Selective hydrogenation of levulinic acid to \( \gamma \)-valerolactone using bimetallic Pd-Fe catalyst supported on titanium oxide

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Abstract. The synthesis of \( \gamma \)-valerolactone (GVL), a versatile precursor in the manufacture of high-value chemicals such as polymer plasticizer, solvent, jet fuel, and, agrochemicals, has been targeted by many research groups. In this study, we report the catalytic performance of iron-modified palladium supported on titanium oxide (denoted as Pd(5.0)-Fe(5.0)/TiO\textsubscript{2}; 5.0 was the loading amount of Pd and Fe, respectively) in the selective hydrogenation of levulinic acid (LA) to \( \gamma \)-valerolactone (GVL) in stainless-steel batch reactor system. Pd(5.0)-Fe(5.0)/TiO\textsubscript{2} catalyst was synthesized by a simple hydrothermal method at 150\textdegree C for 24 h, then followed by reduction with H\textsubscript{2} at 500\textdegree C for 3 h. The X-ray diffraction (XRD) patterns of Pd(5.0)-Fe(5.0)/TiO\textsubscript{2} before and after reduction showed the formation of metallic Pd at 2\texttheta\textdegree = 40.34\textdegree and 47.2\textdegree corresponding to Pd(111) and Pd(200), respectively. The hydrogenation of LA to GVL effectively occurred in the H\textsubscript{2}O solvent, whereas in 2-propanol the formation of ester was the main side product. The highest yield of GVL (52.5\%) was obtained over Pd(5.0)-Fe(5.0)/TiO\textsubscript{2} catalyst at a temperature of 170\textdegree C, initial H\textsubscript{2} pressure of 4.0 MPa, solvent H\textsubscript{2}O 3 ml at a reaction time of 7 h. The yield of GVL slightly increased to 63.3\% when the reaction time was prolonged to 15 h.

1. Introduction

Biomass feedstock valorizations are currently being explored for the production of bio-based platform chemicals, fuels, and various commodity products by using bimetallic-based heterogeneous catalysts. The use of bimetallic catalysts is a promising option for biomass feedstock upgrading, as the interaction between metals can modify the surface properties of the catalyst that meet with the complex surface [1–3]. Furfural (FFald) and levulinic acid (LA) have been identified to be the most promising platform molecules that can turn into a variety of value-added derivative molecules including polymer, plasticizer, solvent, jet fuel precursor, and agrochemicals [4]. FFald and LA were produced effectively from C-5 sugars in hemicellulosic biomasses, such as xylan and arabinose or C-6 sugars in form of glucose or fructose via acidic hydrolysis [5].

In the hydrogenation of LA into \( \gamma \)-valerolactone, heterogeneous catalysts of the monometallic bimetallic precious metal transition have been widely used to achieve high yields of GVL. This hydrogenation reaction is important because the resulting products are used in the chemical industry in the production of high-yield chemicals. Additionally, the study is interesting because there is a combination of two metals with just the right reaction condition. Bourne et al. [6] used Ru/SiO\textsubscript{2} catalyst under supercritical-CO\textsubscript{2} and H\textsubscript{2} up to 4.5 MPa at 473 K to give $>99\%$ GVL yield, while Wettstein et al. employed bimetallic Ru-Sn for LA hydrogenation to give GVL in o-iso-butylphenol at a relatively high reaction temperature of 453 K. They claimed that the formation of intermetallic such
as Ru₂Sn₃ and Ru₃Sn₇ slowed the leaching of Sn into the reaction solution [7]. Recently, Luo et al. reported bimetallic Au-Pd/TiO₂ and Ru-Pd/TiO₂ catalysts for hydrogenation of LA into GVL. The formation of bimetallic alloy or dilution of Au or Ru by Pd improved the selectivity and stability of the catalysts [8]. We have reported the catalytic performance of the bulk structure of intermetallic Ni-Sn catalysts in LA hydrogenation and showed high selectivity in aqueous phase hydrogenation of LA into GVL at 433 K, 4.0 MPa for 6 h and produced GVL yield of >99%. The activity and selectivity of used bulk Ni-Sn catalysts slightly decreased after several reaction runs that might be due to the leaching of metals (Ni and Sn) into the reaction solution [9]. In our most recent extended work, Ni-Sn alloy supported on aluminum hydroxide (denoted as prepared Ni-Sn(x)/AlOH; x = Ni/Sn molar ratio, 7.9 to 1.0) demonstrated highly active and stable catalysts for aqueous-phase hydrogenation of LA into exclusive GVL product. The used solvent reaction and the high dispersion of Ni-Sn alloy on aluminum hydroxide (bayerite and gibbsite) facilitated reaction rate at a much lower temperature than that of bulk ones. Moreover, the Ni–Sn(1.4)/AlOH catalyst was reusable for at least six consecutive runs without any significant loss of activity and selectivity [10].

In the present paper, we report the catalytic performance of iron-modified palladium supported on titanium oxide (denoted as Pd(5.0)–Fe(5.0)/TiO₂; 5.0 was the loading amount of Pd and Fe, respectively) in the selective hydrogenation of levulinic acid to γ-valerolactone in stainless-steel batch reactor system in various solvents. The purpose of this work is to study the effect of Fe loading amount to Pd (%wt), the solvent used, and initial H₂ pressure on the conversion of LA and the yield of GVL. The structure-activity relationship of Pd(5.0)-Fe(5.0)/TiO₂ catalyst in LA hydrogenation to GVL is discussed.

![Reaction Pathway Diagram](image_url)

**Figure 1.** Possible reaction pathways for hydrogenation of levulinic acid in various solvents in the presence of bimetallic Pd(5.0)-Fe(x)/TiO₂ catalysts [10].

### 2. Materials and methods

#### 2.1. Material

Palladium (II) chloride (PdCl₂) (98%; Tokyo Chemical Industry), Iron (III) chloride hexahydrate (FeCl₃·6H₂O) (99%; Merck Millipore), 2-propanol (98%, Merck Millipore), TiO₂ anatase, ethanol (96%; Merck Millipore), ethylene glycol (EG) (99.5%; Merck Millipore), Sodium tetra hydroborate
(NaBH₄) (95%; Tokyo Chemical Industry), NaOH (99%; Merck Millipore), H₂ gas (99.99%), N₂ gas (99.99%), lauric acid (97%; Tokyo Chemical Industry).

2.2. Catalyst preparation
A typical procedure for the synthesis of Pd(5.0)–Fe(5.0)/TiO₂ (5.0 was the loading amount of Pd and Fe, respectively) described as follows (11): PdCl₂ (0.0638 g) was dissolved in deionized water (denoted as solution A) and FeCl₃·6H₂O (0.0605 g) was dissolved in ethanol/ethylene glycol (2.0/1.0 volume ratio) (denoted as solution B) at room temperature. Solutions A, B, and TiO₂ (as support material; 1.0 g) were mixed at room temperature; the temperature was subsequently raised to 70 °C under gentle stirring for 12 h. The NH₃ gas (5.0 ml) was introduced at 100 °C for 1 h to remove physisorbed gases prior to the measurement. The amount of nitrogen adsorbed onto the samples was used to calculate the Brunauer–Emmett–Teller (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 (12). The NH₃-TPD was carried out 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 Brunauer–Emmett–Teller (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 (12). The NH₃-TPD was carried out on a Belsorp Max (BEL Japan). The samples were degassed at an 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. NH₃ gas (balanced NH₃, 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 a temperature of 100–800 °C and the desorbed NH₃ was monitored by TCD.

2.3. Catalyst characterization
The X-ray diffraction (XRD) analysis was performed on a Miniflex 600 Rigaku instrument with Cu as a monochromatic source of CuKα radiation (λ = 0.154444 nm). The XRD was operated at 40 kV and 15 mA with a step width of 0.02°, a scan speed of 4° min⁻¹ (α₁ = 0.154057 nm, α₂ = 0.154433 nm), solar slits 1.25°, and using a Ni Kβ filter. The BET surface area (S_BET) and pore volume (V_p) were measured using N₂ 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 Brunauer–Emmett–Teller (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 (12). The NH₃-TPD was carried out on a Belsorp Max (BEL Japan). The samples were degassed at an 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. NH₃ gas (balanced NH₃, 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 a temperature of 100–800 °C and the desorbed NH₃ was monitored by TCD.

2.4. Catalytic reaction
The typical procedure for hydrogenation of lauric acid is described as follows: Catalysts (0.04 g), levulinic acid (0.23 g), and H₂O (5 ml) as the solvent, and 1,6-hexanediol (0.025 g) were placed into a glass reaction tube in an autoclave reactor system of TAIATSU Techno reactor (a Pyrex tube was fitted inside of a sus316 jacket to protect the vessel from corrosion in acidic media. The reactor was flushed with 1.0 MPa H₂ gas 10 times before removing undesired gases. After H₂ was introduced into the reactor with an initial H₂ pressure of 4.0 MPa at room temperature, the temperature of the reactor was increased to 170 °C. After 7 h, the conversion of levulinic acid and the yield of γ-valerolactone were determined by gas chromatography (GC) analysis.

2.5. Product analysis
GC analysis of the reactant (levulinic acid) and product (γ-valerolactone) was performed on a Perkin Elmer Auto System XL equipped with a flame ionization detector and Restek Rtx® BAC Plus capillary column. GC analysis was operated at the detector and injector temperatures of 250 °C, N₂ as a carrier gas, rates of air, and H₂ were 450 ml/min and H₂ 45 ml/min, respectively. The used 5.0Pd–5.0Fe/TiO₂ catalyst was easily separated using either simple centrifugation or filtration, then finally dried overnight under vacuum at room temperature prior to the reusability testing.
3. Results and discussion

3.1. Screening of solvent

In the first experiments, we evaluated the use of various solvents as solvent media for the hydrogenation of levulinic acid (LA) to \(\gamma\)-valerolactone (GVL) using Pd(5.0)-Fe(5.0)/TiO\(_2\) catalyst as shown in figure 1 and the results are summarised in table 1. Three types of solvents such as 1,4-dioxane, 2-propanol, and water which are corresponding to polar aprotic, polar semi-protic, and polar protic, respectively, were employed. In polar aprotic solvent (1,4-dioxane), 29.3% yield of \(\gamma\)-valerolacton at 29.3% conversion of levulinic acid was obtained (entry 1). In the polar semi-protic solvent of 2-propanol, the products were GVL (27.4%) and isopropyl levulinate (39.8%) at the relatively high conversion of levulinic acid (c.a. 67.2%) under the same reaction conditions (entry 2). In H\(_2\)O, 52.4% yield of GVL and 10.4% yield of pseudo-LA were obtained at 62.7% conversion of LA (entry 3). After reaction temperature was prolonged to 15 h, conversion of LA as well as the yield of GVL slightly increased to 68.6% and 63.3%, respectively, suggesting the extended reaction time caused a further reaction of pseudo-LA to the final product of GVL (entry 4). In the H\(_2\)O/2-propanol and H\(_2\)O/1,4-dioxane mixture solvents, the hydrogenation of levulinic acid occurred with unsatisfactory results (entries 5 and 6) as well as in absence of solvent (entry 7).

Table 1. Results of levulinic acid hydrogenation over Pd(5.0)-Fe(5.0)/TiO\(_2\) catalyst in various solvents.

| Entry | Solvent                              | Conversion\(^a\) (%) | Yield\(^b\) (%) |
|-------|--------------------------------------|----------------------|-----------------|
| 1     | 1,4-Dioxane                          | 29.3                 | 29.3            |
| 2     | 2-Propanol (2-PrOH)                  | 67.2                 | 27.4            |
| 3     | H\(_2\)O                             | 62.7                 | 52.4            |
| 4\(^c\) | H\(_2\)O                            | 68.6                 | 63.3            |
| 5     | H\(_2\)O: 2-PrOH (3: 2 in ml)        | 26.7                 | 7.4             |
| 6     | H\(_2\)O/1,4-Dioxane (3:2 in ml)     | 38.3                 | 30.2            |
| 7     | Neat (without solvent)               | 21.8                 | 11.2            |

\(^a\)Conversion and yield were determined by GC analysis using an internal standard technique. \(^b\)Yields of pseudo-LA and ester were determined by GC area. \(^c\)Reaction time was 15 h.

The relatively high yield of \(\gamma\)-valerolactone in water solvent could be attributed to the presence of H-bonded water molecule or single chemisorbed water on metallic surfaces that could dramatically reduce the energy span of the reaction pathway, hence enhancing the catalytic activity [13]. Alternatively, the increase of surface concentration in hydrogen atom due to dissociated water and strong interaction between water with the substrate by hydrogen bonding lowered the activation energy barrier and led to high hydrogenation rates [14,15].

3.2. Effect of Fe loading amount

The influence of Fe intercalation on the catalytic performance of the Pd/TiO\(_2\) catalyst in levulinic acid hydrogenation was evaluated and the Fe amounts were 1.0, 3.0, and 5.0 %wt to the amount of Pd and the results are summarised in table 2.
Table 2. Results of levulinic acid hydrogenation over Pd(5.0)-Fe(x)/TiO2 catalysts with different loading amounts of Fe.

| Entry | Catalysta | Conversionb (%) | Yieldb (%) | GVL | pseudo-LAc |
|-------|-----------|-----------------|------------|-----|-------------|
| 1     | Pd(5.0)/TiO2 | 25.9           | 22.7       | 3.0 |              |
| 2     | Pd(5.0)-Fe(1.0)/TiO2 | 11.6         | 11.6       | 0.0 |              |
| 3     | Pd(5.0)-Fe(3.0)/TiO2 | 22.7         | 22.7       | 0.0 |              |
| 4     | Pd(5.0)-Fe(5.0)/TiO2 | 62.7         | 52.4       | 10.4|              |
| 5d    | Pd(5.0)-Fe(5.0)/TiO2 | 35.0         | 35.0       | 0.0 |              |
| 6e    | Pd(5.0)-Fe(5.0)/TiO2 | 7.1          | 1.5        | 5.6 |              |

Reaction conditions: catalyst 0.04 g; levulinic acid 0.23 g; solvent 3 ml; initial H2 pressure 3 MPa; temperature 170 °C; reaction time 7 h. Conversion and yield were determined by GC analysis using an internal standard technique. btemperature reaction was 150 °C. cThe as-prepared Pd(5.0)-Fe(5.0)/TiO2 catalyst (without reduction with H2 at 500 °C for 3 h).

A reference catalyst of Pd(5.0)/TiO2 was synthesized and reduced with H2 at 500 °C for 3 h and showed low conversion of levulinic acid (25.9%), whereas the yields of pseudoLA were 22.7% and 3.0%, respectively (entry 1). The addition of 1wt% Fe to Pd (5.0) / TiO2 reduced the conversion significantly in more than half (entry 2). The conversion of LA increased to 22.7% over Pd(5.0)-Fe(3.0)/TiO2 catalyst and no pseudo-LA was observed under the same reaction conditions (entry 3). A remarkable increase in conversion of LA (62.7%) and yield of GVL (52.4%) as well as the amount of pseudo-LA (10.4%) were obtained over Pd(5.0)-Fe(5.0)/TiO2 catalyst (entry 4). The conversion of LA decreased to 35% when the reaction temperature was reduced to 150 °C without decreasing the selectivity of GVL (entry 5). In addition, the as-prepared Pd(5.0)-Fe(5.0)/TiO2 catalyst (without reduction with H2 at 500 °C) was completely inert for the hydrogenation of LA (entry 6).

3.3. Effect of initial H2 pressure
The effect of initial H2 pressure on the conversion and yield in the levulinic acid hydrogenation was evaluated using Pd(5.0)-Fe(5.0)/TiO2 catalyst and the results are summarised in table 3. At initial H2 pressure of 1.0 MPa, an 18.8% yield of GVL was obtained (entry 1). Both conversions of levulinic acid and yield of GVL increased gradually when the initial H2 pressure was increased up to 3.0 MPa (entries 2 and 3) then tended to remain unchanged at initial H2 of 4.0 MPa which decreased in yield of pseudo-LA (entry 4).

Table 3. Results of levulinic acid hydrogenation over Pd(5.0)-Fe(5.0)/TiO2 catalyst at different initial H2 pressure.

| Entry | Initial H2 (MPa) | Conversion (%) | Yield (%) | GVL | pseudo-LA |
|-------|-----------------|---------------|-----------|-----|-----------|
| 1     | 1.0             | 18.8          | 18.8      | 0.0 |           |
| 2     | 2.0             | 20.8          | 20.8      | 0.0 |           |
| 3     | 3.0             | 62.7          | 52.4      | 10.4|           |
| 4     | 4.0             | 56.5          | 52.5      | 3.7 |           |

Reaction conditions: catalyst 0.04 g; levulinic acid 0.23 g; solvent 3 ml; initial H2 pressure 1.0 – 4.0 MPa; temperature 170 °C; reaction time 7 h. Conversion and yield were determined by GC analysis using an internal standard technique.

3.4. Structure-activity relationship
Based on XRD analysis and reaction profiles, we discuss the structure of active Pd and the presence of FeOx species in bimetallic Pd(5.0)-Fe(x)/TiO2 catalysts after reduction with H2 at 500 °C for 3 h. The
as-prepared Pd(5.0)-Fe(5.0)/TiO₂ (without reduction with H₂) was as referenced catalysts and inactive for hydrogenation of lauric acid (table 1, entry 6). The XRD patterns of Pd(5.0)-Fe(x)/TiO₂ catalysts before and after reduction with H₂ at 500 °C for 3 h (figures 2 (a) and (b), respectively) suggest that the formation of metallic Pd(0) was observed at 20 = 40.34° and 47.2° corresponding to Pd(111) and Pd(200), respectively [16]. On the other hand, the metallic or oxide Fe species were unable to detect due to its crystallite sizes were lower than that the detection limit of XRD.

Figure 2. XRD patterns of (a) before and (b) after reduction with H₂ at 500 °C for 3 h with different amounts of Fe.

4. Conclusion
A series iron-modified palladium supported on titanium oxide (Pd(5.0)-Fe(x)/TiO₂ (5.0 and x are loading amount of Pd and Fe, respectively) catalysts were successfully synthesized using a simple hydrothermal method at 150 °C for 24 h followed by reduction with H₂ at 500 °C for 3 h. Results of XRD analysis of Pd(5.0)-Fe(x)/TiO₂ catalysts suggest that the formation of metallic Pd(0) was observed at 20 = 40.34° and 47.2° corresponding to Pd(111) and Pd(200), respectively. The hydrogenation of LA to GVL effectively occurred in the H₂O solvent, whereas in 2-propanol the formation of ester (iso-propyl levulinate (39.8%) was the main side product at the relatively high conversion of levulinic acid (67.2%). The highest yield of GVL (52.5%) was obtained over Pd(5.0)-Fe(5.0)/TiO₂ catalyst at a temperature of 170 °C, initial H₂ pressure of 4.0 MPa, solvent H₂O 3 ml at a reaction time of 7 h. The yield of GVL slightly increased to 63.3% when the reaction time was prolonged to 15 h.

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