Short Paper

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

Haruo KAWAMOTO, Tomoya FUJII, Yuta ITO, and Shiro SAKA

(Received December 2, 2015)

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

酢酸発酵を用いることで、従来のアルコール発酵法よりも高い炭素利用効率でリグノセルロースからバイオエタノールが生産できることが期待される。この酢酸発酵法において酢酸からエタノールへの水素化工程は最後の重要なステップである。本論文では、チタニア (TiO₂) に白金 (Pt) を担持した Pt/TiO₂ 触媒を用い、酢酸のエタノールへの水素化活性に及ぼす溶媒の影響を調べるとともに、触媒の作用機構について検討した。その結果、Pt/TiO₂ 触媒は非極性溶媒であるヘキサン中では高収率にエタノールと酢酸エチルを与えたが、極性溶媒であるテトラヒドロフラン及び水中では、この順でその活性が低下することがわかった。これらの結果は、Pt と TiO₂ の界面で Ti 原子がルイス酸として作用し、酢酸のカルボニル炭素が活性化されることで水素化が促進される機構を支持する。またこの機構は、共通の活性酢酸を経て生成する酢酸エチルの生成が極性溶媒中で抑制されることから支持された。

キーワード

バイオエタノール, 酢酸, 水素化, Pt/TiO₂, 溶媒効果, 触媒機構, ルイス酸

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^{1) 2)}. 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^{3) 4)}. Furthermore, carbon utilization efficiency from glucose to acetic acid is

Graduate School of Energy Science, Kyoto University
Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

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^{5) 6)}, 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^{7) ~ 9)}. Reactive distillation is an alternative potential way to isolate ethyl acetate from aqueous acetic acid^{10) 11)}, 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^{12) 13)} and other biomass-derived substances^{14) ~ 18)}. In particular, titania (TiO_2)-^{13) 18) ~ 20)} and alumina (Al_2O_3)-^{12) 18) ~ 21)} 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/ TiO_2 in acetic acid hydrogenation is discussed based on the solvent effects. If TiO_2 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 TiO_2 P25, 80% anatase/20% rutile, BET surface area 50 m^2/g , Nippon Aerosil Co., Tokyo, Japan) and hexahydroxy-platinic acid [$\text{H}_2\text{Pt}(\text{OH})_6$] (99.9%, Sigma-Aldrich, St Louis, MO, USA) were used for the preparation of Pt/ TiO_2 catalyst. 3%Pt/C (BET surface area 1000 m^2/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% HNO_3 , and then the suspension was stirred with a magnetic stirrer for 1 h. The resulting suspension was evaporated and then oven-dried at 105 $^\circ\text{C}$ for overnight. 4 wt%Pt/ TiO_2 catalyst was obtained by the calcination at 400 $^\circ\text{C}$ under an air flow (100 mL/min) for 5 h, followed by the reduction at 400 $^\circ\text{C}$ under a H_2 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 $\text{Cu-K}\alpha$ radiation (40 kV, 30 mA). Several signals assigned to Pt were observed along with the TiO_2 signals. The latter signals showed very similar shape to that of the original TiO_2 , which indicates that the structure of TiO_2 including the anatase/rutile ratio was not changed significantly during the preparation process.

2.3 Hydrogenation

Catalytic activities of 4 wt% Pt/ TiO_2 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

Fig. 1 X-Ray diffraction pattern of 4 wt%Pt/ TiO_2 catalyst as compared with the commercial TiO_2 used for catalyst preparation
● : anatase, ○ : rutile, ★ : Pt

100 mL reactor made of Hastelloy C-278 (model 4560, Parr Instrument Company, Moline, IL, USA). After the activation of 4 wt%Pt/TiO₂ catalyst (0.30 g) by stirring with hexane, THF or water (40 mL) under H₂ (2.0 MPa) at 120 °C 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% H₂SO₄/ flow rate: 0.6 mL/min, column temperature: 60 °C, 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 °C/ H₂ 6.0MPa for 12 h, the yields of EtOH (45.2 mol%) and EtOAc (26.8 mol%) on Pt/TiO₂ 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/TiO₂ (50 m²/g) was rather smaller than that of Pt/C (1000 m²/g). These results confirm that Pt on TiO₂ is more effective than that on C during the acetic acid hydrogenation in hexane.

Higher catalytic activity of Pt/TiO₂ 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 TiO₂ has been well characterized by IR spectroscopic methods^{20) 22) 23)}. 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 H₂ 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 H₂

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

Ex No	Catalyst	Catalyst (wt%)	Solvent	aq AcOH (g/L)	Temperature (°C)	H ₂ (MPa)	Yield (mol%)		
							AcOH	EtOH	EtOAc
1	3wt%Pt/C	1	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	1	Hexane	10	130	2.0	18.9	22.1	29.5
4						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	2.0	79.6	13.3	7.2
8		10	H ₂ O	100	130	15.0	71.5	23.3	0
9					130		91.6	2.2	0
10		1	H ₂ O	10	150		70.1	25.5	0
11					175	15.0	43.3	52.6	0
12					200		31.2	61.1	0
13					225		4.3	67.4	0

Fig. 2 Proposed hydrogenation and esterification mechanisms on Pt/TiO₂ in various solvents

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 7.1 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.

Acknowledgments

This work was supported by the Japan Science and Technology Agency (JST) under the Advanced Low Carbon Technology Research and Development Program (ALCA), for which the authors are extremely grateful.

References

- 1) Saka, S.; Kawamoto, H.; Miyafuji, H.; Yamauchi, K.; Masuda, S.; Nakamura, Y.; Phaiboonsilpa, N.; Sera, Y.; Tomiyama, S.; Nakamori, K., Japan Patent 2010, JP2010239913
- 2) Saka, S.; Miyafuji, H.; Kohara, Y.; Kawamoto, H., US patent 2013, 8409832
- 3) Nakamura, Y.; Miyafuji, H.; Kawamoto, H.; Saka, S., *J. Wood Sci.*, **57**, 331-337 (2011)
- 4) Rabemanolontsoa, H.; Yoshimizu, K.; Saka, S., *J. Chem. Technol. Biotechnol.*, in press
- 5) Evans, J. W.; Wainwright, M. S.; Cant, N. W.; Trimm, D. L., *J. Catal.*, **88**, 203-213 (1984)
- 6) Turek, T.; Trimm, D. L., *Catal. Rev.-Sci. Eng.*, **36**, 645-683 (1994)
- 7) Yu, L. X.; Guo, Q. F.; Hao, J. H.; Jiang, W. J., *Desalination*, **129**, 283-288 (2000)
- 8) Lei, Z. G.; Li, C. Y.; Li, Y. X.; Chen, B. H., *Sep. Purif. Technol.*, **36**, 131-138 (2004)
- 9) Chien, I. L.; Zeng, K. L.; Chao, H. Y.; Liu, J. H., *Chem. Eng. Sci.*, **59**, 4547-4567 (2004)
- 10) Saha, B.; Chopade, S. P.; Mahajani, S. M., *Catal. Today*, **60**, 147-157 (2000)
- 11) Tang, Y. T.; Chen, Y. W.; Huang, H. P.; Yu, C. C.; Hung, S. B.; Lee, M. J., *AIChE J.*, **51**, 1683-1699 (2005)

- 12) Cheah, K. Y.; Tang, T. S.; Mizukami, F.; Niwa, S.; Toba, M.; Choo, Y. M., *J. Am. Oil. Chem. Soc.*, **69**, 410-416 (1992)
 - 13) Mendes, M. J.; Santos, O. A. A.; Jordao, E.; Silva, A. M., *Appl. Catal. A-Gen.*, **217**, 253-262 (2001)
 - 14) Zhang, Z. G.; Jackson, J. E.; Miller, D. J., *Appl. Catal. A-Gen.*, **219**, 89-98 (2001)
 - 15) Olcay, H.; Xu, L. J.; Xu, Y.; Huber, G. W., *ChemCatChem*, **2**, 1420-1424 (2010)
 - 16) Li, W. J.; Ye, L. M.; Long, P.; Chen, J.; Ariga, H.; Asakura, K., *RSC Adv.*, **4**, 29072-29082 (2014)
 - 17) Lee, J. M.; Upare, P. P.; Chang, J. S.; Hwang, Y. K.; Lee, J. H.; Hwang, D. W., *ChemSusChem*, **7**, 2998-3001 (2014)
 - 18) Besson, M.; Gallezot, P.; Pinel, C., *Chem. Rev.*, **114**, 1827-1870 (2014)
 - 19) Rachmady, W.; Vannice, M. A., *J. Catal.*, **192**, 322-334 (2000)
 - 20) Chen, L. G.; Li, Y. P.; Zhang, X. H.; Zhang, Q.; Wang, T. J.; Ma, L. L., *Appl. Catal. A-Gen.*, **478**, 117-128 (2014)
 - 21) Tahara, K.; Nagahara, E.; Itoi, Y.; Nishiyama, S.; Tsuruya, S.; Masai, M., *Appl. Catal. A-Gen.*, **154**, 75-86 (1997)
 - 22) Busca, G., *Phys. Chem. Chem. Phys.*, **1**, 723-736 (1999)
 - 23) Chen, L. A.; Zhu, Y. L.; Zheng, H. Y.; Zhang, C. H.; Zhang, B.; Li, Y. W., *J. Mol. Catal. A-Chem.*, **351**, 217-227 (2011)
-