1 Efficient and selective hydrogenation of aqueous acetic acid on Ru-Sn/TiO₂
2 for bioethanol production from lignocellulosics
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Abstract

Process via acetic acid fermentation has been proposed as a potential way to produce bioethanol from lignocellulosics with improved carbon utilization efficiency as compared to the conventional alcoholic fermentation. This article reports Ru-Sn/TiO₂ as an effective hydrogenation catalyst for aqueous acetic acid as the last step of this process. Although a larger loading of Ru to TiO₂ rather increased the gas by-production, the additional use of Sn significantly improved the ethanol selectivity by the stronger suppression effect on the gas by-production. Finally, the loading levels of 2-4wt% of Sn to 4wt%Ru/TiO₂ were found to be optimal for efficient and selective hydrogenation of acetic acid to ethanol in water. With 4wt%Ru-4wt%Sn/TiO₂ catalyst, aqueous acetic acid solutions (10, 45 and 100g/L) were converted to ethanol in 98.2, 92.7 and 92.8 mol%, respectively, at 170°C/ H₂ 15MPa. This catalytic system would make the acetic acid-based bioethanol production practical.

Keywords

Bioethanol, hydrogenation, acetic acid, Ru-Sn/TiO₂, aqueous media

1. Introduction

Bioethanol is receiving a lot of attraction to substitute gasoline for mitigation of the carbon dioxide emission to the atmosphere. Particularly, lignocellulose-based bioethanol production is strongly desired as one of the second generation biofuels. Our research group has proposed a new bioethanol production process from lignocellulosics, which includes two step hot-compressed water treatment, acetic acid fermentation and hydrogenation [1,2].

This acetic acid-based process is expected to have an advantage over the alcoholic fermentation process in carbon utilization efficiency [3,4]. Carbon utilization efficiency of alcoholic fermentation of glucose with *Saccharomyces cerevisiae* is limited to the theoretical maximum as low as 67%, since two carbons of glucose are emitted as CO₂. On the other hand, all of the carbons of glucose can be converted theoretically into acetic acid by acetic acid fermentation. Furthermore, we have reported that co-cultures of *Clostridium thermocellum* and *C. thermoaceticum* can utilize 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].

Hydrogenation of acetic acid to ethanol is the last step of this acetic acid-based process. Direct hydrogenation of aqueous acetic acid solution is desirable, because the alternative two stage process via ethyl acetate requires purification (dehydration) of acetic acid before esterification, which is very costly in both energetically and economically [5,-9]. Accordingly, direct hydrogenation of aqueous acetic acid solution to ethanol is strongly desired for efficient bioethanol production via acetic acid fermentation.

Low reactivity of acid, however, makes the direct hydrogenation of acid to alcohol difficult [10-13]. Various types of Pt and Ru catalysts supported on titania (TiO₂) and Alumina (Al₂O₃) have been reported to increase the reactivity in acid hydrogenation [10, 11, 14-17]. We reported Pt supported catalyst on TiO₂ being potential for the conversion of acetic acid into ethanol even in water [18]. Activation of carbonyl carbon of acetic acid through coordination to Ti, a Lewis acid site, significantly enhanced the hydrogenation to ethanol in hexane, a non-polar solvent. However, the catalytic reactivity was reduced in water greatly due to the intrinsic nature of water to coordinate Ti, which competes with the coordination of acetic acid to Ti. Fragmentation into methane and ethane was also pointed out as another problem to be solved for the water system at higher temperatures. Accordingly, more effective catalytic systems were still desired for hydrogenation of aqueous acetic acid to ethanol.

This paper reports the Ru-Sn/TiO₂ catalyst systems which were effective to hydrogenate aqueous acetic acid with concentrations of 10, 45 and 100g/L to ethanol. Generally, Ru is expected to be more effective for hydrogenation and less expensive than Pt.

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), titanium tetraisopropoxide (TTIP, >95%, Nacalai Tesque, Kyoto, Japan), ruthenium (III) chloride (RuCl₃, >97.0%, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan), tin (II) chloride (SnCl₂, 97.0%, Nacalai Tesque, Kyoto, Japan) and hexahydroxy-platinic acid [H₂Pt(OH)₆, 99.9%, Sigma-Aldrich,

St Louis, MO, USA] were used for the preparation of Ru/TiO₂, Ru-Sn/TiO₂ and Pt/TiO₂ catalysts. Acetic acid and isopropanol were purchased as guaranteed grade from Nacalai Tesque (Kyoto, Japan).

2.2 Catalyst preparation

Catalysts were prepared by the following impregnation and sol-gel methods A-C separately:

Impregnation method Titanium oxide (1.0 g) was added to an aqueous solution (10 mL) of RuCl₃ (0.082 g, corresponding to Ru 40 mg), and then the suspension was stirred with a magnetic stirrer for 24 h. The resulting suspension was evaporated *in vacuo* and then oven-dried at 105 °C for overnight. 4wt%Ru/TiO₂ catalyst was obtained by further reduction at 400 °C under a H₂ flow (100 mL/min) for 1 h (method A), without calcinations process. Alternatively, heat-treatment at higher reduction temperature [700 °C/ H₂ flow (100 mL/min)/ 1 h] followed by calcination [700 °C/ air flow (100 mL/min) / 4 h] was also conducted separately to check the influences of the treatment temperature (method B).

Sol-gel method A mixture of TTIP (37.2 mL) and isopropanol (20 mL) was poured dropwise to a solution of RuCl₃ (0.205-4.11 g, corresponding to 1.0-20 wt% of Ru against TiO₂) at 60 °C with vigorously stirring. After the additional agitation for 30 min, the mixture was evaporated *in vacuo* and then completely dried in an oven at 105 °C for overnight. The obtained solid was calcinated at 450 °C under an air flow (100 mL/min) for 1 h and then reduced at 400 °C under a H₂ flow (100 mL/min) for 2 h to give 1-20wt%Ru/TiO₂ catalysts (method C). The percentages of 1-20wt% represent the Ru contents (% , w/w) against TiO₂.

Preparation of Ru-Sn/TiO₂ catalysts were conducted by the similar sol-gel method C using the mixtures of RuCl₃ and SnCl₂ instead of RuCl₃. Preparation of Pt/TiO₂ was also conducted by the impregnation method A using H₂Pt(OH)₆ instead of RuCl₃.

2.3 Catalyst characterization

X-Ray diffraction (XRD) patterns of the catalysts were measured with a RINT 2000V (Rigaku Co. Ltd., Tokyo, Japan) using Cu-K α radiation (40 kV, 30 mA). The crystallite diameter L (nm) was estimated according to the Scherrer equation (1)

$$L = 0.94\lambda/\beta\cos\theta \quad (1)$$

where λ is the X-ray wavelength (0.1542 nm), β is full width at half maximum of the peak at $2\theta = 25.2^\circ$ assigned to the (101) faces of anatase-form TiO₂ and θ is the Bragg angle. The surface areas of the catalysts were measured by nitrogen adsorption with a FlowSorb III 2305 BET surface area analyzer (Shimadzu, Kyoto, Japan).

2.4 Hydrogenation

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 catalyst by stirring in water (20 mL) under H₂ (2.0 MPa) at 120 °C for 1 h, an aqueous acetic acid solution (10 mL) was added to the solution, and the mixture was stirred at the designated temperature and pressure for 12-24 h. Hydrogenation was conducted by using different loading levels of catalyst: 1.0, 4.0 and 18 wt% against the acetic acid solutions.

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 x 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. The recovery of acetic acid and the yield of ethanol were determined as mol % based on the acetic acid used in this study. These values were obtained from the areas of the peaks observed at the retention times of 14.9 and 22.5 min, respectively, by using the calibration curves which had been prepared with the solutions with known concentrations.

The gaseous products were recovered into a gas bag and analyzed on a Varian CP-4900 micro gas chromatograph, under the following chromatographic conditions: channel (1) column: MS5A 10 m; carrier gas: argon; column temperature: 100 °C; column pressure: 170 kPa; detector: thermal conductivity detector (TCD); channel (2) column: PoraPLOT Q 10 m; carrier gas: helium; column temperature: 80 °C: column pressure: 190 kPa; detector: TCD.

Most of the experiments were repeated twice to ensure the reproducibility, although the data presented in this article were not treated statistically.

3. Results and discussion

3.1 Characterization of catalyst

The XRD patterns measured for the 4wt%Ru/TiO₂ catalysts prepared by the impregnation and sol-gel methods (A-C) are illustrated in Fig. 1, along with that of commercial TiO₂ [anatase (A) : rutile (R) = 4:1] used for the impregnation. Table 1 summarizes the A/(A + R) ratios, crystallite diameters and BET surface areas of the catalysts. The A/(A + R) ratios were evaluated from the areas of the peaks at 2θ 25.2°

and 27.4°, which are assigned to anatase and rutile type of crystal forms, respectively [19]. No signals assigned to Ru were observed for all Ru/TiO₂ catalysts, probably due to the dispersion as small particles.

The XRD patterns were quite different depending on the preparation method. The catalyst prepared by the impregnation method A with a relatively low reduction temperature of 400°C without calcination exhibited very similar pattern (b) to that (a) of the original TiO₂ used for preparation. By increasing the reduction temperature to 700 °C following calcination at 700 °C [method B, pattern (c)], content of the rutile form increased significantly, which reduced the A/(A + R) ratio from 0.62 to 0.38. Accordingly, crystalline transformation from anatase to rutile form occurred during the heat-treatment at 700°C. This kind of transformation is a well-known process for TiO₂ at high temperatures [19]. A growth in the crystallite diameter from 17.7 to 26.5 nm and a decrease in the BET surface area from 50.4 to 22.7 m²/g were accompanied with this crystalline transformation.

The catalyst prepared by the sol-gel method C had a greater BET surface area (84.5 m²/g) and exhibited much broader XRD signals [pattern (d)], which attributes to the smaller crystallite diameter (7.7 nm). Milder calcination and reduction temperatures (400/450°C) may not be enough for the extensive crystallization to grow the crystallite size. The anatase form was dominant along with a smaller content of the brookite form, while the signals assigned to rutile form was not observed.

3.2 Hydrogenation of aqueous acetic acid

Catalytic activities of 4wt% Ru/TiO₂ and 4wt% Pt/TiO₂, both of which were prepared by the same impregnation method A, were compared for the hydrogenation of 10 g/L

aqueous acetic acid under the following reaction conditions: catalyst load: 1.0 wt% in solution/ H₂ 15MPa/ 130°C/ 12 h. The ethanol yield (35.3 mol%) obtained with 4wt%Ru/TiO₂ was greater than that (2.2 mol%) with 4wt%Pt/TiO₂, which confirms that Ru is a better catalyst metal than Pt for hydrogenation of acetic acid.

As for the influences of the catalyst preparation method, activities of three kinds of the catalysts as characterized in Fig. 1 and Table 1 were evaluated under the similar reaction conditions. The resulting ethanol yields are plotted against three parameters, i.e., A/(A + R) ratio, BET surface area and crystallite diameter in Fig. 2. The ethanol yield varied depending on the catalysts, and the catalyst prepared by the sol-gel method was found to be better than the impregnation methods for Ru/TiO₂ preparation. Thus, the following discussion is focused on the catalysts prepared by the sol-gel method.

The influences of the Ru content on the catalytic activity as evaluated by changing the Ru content from 1.0 to 20 wt% against TiO₂ are shown in Fig. 3. Gaseous products including methane, ethane, and smaller amount of propane were formed along with ethanol as a major type of the by-product, and the rest of the reaction mixtures was only acetic acid. For example, methane, ethane and propane formed in 32.1, 9.7 and 1.7 % (C-based), respectively, on 14wt%Ru/TiO₂. These results indicate that homolysis of the C–C bond is also catalyzed by Ru/TiO₂. Propane would form by the coupling of methyl radical and ethyl radical intermediates.

The ethanol yield increased with an increase in the Ru content up to 8.0 wt% against TiO₂, while rather decreased at the higher Ru contents by enhancing the gas formation. Thus, the optimum Ru content exists for ethanol production. In terms of the selectivity to ethanol against the gaseous by-products, 4wt%Ru against TiO₂ was chosen as the optimal content of Ru for ethanol production.

Addition of Sn to some metal catalysts has been reported to reduce the gas formation during catalytic hydrogenation [20-23]. To evaluate the effectiveness of Sn for suppression of the gaseous products formation, reactivities of various 4wt%Ru-Sn/TiO₂ catalysts were evaluated, which had different addition levels of Sn from 2.0 to 8.0 wt% against TiO₂ (Fig. 4). Without the addition of Sn, approximately 30 % (C-based) of the gaseous by-products were produced, while the gas formation was effectively suppressed even at 2.0 wt% addition against TiO₂ and became almost negligible at >4.0 wt% with the reaction mixtures being acetic acid and ethanol only. The addition levels of 2-4 wt% of Sn against TiO₂ were therefore found to be the optimal catalyst composition at 130°C for selective hydrogenation of aqueous acetic acid to ethanol.

Tin is also known to be a potential Lewis acid site to activate carbonyl group, and this property has been utilized for selective reduction of aldehyde/ketone to alcohol in the presence of unsaturated >C=C< group [11, 24-28]. The ethanol yield from aqueous acetic acid, however, was rather reduced with the introduction of the increasing amounts of Sn to 4wt%Ru/TiO₂. Thus, Sn in Ru-Sn/TiO₂ catalyst does not exhibit any positive roles for the catalytic hydrogenation of acetic acid into ethanol.

As illustrated in Fig. 5, hydrogenation of acetic acid to ethanol may occur at the interface between Ru and TiO₂, where hydrogen anion as activated on Ru can attack the activated carbonyl carbon of acetic acid. This mechanism has been postulated based on the solvent effects reported in our previous paper [18]; the catalytic activities of Pt/TiO₂ for the production of ethanol and ethyl acetate from acetic acid, both of which are expected to proceed via the same activated species of acetic acid, were reduced in polar solvent [reactivity: n-hexane > tetrahydrofuran (THF) > H₂O]. These results could be explained reasonably with the competitive coordination of the oxygen lone pairs of THF

or H₂O and that of acetic acid to the Lewis acid site (TiO₂). On the other hand, gas formation via the C–C bond cleavage of acetic acid may occur on the Ru surface, since such a reaction did not proceed with the pure TiO₂.

The results in Fig. 3 are explainable with this postulated mechanism. Although the gas yield increased linearly with the increasing content of Ru against TiO₂, the ethanol yield tended to level off around 4-8 wt%. The increasing amount of Ru contributes its greater surface against the Ru-TiO₂ interface, which is not beneficial to the hydrogenation but the gas formation. The proposed spill-over mechanism [29, 30], in which the hydrogen atoms activated on metal migrate to the metal-support interface, cannot explain the influence of Ru content in Fig.3 on production of ethanol, although this may increase the reactivity of ethanol production at the Ru-TiO₂ interface.

Literature [31-33] indicates that Ru and Sn form alloys, although any evidence was not obtained in this study due to no apparent XRD signals assigned to Ru and Sn, which would arise from the highly dispersed distribution of these elements in the catalysts. Based on the results in Fig. 4, the Ru-Sn alloys may have the lower catalytic activities than Ru particularly for the gas by-production. This would improve the ethanol selectivity, although the ethanol productivity also decreases.

Hydrogenation was conducted on 4wt%Ru-4wt%Sn/TiO₂ at higher temperatures than 130°C (Fig. 6). Gas formation was effectively inhibited at the temperatures up to 170°C, where acetic acid was converted into ethanol in a 98.2 mol% yield. Even with this catalyst system, the ethanol yield rather decreased at 175°C due to the occurrence of the gas by-production. Consequently, 170°C was found to be the optimal temperature condition for selective ethanol production. We also confirmed that no ethanol formation was observed without using the catalyst even at such high temperatures.

In conventional alcoholic fermentation process, sugar (ethanol) concentration is one of the important factors which influence the overall energy efficiency, since the energy required for the purification through distillation tends to correlate inversely to the ethanol concentration. The situation is also true for the acetic acid-based bioethanol production. We estimated that the acetic acid concentration greater than 45 g/L is desirable for energy-efficient production of bioethanol from lignocellulosics [34]. Accordingly, higher concentrations of aqueous acetic acid solutions at 45 and 100 g/L were also investigated with the optimal catalytic conditions (Table 2). Although the higher concentrations of 45 and 100 g/L required longer reaction times to complete the hydrogenation reaction, ethanol was similarly obtained in high yields: 92.7 mol% (45 g/L) and 92.6 mol% (100 g/L) after 24 h treatment. Increasing the catalyst load from 4.0 to 18 wt% in solution was effective to shorten the reaction time with maintaining the high yield ethanol production, and hence 45 g/L of acetic acid was converted into ethanol in a 95 mol% yield after 12 h treatment. Consequently, this catalyst system was found to be effective for aqueous acetic acid solution at least up to 100 g/L.

4. Conclusions

Efficient and selective hydrogenation of aqueous acetic acid on Ru-Sn/TiO₂ for bioethanol production from lignocellulosics has been studied in this work and the following conclusions were obtained:

1. Ru/TiO₂ catalyzed both ethanol and gas productions from aqueous acetic acid.
2. The addition of Sn to Ru/TiO₂ significantly improved the ethanol selectivity by the stronger suppression effect on the gas by-production, although this also tends to reduce the ethanol productivity.

3. The Sn loading levels of 2-4wt% against TiO₂ to 4wt%Ru/TiO₂ were found to be optimal for the ethanol production from aqueous acetic acid.
4. 4wt%Ru-4wt%Sn /TiO₂ effectively converted the aqueous acetic acid solutions (10, 45 and 100g/L) to ethanol in 98.2, 92.7 and 92.8 mol%, respectively, at 170°C.

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Legends of figures and tables

Fig.1 X-Ray diffraction patterns of 4wt%Ru/TiO₂ catalysts obtained by various preparation methods.

a): commercial TiO₂ used for impregnation, b): impregnation (method A), c): impregnation (method B), d): sol-gel (method C), ●: anatase, ○: rutile, ◆: brookite.

Fig. 2 Ethanol yields plotted against three catalyst parameters, A/(A + R) ratios, BET surface areas and crystallite diameters of 4wt%Ru/TiO₂ catalysts (reaction conditions: 10g/L aqueous acetic acid/ catalyst load: 1.0 wt% in solution/ H₂ 15MPa/ 130°C/ 12 h).

①: sol-gel (450°C /400°C) (method C), ②: impregnation (-/400°C) (method A), ③: impregnation (700°C/700°C) (method B), values in parenthesis are the temperatures used for (calcination/reduction).

Fig. 3 Influences of the Ru content (wt% against TiO₂) in Ru/TiO₂ on the yields (% , C-based) of ethanol and gaseous by-products (reaction conditions: 10g/L aqueous acetic acid/ catalyst load: 1.0 wt% in solution/ H₂ 15MPa/ 130°C/ 12 h).

○: ethanol, +: gaseous by-products.

Fig. 4 Influences of the addition of Sn (wt% against TiO₂) to 4wt%Ru/TiO₂ on the yields (% , C-based) of ethanol and gaseous by-products (reaction conditions: 10g/L aqueous acetic acid/ catalyst load: 4.0 wt% in solution/ H₂ 15MPa/ 130°C/ 12 h).

○: ethanol, +: gaseous by-products.

Fig. 5 Postulated role of TiO₂ for the formation of ethanol and gaseous by-products from acetic acid on Ru/TiO₂.

Fig. 6 Temperature dependency in hydrogenation of aqueous acetic acid on 4wt%Ru-4wt%Sn/TiO₂ catalyst (reaction conditions: 10g/L acetic acid/ catalyst load: 4.0 wt% in solution/ H₂ 15MPa/ 12 h).

Table 1 A/(A + R) ratios, crystallite diameters and BET surface areas measured for various Ru/TiO₂ catalysts.

Table 2 Hydrogenation of 45 and 100g/L aqueous acetic acid on 4wt%Ru-4wt%Sn/TiO₂ (reaction conditions: H₂ 15MPa/ 170°C).

Table 1

Preparation method	A/(A + R) ^{*2}	Crystallite diameter L (nm)	BET surface area (m ² /g)
A. Impregnation (–/400°C) ^{*1}	0.62	17.7	50.4
B. Impregnation (700°C/700°C)	0.38	28.5	22.7
C. Sol-gel (450°C/400°C)	1.0	7.7	84.5

^{*1} Temperatures used for (calcination / reduction) .

^{*2} Ratio of peak area [anatase (A, 2 θ 25.2°)] / [anatase (A, 2 θ 25.2°) + rutile (R, 2 θ 27.4°)]

Table 2

Concentration of AcOH (g/L)	Catalyst load (wt% in solution)	Reaction time (h)	Recovery of AcOH (mol%)	Yield of EtOH (mol%)
45	18	12	0.1	95.0
	4.0	12	20.8	74.7
		18	4.5	89.2
		24	0.5	92.7
100	4.0	12	28.7	62.6
		18	6.6	86.0
		24	0.2	92.6

Figure

Fig.1

Figure

Fig.2

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Fig.6