Effects of Different Solvents on Hydrogenation of Acetic Acid over Pt/TiO₂ for Bioethanol Production

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Bioethanol production from lignocellulosics via acetic acid fermentation is a potential way to substitute gasoline with more improved carbon utilization efficiency than the conventional alcoholic fermentation processes. Accordingly, hydrogenation of acetic acid to ethanol is a very important step to realize this acetic acid-based process. In this communication, hydrogenation mechanism of acetic acid into ethanol on a Pt catalyst supported on TiO₂ (titania) was characterized from the solvent effects. The Pt/TiO₂ catalyst was quite effective in hexane, a non-polar solvent, to give ethanol and ethyl acetate from acetic acid in relatively high yields, while the catalytic activities were reduced in tetrahydrofuran (THF) and water, polar solvents. These results evidently support the catalytic mechanism: Ti atoms of the TiO₂ surface act as a Lewis acid to activate the carbonyl carbon of acetic acid, which leads to the efficient hydrogenation of acetic acid at the interface between Pt and TiO₂. Suppression of the ethyl acetate formation in THF and water, which could be formed via the common activated state of acetic acid on TiO₂, also supports this catalytic mechanism.

Key Words
Bioethanol, Acetic acid, Hydrogenation, Pt/TiO₂, Solvent effect, Catalytic mechanism, Lewis acid

1. Introduction

Bioethanol produced from lignocellulosics is a potential renewable fuel which can be utilized as a substitute for gasoline to mitigate the emission of additional carbon dioxide to the atmosphere. It is conventionally produced by alcoholic fermentation of sugars with *Saccharomyces cerevisiae*. The carbon utilization efficiency of this system, however, is low as indicated by the following theoretical consideration: only four carbons of glucose can be converted into ethanol with releasing the rest of carbons (two carbons) as CO₂ during alcoholic fermentation.

To overcome this drawback, our research group has recently proposed a new process based on acetic acid fermentation of the products of two-step hot-compressed water treatment of lignocellulosics. We also have reported that acetic acid fermentation with co-cultures of *Clostridium thermocellum* and *C. thermoaceticum* can utilize much wider range of substrates than alcoholic fermentation, which include not only C5/C6 mono-/oligo-saccharides, their decomposition products such as organic acids and furans, but also lignin-derived products. Furthermore, carbon utilization efficiency from glucose to acetic acid is
theoretically 100%. Accordingly, efficient hydrogenation of aqueous acetic acid into aqueous ethanol is a quite important step for this bioethanol production.

Hydrogenation of acetic acid to ethanol has been conventionally conducted by a two-step method, which includes the esterification with ethanol to produce ethyl acetate followed by catalytic hydrogenation. In this method, complete dehydration of aqueous acetic acid solutions is necessary before esterification. However, it should be noted that dehydration of aqueous acetic acid solutions is very costly in both energetically and economically. No azeotrope mixtures formation between acetic acid and water makes the purification with distillation quite difficult. Reactive distillation is an alternative potential way to isolate ethyl acetate from aqueous acetic acid, but this technique has not been established yet. Therefore, so far there have been no mature technologies for purification of acetic acid or ethyl acetate from dilute aqueous acetic acid solutions.

On the other hand, direct hydrogenation of acetic acid is normally less effective than that of ethyl acetate due to the lower carbonyl reactivity of acetic acid. Accordingly, substantial efforts have recently been made to exploit the effective catalysts for direct hydrogenation of organic acids, mainly focusing on the utilization of fatty acids and other biomass-derived substances. In particular, titania-supported catalysts have been reported as effective catalysts with higher alcohol selectivity. However, role of the support in the hydrogenation mechanism has not been fully clarified, and it is not clear whether these catalysts can be used for aqueous acetic acid solutions.

In this communication, catalytic mechanism of Pt/TiO₂ in acetic acid hydrogenation is discussed based on the solvent effects. If TiO₂ could act as a Lewis acid for carbonyl group of acetic acid, solvent polarity must affect the activity greatly. The applicability to aqueous acetic acid solutions is also discussed based on the present results, since acetic acid is obtained as the aqueous solutions from the fermentation step.

2. Experimental

2.1 Materials

Titanium oxide (Aeroxide TiO₂ P25, 80% anatase/20% rutile, BET surface area 50 m²/g, Nippon Aerosil Co., Tokyo, Japan) and hexahydroxy-platinic acid [H₂Pt(OH)₆] (99.9%, Sigma-Aldrich, St Louis, MO, USA) were used for the preparation of Pt/TiO₂ catalyst. 3%Pt/C (BET surface area 1000 m²/g) was purchased from JGC Chemicals and Catalyst Ltd. (Kawasaki, Japan). Acetic acid (AcOH), ethyl acetate (EtOAc), hexane and tetrahydrofuran (THF) were purchased as guaranteed grade from Nacalai Tesque (Kyoto, Japan).

2.2 Catalyst preparation

Titanium oxide (1.0 g) was added to a solution of hexahydroxy-platinic acid (0.0613 g, corresponding to Pt 0.040 g) in 5% HNO₃, and then the suspension was stirred with a magnetic stirrer for 1 h. The resulting suspension was evaporated and then oven-dried at 105 °C for overnight. 4 wt%Pt/TiO₂ catalyst was obtained by the calcination at 400 °C under an air flow (100 mL/min) for 5 h, followed by the reduction at 400 °C under a H₂ flow (100 mL/min) for 4 h. X-Ray diffraction (XRD) pattern of the catalyst (Fig. 1) was measured with a RINT 2000V (Rigaku Co. Ltd., Tokyo, Japan) using Cu-Kα radiation (40 kV, 30 mA). Several signals assigned to Pt were observed along with the TiO₂ signals. The latter signals showed very similar shape to that of the original TiO₂, which indicates that the structure of TiO₂ including the anatase/rutile ratio was not changed significantly during the preparation process.

2.3 Hydrogenation

Catalytic activities of 4 wt% Pt/TiO₂ catalyst were evaluated for acetic acid (10 g/L or 100 g/L) in hexane (a non-polar solvent) and THF and water (polar solvents). Some results were compared with those of commercial 3 wt%Pt/C catalyst. Hydrogenation was conducted with a high-pressure
100 mL reactor made of Hastelloy C-278 (model 4560, Parr Instrument Company, Moline, IL, USA). After the activation of 4 wt%Pt/TiO$_2$ catalyst (0.30 g) by stirring with hexane, THF or water (40 mL) under H$_2$ (2.0 MPa) at 120 ºC for 1 h, an acetic acid solution (20 mL) in the same solvent was added to the solution, and the mixture (final concentration: 10 g/L or 100 g/l) was stirred at the designated temperature and pressure for 12 h. The products and acetic acid in the liquid phase were determined by high-performance liquid chromatography (HPLC) with a LC-20A (Shimadzu, Kyoto, Japan) under the chromatographic conditions: column: Aminex HPX-87H (300 mm × 7.8 mm, Bio-Rad, Helucles, CA, USA), eluent: 5 mmol% H$_2$SO$_4$/ flow rate: 0.6 mL/min, column temperature: 60 ºC, detector: refractive index.

### 3. Results and discussion

The reaction conditions and the yields of AcOH, EtOH and ethyl acetate (EtOAc) are summarized in Table 1. From the comparison between Ex1 and Ex4, both of which were conducted in hexane at 130 ºC/ H$_2$ 6.0 MPa for 12 h, the yields of EtOH (45.2 mol%) and EtOAc (26.8 mol%) on Pt/TiO$_2$ catalyst were much higher than those (0.2 and 0.7 mol%, respectively) on the Pt/C. A similar tendency was obtained in water (Ex2 and Ex12). In general, surface area is known to be positively related to the catalytic activity, while the specific surface area of Pt/TiO$_2$ (50 m$^2$/g) was rather smaller than that of Pt/C (1000 m$^2$/g). These results confirm that Pt on TiO$_2$ is more effective than that on C during the acetic acid hydrogenation in hexane.

Higher catalytic activity of Pt/TiO$_2$ is explainable with the increasing δ+ of the carbonyl carbon of acetic acid by the coordination of the vacant orbital of Ti to the lone pair of carbonyl oxygen, which makes an attack of hydrogen anion as activated on Pt occur more efficiently (Fig. 2). Lewis acidity of TiO$_2$ has been well characterized by IR spectropic methods. Formation of EtOAc is also reasonably explained by the attack of EtOH, which is formed in the vicinity of the same catalyst surface, to the activated carbonyl carbon as the common reactive intermediate.

In hexane, the EtOH yield increased linearly with increasing the H$_2$ pressure up to 15.0 MPa, where acetic acid was completely consumed to give EtOH (85.8 mol%) along with EtOAc (7.1 mol%) as a by-product (Ex3-Ex6). Acetic acid was almost completely consumed even at a lower H$_2$

| Ex | Catalyst | Solvent | aq AcOH (g/L) | Temperature (°C) | H$_2$ (MPa) | Yield (mol%) |
|----|---------|---------|--------------|-----------------|-------------|--------------|
|   | 3wt%Pt/C | Hexane | 10 | 130 | 6.0 | 99.1 | 0.2 | 0.7 |
| 2 | H$_2$O | 200 | 15.0 | 86.6 | 8.4 | 0 |
| 3 | 4wt%Pt/TiO$_2$ | Hexane | 10 | 130 | 20 | 18.9 | 22.1 | 29.5 |
| 4 | | | 200 | 6.0 | 1.3 | 45.2 | 26.8 |
| 5 | | | 10.0 | 0 | 68.9 | 15.5 |
| 6 | | | 15.0 | 0 | 85.8 | 7.1 |
| 7 | THF | 10 | 130 | 20 | 79.6 | 13.3 | 72 |
| 8 | H$_2$O | 100 | 130 | 15.0 | 71.5 | 23.3 | 0 |
| 9 | | | 130 | 130 | 91.6 | 22 | 0 |
| 10 | | | 150 | 150 | 70.1 | 25.5 | 0 |
| 11 | | | 175 | 150 | 43.3 | 52.6 | 0 |
| 12 | | | 200 | 200 | 31.2 | 61.1 | 0 |
| 13 | | | 225 | 225 | 4.3 | 67.4 | 0 |

**Table 1** Influences of the solvent and other reaction conditions on the yields of ethanol and ethyl acetate from acetic acid

![Fig. 2](image-url)
pressure of 6.0 MPa to give 26.8 mol% of EtOAc and EtOH (45.2 mol%). Thus, the esterification to EtOAc proceeds quite effectively in hexane, and EtOAc is hydrogenated further into two mol-equivalents of EtOH in rather smaller rate than the hydrogenation of acetic acid. Sterically bulky ethyl group of EtOAc may suppress the coordination of Ti to the carbonyl group. Use of THF instead of hexane reduced the yields of EtOH (22.1 to 13.3 mol%) and EtOAc (29.5 to 71 mol%) (Ex7 and Ex3). This is explainable by considering the competitive coordination of the oxygen lone pair of THF to Ti. In particular, the greater influence on the EtOAc formation would attribute to the separation of the activated acetic acid from EtOH by the THF molecules coordinating to Ti as illustrated in Fig. 2.

In water, which is expected to be a better ligand to Ti, the hydrogenation activity of Pt/TiO2 was reduced further at 130 °C (Ex9). The other characteristic point observed in water is no formation of EtOAc as a by-product or a more stable intermediate to EtOH. These results are also explainable by the extensive hydration to Ti. In the hydrated state, water, rather than EtOH, tends to attack to the activated carbonyl carbons. To check the Lewis acid activity of TiO2 in water, the experiment Ex8 was conducted, in which both of the concentrations of acetic acid and catalyst were twice of those of Ex9. If the Lewis acid mechanism (Fig. 2) is involved even in the water system, the increasing acetic acid/water ratio would be favorable for hydrogenation of acetic acid. Accordingly, the improved EtOH yield (23.3 mol%) as compared to 2.2 mol% in Ex9 suggests the Lewis acid mechanism also being active in water, although the effectiveness reduces in the order of hexane > THF > water.

All of these results are consistent with the Lewis acid mechanism of Fig. 2. Although water is not an ideal solvent for hydrogenation of acetic acid, higher temperature reactions (Ex9-Ex13) improved the EtOH yield, and 67.4 mol% of EtOH was obtained at 225 °C with 4.3 mol% of recovered acetic acid. However, total yield of EtOH and acetic acid recovered amounted to 71.7 mol%, and the rest of the components (~28 mol%) were found to be the gaseous products (methane and ethane). These gaseous products would form through C–C bond cleavage of acetic acid, which reduces the EtOH yield. Thus, suppression of this gasification would be important to improve the EtOH yield from direct hydrogenation of aqueous acetic acid solutions.

4. Conclusions

Catalytic activity of 4wt% Pt/TiO2 was evaluated for acetic acid in various solvents for better understanding of the catalytic mechanism and applicability to aqueous acetic acid solutions obtained by fermentation. The following results were obtained:

1. 4wt% Pt/TiO2 catalyst was very active in hexane, a non-polar solvent, to give ethanol and ethyl acetate in relatively high yields.

2. The catalytic activity became lower by changing the polarity of the solvent, in the order of hexane > THF > water. These results evidently supported the catalytic mechanism in which the carbonyl carbon is activated through coordination to Ti, a Lewis acid.

3. Water is not an ideal solvent because TiO2 is extensively hydrated, although Lewis acidity of Ti was still active in hydrogenation of acetic acid.

4. Increasing the reaction temperature up to 225 °C was effective to improve the EtOH yield from aqueous acetic acid solution, although this also enhanced the formation of the gaseous by-products.

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