

Article

Reaction Mechanisms and Production of Hydrogen and Acetic Acid from Aqueous Ethanol Using a Ru-Sn/TiO₂ Catalyst in a Continuous Flow Reactor

Takashi Nomura , Yuanyuan Zhao, Eiji Minami and Haruo Kawamoto * 

Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan; nomura.takashi.2n@kyoto-u.ac.jp (T.N.); papalena@live.cn (Y.Z.); minami.eiji.4z@kyoto-u.ac.jp (E.M.)

* Correspondence: kawamoto@energy.kyoto-u.ac.jp; Tel.: +81-75-753-4737

Abstract: The catalytic reforming of bioethanol can produce green hydrogen (H₂) and acetic acid (AcOH). In the present study, the conversion of aqueous ethanol (EtOH) over 4 wt%Ru-4 wt%Sn/TiO₂ in a flow reactor was investigated at different temperatures at 0.1 MPa or at various pressures at 260 °C. The ethanol conversion was rather slow in liquid water, while the reactivity increased significantly when water was evaporated. Under gas-phase conditions at 0.1 MPa, the conversion rate increased with increasing reaction temperature, but the AcOH yield and H₂ purity decreased due to by-production of CH₄, CO, and CO₂. The CH₄ and CO generated by fragmentation of acetaldehyde (AA), an intermediate, were suppressed by increasing reaction pressure, although the formation of CH₄ and CO₂ generated from AcOH was pressure independent. Thus, the highest-pressure conditions in steam at a given reaction temperature are preferred for the production of pure H₂. The initial step, EtOH → AA, was the rate-determining reaction, and the model experiments using AA as a substrate showed that the Cannizzaro reaction of two AA molecules to form EtOH and AcOH occurred preferentially. This oxidation system was confirmed to be effective at EtOH concentrations of up to 500 g/L in water.

Keywords: ethanol; green hydrogen; acetic acid; Ru-Sn/TiO₂ catalyst; biomass; reaction mechanism



Citation: Nomura, T.; Zhao, Y.; Minami, E.; Kawamoto, H. Reaction Mechanisms and Production of Hydrogen and Acetic Acid from Aqueous Ethanol Using a Ru-Sn/TiO₂ Catalyst in a Continuous Flow Reactor. *Catalysts* **2024**, *14*, 249. <https://doi.org/10.3390/catal14040249>

Academic Editor: Anjie Wang

Received: 29 February 2024

Revised: 3 April 2024

Accepted: 8 April 2024

Published: 9 April 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The efficient use of biomass as an alternative to fossil resources is attracting attention as a means of mitigating climate change caused by increasing emissions of greenhouse gases. Specifically, bioethanol produced by the fermentation of sugars derived from biomass can be used as a substitute for gasoline. However, the demand for bioethanol as a fuel is expected to decline as electric and fuel cell vehicles become more widespread in the future. Therefore, it is important to develop alternative utilization technologies for bioethanol.

Because bioethanol produced by fermentation contains a large amount of water, it would be preferable to develop techniques that allow the utilization of aqueous ethanol (EtOH) solutions without removing this water. The reforming of EtOH with water is a potential method of converting aqueous EtOH to hydrogen (H₂) and acetic acid (AcOH) via the reaction shown in Equation (1).



Hydrogen is a clean energy carrier, producing only water as a by-product during combustion, but the extent to which this fuel is carbon neutral depends on the manner in which it is produced. Carbon dioxide is emitted in the process of producing H₂ from fossil resources, whereas green H₂ production without CO₂ emissions would be highly desirable. The reforming of bioethanol to generate H₂ is therefore a promising means of reducing CO₂ emissions and the H₂ produced in this manner also has numerous applications such

as a clean fuel and in the synthesis of various chemicals. AcOH is an important industrial chemical feedstock with a global demand of 16.1 million tons in 2022 [1] and can be used as a raw material for the generation of vinyl acetate, cellulose acetate, and other compounds, the majority of which are currently produced from petroleum-based AcOH.

Various organometallic complexes [2,3] and metal catalysts [4–8] have been investigated for the reforming of EtOH with water. Iridium complexes with bipyridonate ligands bearing *N,N*-dimethylamino substituents have been reported to convert aqueous EtOH to H₂ and AcOH with high yields and good selectivity [3]. In this catalytic system, the oxidation is able to proceed under mildly basic conditions, providing a 99% sodium acetate yield (based on the amount of EtOH used) and a 95% theoretical H₂ yield under reflux conditions. Even so, the required reaction time is very long (over 18 h) and the resulting sodium acetate must be protonated to generate pure AcOH. In addition, the spent catalyst must be dried under reduced pressure and then extracted with dichloromethane in preparation for reuse.

Due to their great advantages in industrial applications, many attempts have been made to use supported metal catalysts [4–8]. Cu/ZnO-ZrO₂-Al₂O₃ has been found to catalyze the conversion of aqueous EtOH to AcOH and H₂ with a maximum AcOH yield of 73.3% [4]. However, the selectivity of this process for AcOH decreases with increases in the EtOH concentration as by-products such as ethyl acetate, acetaldehyde (AA), methyl ethyl ketone, and butanol are produced. This previous work also did not report the purity of the H₂ obtained. CuCr can provide almost complete EtOH conversion but gives a reported AcOH yield of only 48.6% based on the formation of a high proportion of AA (approximately 50%) as an oxidation intermediate [5]. The temperature range used for these metal catalysts is also generally high (250–300 °C for Cu/ZnO-ZrO₂-Al₂O₃ and 350 °C for CuCr).

Supported precious metal catalysts have been used to lower the reaction temperature. Nozawa et al. [6] used Ru/TiO₂ for aqueous-phase reforming of EtOH at 200 °C, but the main products were CH₄ and CO₂ rather than AcOH, resulting in the lower H₂ purity. Such high selectivity of gaseous products in aqueous-phase reforming of EtOH has also been reported for carbon black- and carbon nanotube-supported Pd and PdZn catalysts at 250 °C [7]. The addition of rhenium to the TiO₂ supported Ru, Rh, Ir, and Pt catalysts was reported to improve the selectivity of AcOH and H₂, but the conversion of EtOH was only less than 37% even after 10 h at 200 °C in a batch reactor [8].

For all these reasons, the catalytic reforming of aqueous EtOH to H₂ and AcOH is not yet sufficiently mature to allow for practical applications as an approach to green H₂ production. On this basis, the present study assessed the performance of Ru-Sn/TiO₂ as an efficient and selective catalyst for the production of H₂ and AcOH in a flow reactor and discusses the reaction mechanisms involved in this conversion. In previous studies by the authors on the hydrogenation of AcOH to EtOH while investigating bioethanol production via AcOH fermentation, Ru-Sn/TiO₂ was developed as an effective catalyst capable of functioning in aqueous media [9,10]. The formation of the gaseous products was effectively suppressed by the addition of Sn to Ru/TiO₂ [9], and the hydrogenolysis efficiency of AcOH to EtOH was significantly improved by using a continuous flow reactor [10]. The 4 wt%Ru-4 wt%Sn/TiO₂ (based on the weight of TiO₂) was selected in accordance with the previous investigation to optimize the Ru and Sn contents and to minimize the production of gaseous by-products from the hydrogenolysis of aqueous AcOH [9].

2. Results and Discussion

2.1. Effect of Temperature at 0.1 MPa

The oxidation of a 10 g/L aqueous EtOH solution over 4 wt%Ru-4 wt%Sn/TiO₂ was performed over the temperature range of 190–260 °C at atmospheric pressure (0.1 MPa) in a flow-type reactor. The yields of liquid-phase products, of gaseous products other than H₂, and of H₂, together with the H₂ purity, are summarized in Figure 1A–C, respectively. Under all conditions, water vapor was present in the gas phase. The data show that two

moles of H₂ were obtained from each mole of EtOH (as expected according to Equation (1)) and so the H₂ yields are reported herein relative to the expected theoretical yields. That is, a theoretical yield of 100% H₂ would be equivalent to a yield of 200 mol% based on the initial amount of EtOH. Yields of other products are given as mol% based on the actual amount of EtOH used in the trial.

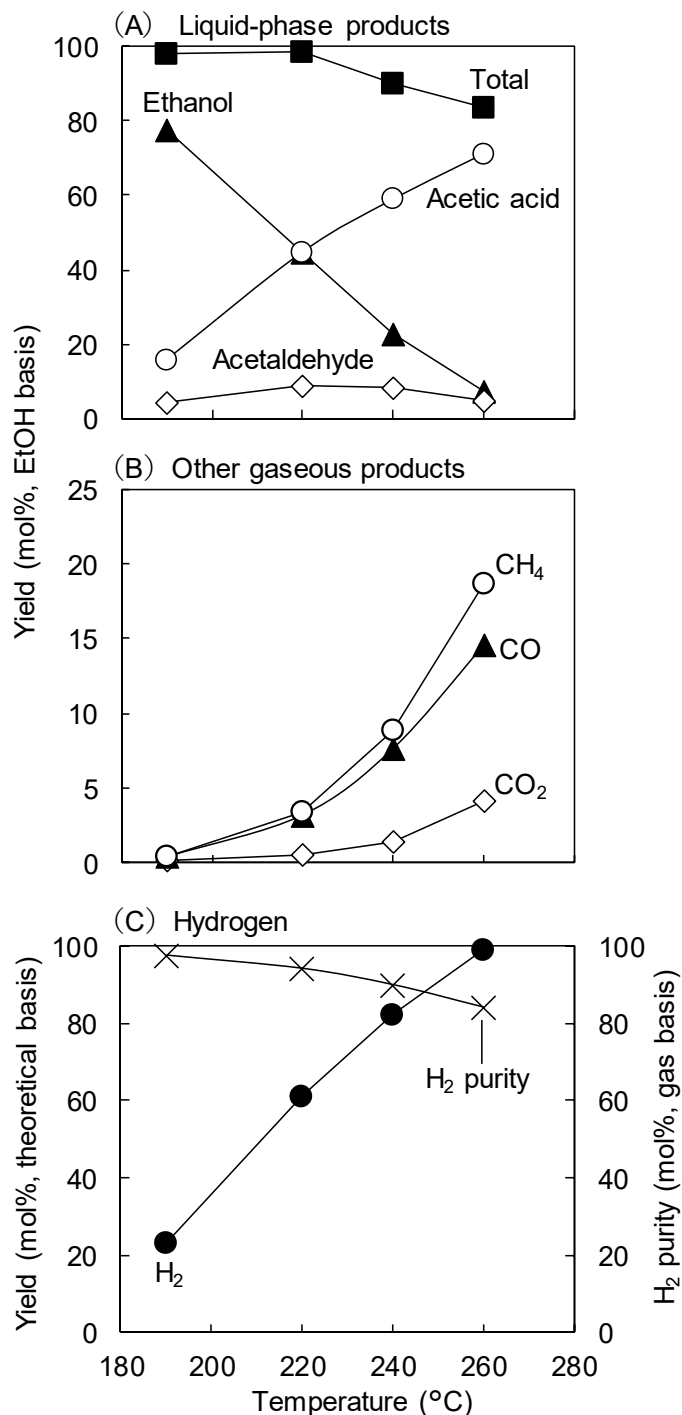
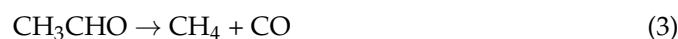


Figure 1. The effects of reaction temperature on the conversion of aqueous EtOH (10 g/L) to AcOH and H₂, based on the outputs of (A) liquid-phase products, (B) gaseous products other than H₂ and (C) H₂. The graph in (C) also plots H₂ purity in the gaseous products as a function of temperature. Data were acquired with a reactor column having a 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at a pressure of 0.1 MPa.

The EtOH conversion efficiency increased from 22.4% to 92.8% as the reaction temperature was increased from 190 to 260 °C. The yields of H₂ and AcOH also increased, from 23.2% to 99.4% (on a theoretical basis) and from 16.0 mol% to 71.2 mol% (on an EtOH basis), respectively. The yield of AA, the intermediate in EtOH oxidation, remained low (from 4.6–8.7 mol% based on EtOH) regardless of the reaction temperature, indicating that the second step in this process (AA → AcOH) occurred more efficiently in the sequential oxidation scheme (EtOH → AA → AcOH).



The yields of all gaseous products, including H₂, increased with increases in the reaction temperature. However, the CH₄, CO, and CO₂ formation rates all increased exponentially, whereas that of H₂ exhibited a linear increase (Figure 1B,C). Consequently, the purity of H₂ decreased from 97.9 mol% at 190 °C to 84.1 mol% at 260 °C at 0.1 MPa. The total combined yield of CH₄, CO, and CO₂ reached 37.4 mol% (EtOH basis) at 260 °C, while the total combined yield of the liquid products (EtOH, AcOH and AA, Figure 1A) decreased from 98.1 mol% at 190 °C to 83.5 mol% at 260 °C. Although the EtOH conversion was low at the lower temperatures, the selectivities for H₂ and AcOH were relatively high, giving almost pure products. At higher temperatures, the conversion of EtOH was increased but the selectivity decreased as a result of the increased fragmentation of AA and AcOH.

2.2. Effect of Pressure at 260 °C

Additional reactions of 10 g/L aqueous EtOH were performed over the pressure range of 0.1 to 6.0 MPa at a fixed temperature of 260 °C (Figure 2). The aqueous phase transitioned from steam to liquid water upon increasing the reaction pressure to the saturated vapor pressure of water, which was estimated to be 4.7 MPa at 260 °C using the Soave–Redlich–Kwong model with the ProII 2022 process simulator. The residence time as shown in this figure was also increased up to 3.1 s at 4.0 MPa by compressing the steam, based on increasing the reaction pressure. The residence time was significantly longer in the liquid aqueous phase (93 s at 6.0 MPa). The amount of unreacted EtOH increased with increases in the reaction pressure, and this trend became more pronounced at 6.0 MPa, at which the water vapor was converted to liquid water even though the residence time increased with increasing pressure. Thus, the oxidation of EtOH was more efficient in the gas phase and a lower pressure improved the conversion of EtOH in the steam. The H₂ yields showed a similar trend to the EtOH conversion throughout the pressure range used in this study.

In contrast, the AcOH yield was almost constant at approximately 70 mol% over the pressure range of 0.1–4.0 MPa based on gas-phase reactions, while the H₂ purity gradually increased from 84.1 mol% at 0.1 MPa to 93.2 mol% at 4.0 MPa. The latter effect is ascribed to decreases in the yields of CO and CH₄ derived from the fragmentation of AA (Equation (3)). The yield of CO became almost zero at pressures of 3 to 4 MPa, indicating that the fragmentation of AA was completely suppressed under such conditions. Conversely, the CO₂ yield was constant over the pressure range of 0.1–4.0 MPa, whereas the CH₄ yield plateaued, suggesting that the fragmentation of AcOH (Equation (2)) also occurred but the progress of the reaction was independent of pressure. Therefore, a reaction pressure slightly lower than the saturated vapor pressure of water at a given reaction temperature was evidently optimal with regard to obtaining high-purity H₂.

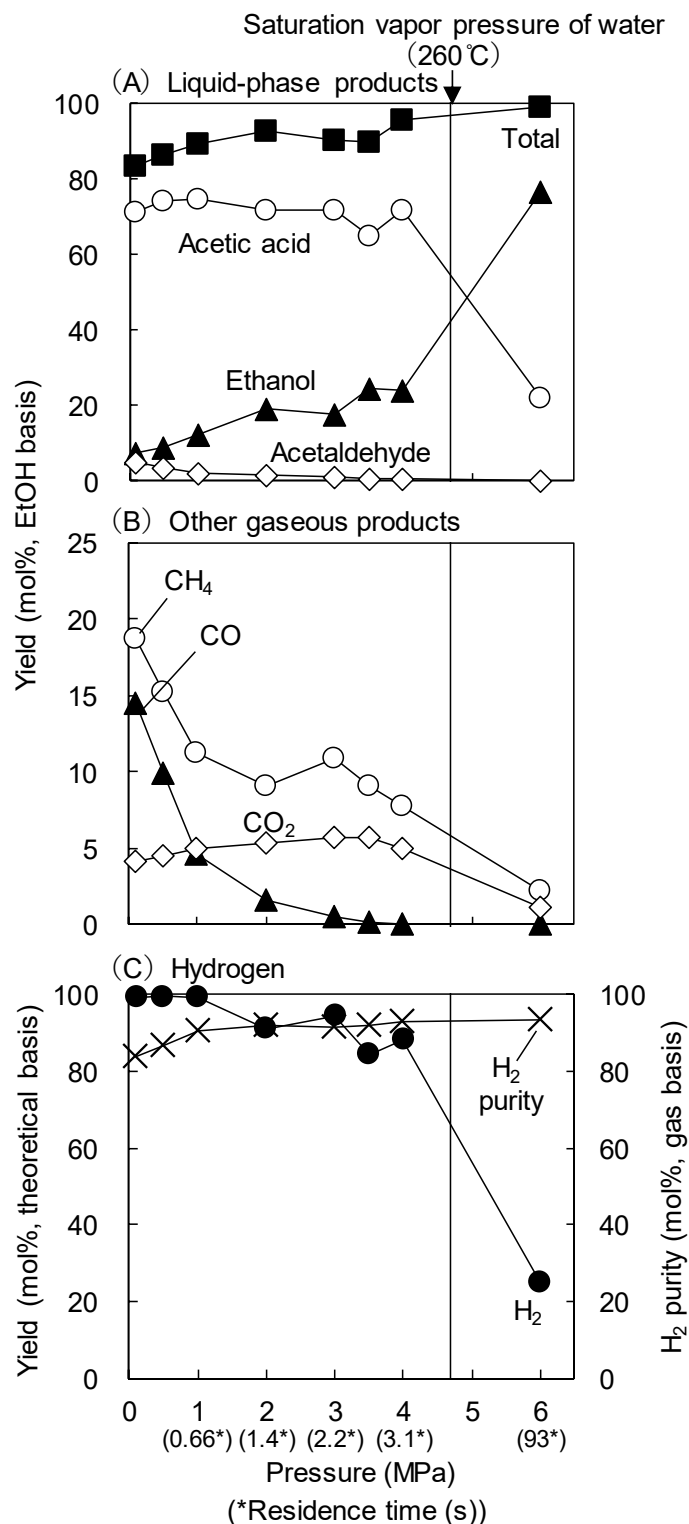


Figure 2. The effects of reaction pressure on the conversion of aqueous EtOH (10 g/L) to AcOH and H₂, based on the outputs of (A) liquid-phase products, (B) gaseous products other than H₂ and (C) H₂. The graph in (C) also plots H₂ purity in the gaseous products as a function of pressure. Data were acquired with a column having a 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at a temperature of 260 °C.

The yield of AA was consistently low, as can be seen from Figure 1, but tended to decrease with increases in reaction pressure. From this outcome, it appears that the conversion of AA to AcOH was more efficient at higher pressures. The opposite trend

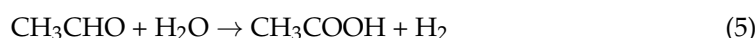
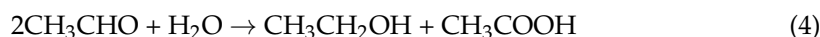
was observed for the fragmentation of AA to CH₄ and CO. The effects of reaction pressure on the various steps involved in the conversion of EtOH in the vapor phase at 260 °C are summarized in Table 1.

Table 1. Summary of the effects of reaction pressure on the steps involved in the conversion of aqueous EtOH in steam over 4 wt%Ru-4 wt%Sn /TiO₂ at 260 °C.

Step	Preferred Condition
EtOH → AA (rate-determining)	Lower pressure (0.1–2 MPa)
AA → AcOH	Higher pressure (2–4 MPa)
AA → CH ₄ + CO	Lower pressure (0.1–2 MPa)
AcOH → CH ₄ + CO ₂	No effect

2.3. Cannizzaro Reaction

To better understand the reactivity of the AA intermediate, a 10 g/L aqueous solution of AA was reacted over 4 wt%Ru-4 wt%Sn/TiO₂ at pressures between 0.1 and 4.0 MPa at 260 °C. The results are shown in Figure 3. At all pressures, the AA was almost completely reacted (with recoveries of 0.0–1.0%) and AcOH and H₂ were formed. The H₂ yields were high (82.2–93.2% on a theoretical basis), indicating that the conversion of AA to AcOH and H₂ was highly selective. Note that, in these trials, a 100% theoretical yield of H₂ was equivalent to 100 mol% based on the amount of AA used. Unexpectedly, EtOH was found to have been produced from the AA, although the yields were less than 10.2 mol%. Evidently, the Cannizzaro reaction occurred. In this reaction, two molecules of a non-enolizable aldehyde give a primary alcohol and a carboxylic acid (Equation (4)) [11,12].



The EtOH produced by the Cannizzaro reaction in these trials was subsequently converted to AA (Figure 4).

In addition to the Cannizzaro reaction, the direct oxidation of AA (Equation (5)) was also expected to take place during the conversion of EtOH to AcOH (Figure 4). To evaluate this phenomenon, the amount of EtOH produced by the Cannizzaro reaction, EtOH (Cannizzaro), was estimated based on Equation (6), assuming that the EtOH obtained from the original AA (Figure 3) had a reactivity similar to that of EtOH during the trials used to generate the data in Figure 2.

$$\text{EtOH (Cannizzaro)} \times \text{Recovery rate (EtOH ex)} = \text{EtOH (O)} \quad (6)$$

In this equation, Recovery rate (EtOH ex) is the percentage of the original EtOH recovered following the EtOH oxidation reaction used to generate the data in Figure 2. EtOH (O) is the amount of EtOH observed in the experiment of AA as a substrate (Figure 3). The estimated EtOH (Cannizzaro) yield values are plotted in Figure 5. Because the theoretical EtOH (Cannizzaro) yield had a maximum of 50 mol% based on the original amount of AA, the approximately 50 mol% values estimated for the trials at 0.1, 0.5, and 1.0 MPa indicate that the conversion of AA occurred primarily via the Cannizzaro reaction rather than the direct oxidation pathway. In contrast, the estimated EtOH (Cannizzaro) yields were lower (30–40 mol%) in the pressure range of 2.0–4.0 MPa, demonstrating that the direct oxidation of AA became competitive with the Cannizzaro reaction at these pressures, although the Cannizzaro reaction was still preferred even under these conditions.

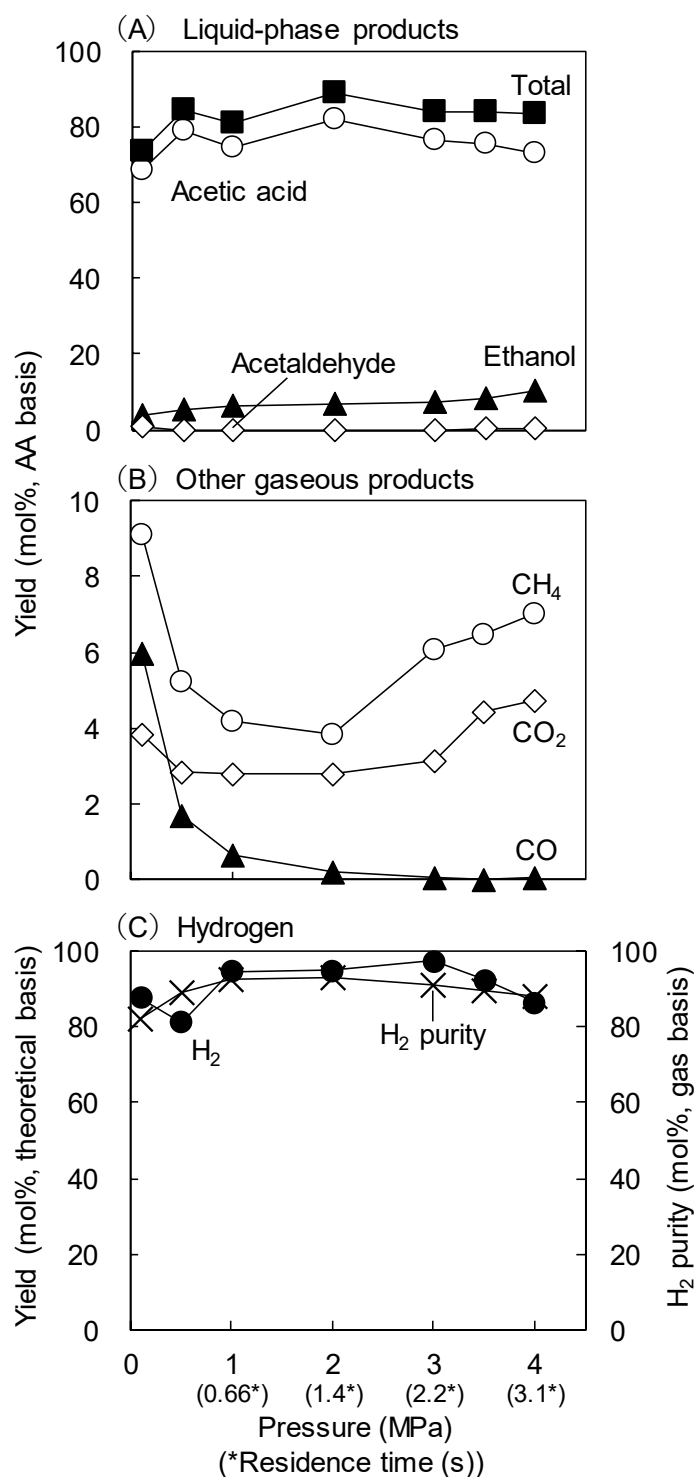


Figure 3. The effects of reaction pressure on the conversion of aqueous AA (10 g/L) to AcOH and H₂, based on the outputs of (A) liquid-phase products, (B) gaseous products other than H₂ and (C) H₂. The graph in (C) also plots H₂ purity in the gaseous products as a function of pressure. Data were acquired using a reactor column with dimensions of 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at 260 °C.

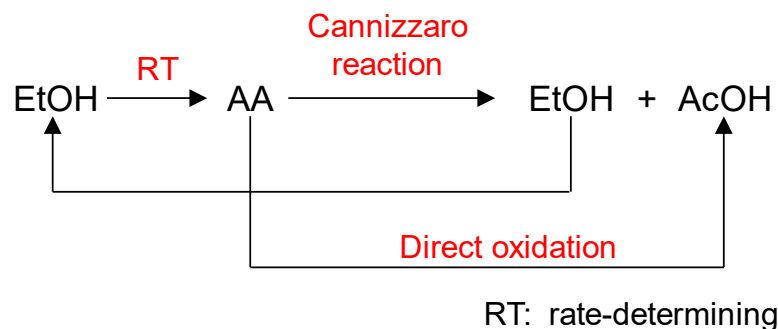


Figure 4. A diagram showing the Cannizzaro reaction and direct oxidation of AA, which represent competing pathways during the oxidation of EtOH.

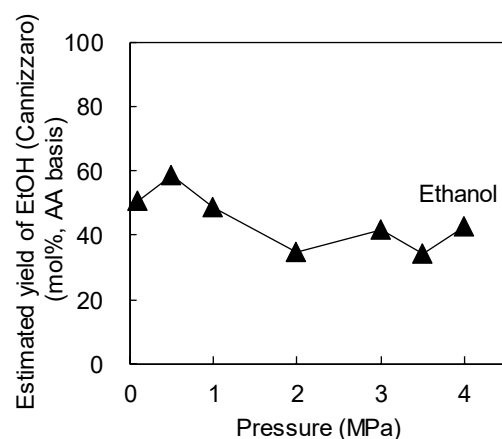


Figure 5. The effects of reaction pressure on the yield of EtOH produced by the Cannizzaro reaction during the reaction of AA. EtOH (Cannizzaro) refers to EtOH produced from AA by the Cannizzaro reaction. Data were acquired using a reaction column having dimensions of 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at a temperature of 260 °C.

The composition of the gaseous by-product mixture provided insights into the fragmentation reactions of AA and AcOH. Similar to the trials using EtOH (as shown in Figure 2), the yields of CO and CH₄ resulting from the fragmentation of AA decreased with increases in reaction pressure (Figure 3B). Interestingly, the yields of CO and CH₄ obtained from the AA experiments were approximately half those obtained from trials using EtOH solutions (CO: 14.5 → 6.0 mol%, CH₄: 18.7 → 9.1 mol%). This change can be explained by considering that the fragmentation reaction of AA occurred only during the conversion of EtOH to AA on the surface of the 4 wt%Ru-4 wt%Sn/TiO₂, as shown in Figure 6. In the trials using the AA solutions, the amount of EtOH involved in the conversion process was approximately half the amount of AA because the Cannizzaro reaction converted AA according to the relationship 2AA → EtOH + AcOH. It is not presently clear why the fragmentation of AA did not occur in conjunction with the Cannizzaro reaction catalyzed by 4 wt%Ru-4 wt%Sn /TiO₂.

In contrast, the CO₂ yields obtained from the fragmentation of AcOH to give CO₂ and CH₄ were approximately 5 mol% when using either AA or EtOH. This outcome suggests that the yields of these compounds were dependent on the amount of AcOH that was produced. The yields of CO₂ and CH₄ during the AA trials (Figure 3B) tended to increase along with pressure on going from 2 to 4 MPa, showing that the fragmentation of AA was more efficient at higher pressures. However, this effect was not as evident during the experiments using the EtOH solution (Figure 2B).

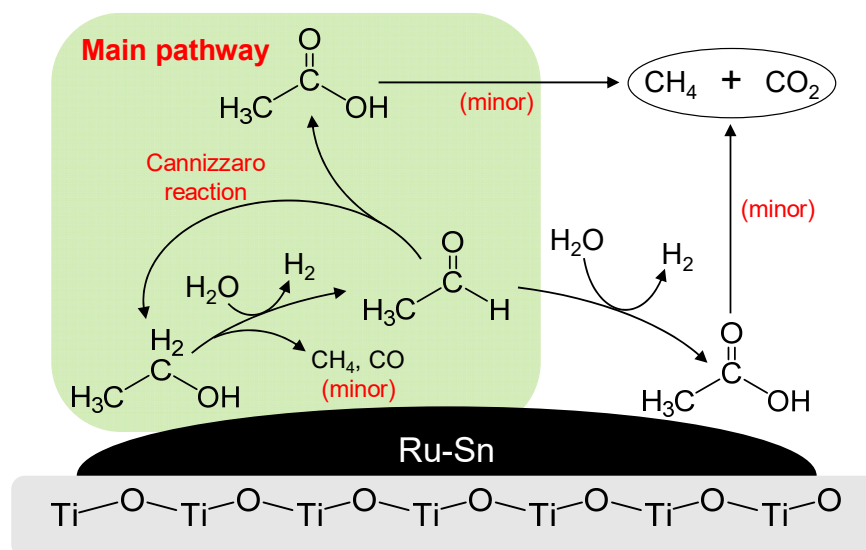


Figure 6. A proposed mechanism for the conversion of aqueous EtOH to AcOH and H₂ with the formation of gaseous by-products over a 4 wt%Ru-4 wt%Sn/TiO₂ catalyst.

Because the Cannizzaro reaction did not produce H₂ and the contribution of the direct oxidation of AA to AcOH was minimal, the majority of the H₂ would have been generated during the oxidation of EtOH to AA on the catalyst (Figure 6).

2.4. Oxidation of High-Concentration Aqueous EtOH Solutions

The oxidation of more highly concentrated aqueous EtOH solutions (100 and 500 g/L) was also attempted at 260 °C and 4 MPa or 320 °C and 10 MPa, with the results presented in Table 2. The latter conditions were the most extreme that could be obtained with the flow-type reactor system used in this study. The conversions obtained using the 100 g/L EtOH were 26.7% and 62.8% at 260 °C (4 MPa) and 320 °C (10 MPa), respectively. The corresponding yields of AcOH/H₂ were 21.4 mol%/30.1% and 50.7 mol%/72.3%, along with H₂ purities of 98.2% and 86.1%, respectively. Although the reactivity was not as high (with an EtOH conversion of just 13.1%) in trials with the 500 g/L EtOH at 320 °C and 10 MPa, the reacted EtOH was selectively converted to both AcOH and H₂ (10.4 mol% AcOH with a H₂ purity of 90.9%). These results suggest that this catalytic system could represent a viable approach to producing green H₂ and AcOH, although further development is needed to produce a larger-scale system capable of processing highly concentrated aqueous EtOH.

Table 2. Conversions of high-concentration aqueous EtOH solutions (10, 100 or 500 g/L) to AcOH and H₂ using a column with dimensions of 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at various temperatures and pressures.

Temp. (°C)	Press. (MPa)	Conc. (g/L)	EtOH Conversion (%)	Yield (mol%)*						H ₂ Purity (%)
				AcOH	AA	CH ₄	CO	CO ₂	H ₂	
260	4	10	76.2	71.9	0.4	7.75	0.06	4.99	88.4	93.2
		100	26.7	21.4	1.0	0.66	0.07	0.38	30.1	98.2
320	10	100	62.8	50.7	2.4	10.89	1.18	7.23	72.3	88.1
		500	13.1	10.4	1.5	2.81	1.39	1.36	29.7	90.9

* The yields of AcOH, AA, CH₄, CO and CO₂ are on an EtOH basis, and the yields of H₂ are on a theoretical basis.

3. Materials and Methods

3.1. Materials and Catalyst Preparation

Titanium isopropoxide (>95%), tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, >97%), ruthenium (III) chloride (RuCl_3), sodium hydroxide (NaOH , >97%), 2-propanol (>99%), and hydrochloric acid (HCl , 6 mol/L) were used for catalyst preparation. EtOH (>99.5%), AcOH (>99%), and AA (>99%) were employed for the catalytic conversion trials. The RuCl_3 was purchased from the Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, while all other reagents were obtained from Nacalai Tesque, Inc., Kyoto, Japan. Hydrogen (>99.9%) was purchased from the Imamura Sanso Co., Ltd., Shiga, Japan.

The 4 wt%Ru-4 wt%Sn/ TiO_2 catalyst was prepared by a sol-gel precipitation technique [10]. In this process, RuCl_3 (0.82 g, corresponding to 4 wt% Ru based on 10 g TiO_2) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.76 g, corresponding to 4 wt% Sn based on 10 g TiO_2) were added to hot water (100 mL, 60 °C). Following this, a mixture of 2-propanol (20 mL) and titanium isopropoxide (37.2 mL) was added dropwise with stirring. After waiting 30 min for TiO_2 to precipitate, an aqueous NaOH solution (100 mL, having a concentration sufficient to neutralize the metal chlorides) was added and the mixture was stirred for 30 min. The mixture was subsequently allowed to stand for 12 h and the resulting precipitate was filtrated and then washed five times with water, oven-dried in air at 105 °C for 12 h, calcined at 450 °C for 1 h, and then reduced under a H_2 flow (100 mL/min) at 400 °C for 5 h. Following this, the material was ground to a powder having an average particle size in the range of approximately 50–70 μm and then packed into a stainless-steel column (internal diameter, 3.9 mm; length, 100 mm).

According to a previous study [9], the crystal structure of the TiO_2 is mostly anatase type, and the BET surface area and crystallite diameter of TiO_2 of the 4 wt%Ru-4 wt%Sn/ TiO_2 catalyst were reported to be 84.5 m^2/g and 7.7 nm, respectively. Regarding the stability of the catalyst, no difference in catalytic activity was observed even after the continuous use in the temperature range of 140–320 °C for 60 h in the hydrogenolysis of aqueous AcOH [10].

3.2. Catalytic Conversion and Product Analysis

A flow-type reactor (H-cube ProTM, ThalesNano Inc., Budapest, Hungary) equipped with an electric furnace (Phoenix, ThalesNano Inc.), as shown in Figure 7, was used for these trials. In each experiment, an aqueous solution of EtOH, AcOH, or AA (10 g/L in each case) was fed into the catalyst column at a flow rate of 0.3 mL/min at a temperature in the range of 190–260 °C and a pressure in the range of 0.1–6.0 MPa. The resulting mixture was fractionated into aqueous and gaseous phases.

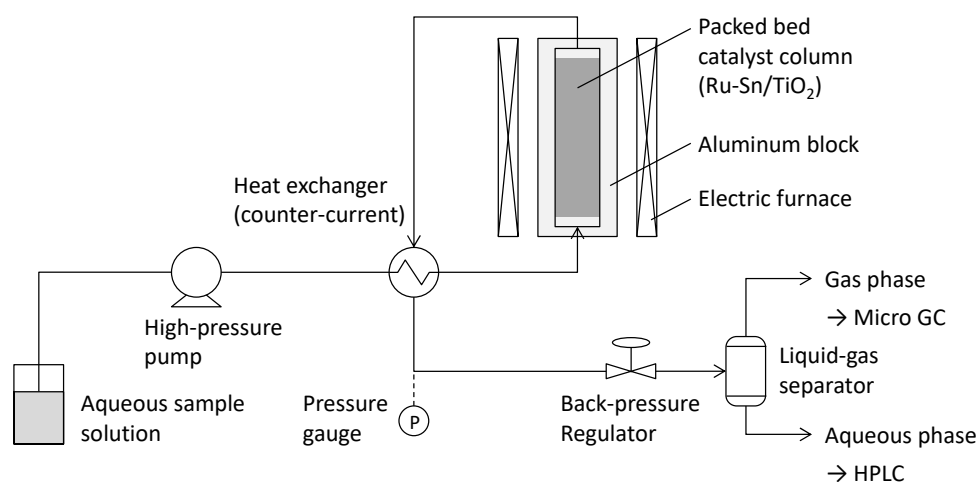


Figure 7. The flow-type reactor used for catalytic conversion trials.

The aqueous phase was analyzed by high-performance liquid chromatography (LC-20 system, Shimadzu Corp., Kyoto, Japan) using an Aminex HPX-87H column (300 mm × 7.8 mm, Bio-Rad Laboratories, Inc., Hercules, CA, USA) with 5 mM sulfuric acid in water as the mobile phase at a flow rate of 0.6 mL/min and a column temperature of 60 °C, employing a refractive index detector (RID-20A, Shimadzu Corp.). The total yield of gaseous products was quantified by the water displacement method using a graduated cylinder. The composition of these products was determined by micro gas chromatography (CP-4900, Varian Medical Systems, Palo Alto, CA, USA). These analyses used a 10 m MS5A column with argon as the carrier gas and a column temperature of 100 °C and inlet pressure of 170 kPa along with a thermal conductivity detector or a 10 m PoraPLOT Q column with helium as the carrier gas and a column temperature of 80 °C and inlet pressure of 190 kPa with a thermal conductivity detector.

4. Conclusions

The oxidation of aqueous EtOH (10 g/L) over 4 wt%Ru-4 wt%Sn/TiO₂ was investigated at various temperatures at a pressure of 0.1 MPa and at various pressures at a temperature of 260 °C. The following conclusions were obtained.

1. The conversion of aqueous EtOH to AcOH and H₂ over 4 wt%Ru-4 wt%Sn/TiO₂ was more efficient in the gas phase than in the liquid aqueous phase.
2. The selectivities for AcOH and H₂ were generally high.
3. Methane, CO, and CO₂ were produced as gaseous by-products via the fragmentation of AA to give CO and CH₄ and of AcOH to give CO₂ and CH₄, thus reducing the H₂ purity.
4. At a fixed reaction temperature of 260 °C in the gas phase, the EtOH conversion decreased with increasing pressure, whereas the H₂ purity increased because of the less-efficient reaction of AA to generate CO and CH₄ at the higher pressure.
5. The fragmentation of AcOH to CO₂ and CH₄ was independent of the reaction pressure.
6. The first reaction, EtOH → AA, was the rate-determining step in this process and AA was converted to AcOH and EtOH by the Cannizzaro reaction rather than undergoing direct oxidation to AcOH.
7. The fragmentation of AA occurred during the conversion of EtOH on the surface of the 4 wt%Ru-4 wt%Sn/TiO₂ catalyst prior to the removal from the surface.
8. Highly concentrated aqueous EtOH solutions (100 and 500 g/L) could also be employed with this process to selectively produce H₂ and AcOH.
9. The reaction pressure should be slightly less than the saturation vapor pressure of water to selectively obtain AcOH and H₂.
10. The use of the 4 wt%Ru-4 wt%Sn/TiO₂ catalyst in a flow reactor was found to be an effective method for the aqueous-phase reforming of EtOH to AcOH and H₂ with high purity. This provides insight into the industrial production of green hydrogen and AcOH.

Author Contributions: Formal analysis, writing—original draft preparation, investigation, data curation, T.N.; data curation, writing—review and editing, Y.Z.; data curation, writing—review and editing, E.M.; funding acquisition, supervision, writing—review and editing, H.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the JST-Mirai Program under grant number JPMJMI20E3. The sponsors had no role in the study design nor in the collection, analysis, and interpretation of data, in the writing of the report or in the decision to submit the article for publication.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Martin-Espejo, J.L.; Gandara-Loe, J.; Odriozola, J.A.; Reina, T.R.; Pastor-Perez, L. Sustainable routes for acetic acid production: Traditional processes vs. a low-carbon, biogas-based strategy. *Sci. Total Environ.* **2022**, *840*, 156663. [[CrossRef](#)] [[PubMed](#)]
2. Sponholz, P.; Mellmann, D.; Cordes, C.; Alsabeh, P.G.; Li, B.; Li, Y.; Nielsen, M.; Junge, H.; Dixneuf, P.; Beller, M. Efficient and selective hydrogen generation from bioethanol using ruthenium pincer-type complexes. *ChemSusChem* **2014**, *7*, 2419–2422. [[CrossRef](#)] [[PubMed](#)]
3. Kuwahara, M.; Nishioka, M.; Yoshida, M.; Fujita, K. A Sustainable method for the synthesis of acetic acid based on dehydrogenation of an ethanol-water solution catalyzed by an iridium complex bearing a functional bipyridonate ligand. *ChemCatChem* **2018**, *10*, 3636–3640. [[CrossRef](#)]
4. Brei, V.V.; Sharanda, M.E.; Prudius, S.V.; Bondarenko, E.A. Synthesis of acetic acid from ethanol-water mixture over Cu/ZnO-ZrO₂-Al₂O₃ catalyst. *Appl. Catal. A-Gen* **2013**, *458*, 196–200. [[CrossRef](#)]
5. Xiang, N.; Xu, P.; Ran, N.; Ye, T. Production of acetic acid from ethanol over CuCr catalysts via dehydrogenation-(aldehyde-water shift) reaction. *RSC Adv.* **2017**, *7*, 38586–38593. [[CrossRef](#)]
6. Nozawa, T.; Mizukoshi, Y.; Yoshida, A.; Naito, S. Aqueous phase reforming of ethanol and acetic acid over TiO₂ supported Ru catalysts. *Appl. Catal. B* **2014**, *146*, 221–226. [[CrossRef](#)]
7. Xiong, H.; DeLaRiva, A.; Wang, Y.; Datye, A.K. Low-temperature aqueous-phase reforming of ethanol on bimetallic PdZn catalysts. *Catal. Sci. Technol.* **2015**, *5*, 254–263. [[CrossRef](#)]
8. Nozawa, T.; Yoshida, A.; Hikichi, S.; Naito, S. Effects of Re addition upon aqueous phase reforming of ethanol over TiO₂ supported Rh and Ir catalysts. *Int. J. Hydrog. Energy* **2015**, *40*, 4129–4140. [[CrossRef](#)]
9. Ito, Y.; Kawamoto, H.; Saka, S. Efficient and selective hydrogenation of aqueous acetic acid on Ru-Sn/TiO₂ for bioethanol production from lignocellulosics. *Fuel* **2016**, *178*, 118–123. [[CrossRef](#)]
10. Zhao, Y.; Konishi, K.; Minami, E.; Saka, S.; Kawamoto, H. Hydrogenation of aqueous acetic acid over Ru-Sn/TiO₂ catalyst in a flow-type reactor, governed by reverse reaction. *Catalysts* **2020**, *10*, 1270. [[CrossRef](#)]
11. Haffad, D.; Kameswari, U.; Bettahar, M.M.; Chambellan, A.; Lavalley, J.C. Reduction of benzaldehyde on metal oxides. *J. Catal.* **1997**, *172*, 85–92. [[CrossRef](#)]
12. Saadi, A.; Rassoul, Z.; Bettahar, M.M. Reduction of benzaldehyde on alkaline earth metal oxides. *J. Mol. Catal. A-Chem* **2006**, *258*, 59–67. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.