46.0      | 1.7       | 39.0           | 5.3   |         |
| 4     | Pd–Sn(3.0)/HZSM–5 | 7                | 91.7      | 6.5       | 80.4           | 5.8   |         |
| 5     | Pd–Sn(3.0)/Al₂O₃ | 7                | 94.7      | 22.7      | 60.6           | 11.4  |         |
| 6     | Pd–Sn(3.0)/Al₂O₃ | 1                | 12.9      | 0.0       | 1.0            | 11.9  |         |
| 7     | Pd–Sn(3.0)/Al₂O₃ | 5                | 84.4      | 12.5      | 65.3           | 6.6   |         |
| 8     | Pd–Sn(3.0)/Al₂O₃ | 13               | 99.1      | 43.2      | 45.0           | 10.9  |         |
| 9     | Pd–Sn/Al₂O₃ | 13               | 81.3      | 2.1       | 26.5           | 52.7  |         |
| 10    | Ni–FeOₓ | 20               | 75        | 20        | 9              | –     | –       |
| 11    | Ru₅Snₓ/SiO₂ | 2–4              | 100       | 99        | 99             | –     | –       |

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 513 K; initial H₂ pressure (2.0 MPa); reaction time (7 h). The value in the parenthesis is the Pd/Sn molar ratio; based on the amount of metal salt precursor.

3.3. Effect of reaction temperature

The effect of reaction temperature on the conversion and product distribution in the catalytic conversion of stearic acid over bimetallic Pd–Sn₃/Al₂O₃ catalyst was investigated. As shown in Table 4, at the reaction temperature of 433 K, the conversion of stearic acid was 22.8%, and the products were distributed to 1-octadecanol (1.1%), ester (19.1%), and other products (2.6%) (entry 1). The increase in reaction temperature to 473 K increased stearic acid conversion (49.6%). However, the yield of 1-octadecanol was remained low (2.0%), whereas the formation of ester and other products increased significantly (entry 2). When the reaction temperature was increased to 513 K, high conversion of stearic acid (94.7%) with remained low 1-octadecanol yield (22.7%) was obtained (entry 3).

In these reaction conditions, the yield of ester (mainly contains isopropyl stearate) and others were still much higher than that of Pd–Sn₃(1.5)/Al₂O₃ catalysts (entry 4). The hydrogenation of fatty acid using Pd–based catalysts required a co–promoter to enhance alcohol selectivity and inhibit the decarboxylation reaction, producing alkanes as the main products [13, 33]. This result suggested that the further reaction of the formed alcohol to another side product occurred during the hydrogenation of stearic acid, as indicated by the number of others.

Table 4. Effect of reaction temperature on conversion and product distribution in the hydrogenation of stearic acid using Pd–Sn₃(3.0)/Al₂O₃

| Entry | Temp. (K) | Conv. (%) | Yield (%) | 1-octadecanol | Ester | Others |
|-------|-----------|-----------|-----------|----------------|-------|---------|
| 1     | 433       | 22.8      | 1.1       | 19.1           | 2.6   |         |
| 2     | 473       | 49.6      | 2.0       | 41.7           | 5.9   |         |
| 3     | 513       | 94.7      | 22.7      | 60.6           | 11.4  |         |
| 4     | 513       | 84.4      | 32.5      | 45.3           | 6.6   |         |

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); 513 K; initial H₂ pressure (3.0 MPa); reaction time (7 h). Conversion was determined by GC using a standard internal technique. Yields were determined by GC using GC area ratio according to GC–MS data. Others were included hydrocarbon and unidentified products based on the GC–MS analysis data. Data was taken from the cited reference of Rodiansono et al. [17].

Figure 6. ATR–FTIR spectra of fresh and recovered catalysts and their possible interaction between Pd–Sn₃(3.0)/Al₂O₃ catalyst and the molecular reactant of stearic acid. (a) 2–propanol; (b) wetted recovered catalyst; (c) dried recovered catalyst; (d) freshly activated catalyst; (e) stearic acid; and (f) 1-octadecanol.
4. Conclusion

We described the selective hydrogenation of stearic acid to corresponding alcohol using Pd–Sn(3.0)/γ-Al₂O₃ catalyst under mild reaction conditions. The highest yield of stearyl alcohol (1–octadecanol) (up to 43.2%) at 99.1% conversion of stearic acid at temperature 240°C, initial H₂ pressure of 2.0 MPa, a reaction time of 13 h, and in 2-propanol/water (4:0.1 v/v) solvent. Under the current reaction conditions, the main product obtained over Pd–Sn(3.0)/γ-Al₂O₃ catalyst was ester stearate (isopropyl stearate) and others. The high yield of ester and other products may be due to the high acidity of catalyst as indicated by NH₃–TPD and ATR–FTIR pyridine adsorption analysis.

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