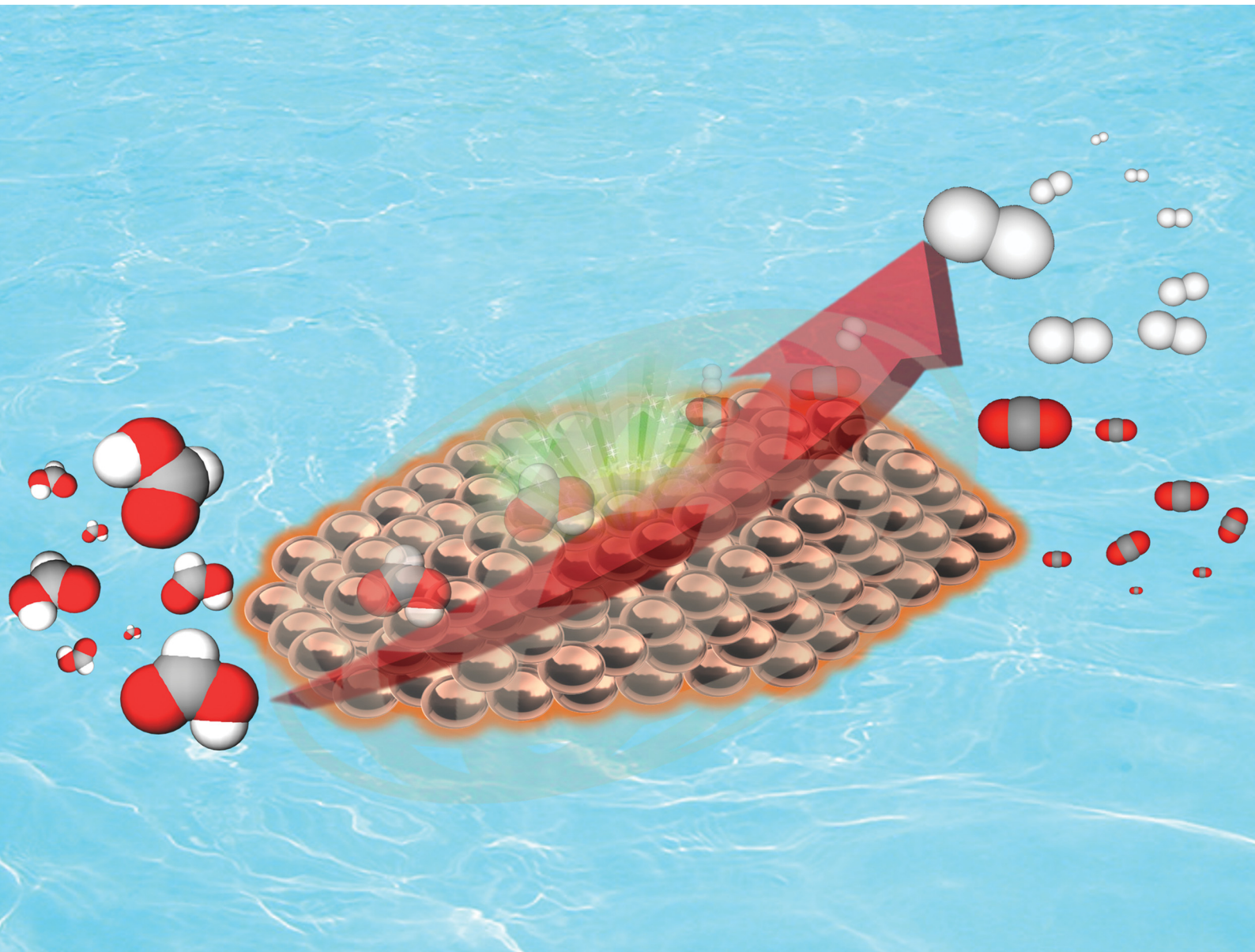


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PAPER

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Effective hydrogen production based on formic acid decomposition catalysed by polyvinylpyrrolidone dispersed colloidal platinum nanoparticles using an isobaric process system†

Koya Kano^a and Yutaka Amao^{id} *^{ab}

With its high-volume capacity (53 g H₂ L⁻¹) and low toxicity and flammability under ambient conditions, formic acid is a promising hydrogen energy carrier. It is desirable to invent a catalyst capable of efficiently and selectively decomposing formic acid into H₂. Among the various catalysts, colloidal platinum nanoparticles dispersed in polyvinylpyrrolidone (Pt-PVP) catalyse the formic acid decomposition into H₂ and CO₂ under ambient conditions. In an isochoric process, the amount of H₂ produced in formic acid decomposition catalysed by Pt-PVP, especially at a reaction temperature of 60 °C, tends to approach a constant value with the incubation time. It is predicted that the internal pressure increases due to H₂ production and reaches the equilibrium pressure. In this study, we attempted to improve the amount of H₂ produced during formic acid decomposition with Pt-PVP by maintaining the internal pressure at 1 atm (= 101.3 kPa) with an isobaric process. As a result, the amount of H₂ produced based on formic acid decomposition catalysed with Pt-PVP using an isobaric process system was more than twice that of using an isochoric process system. 650 μmol of Pt-PVP was added to 90 mmol of formic acid aqueous solution (pH 3.5) and reacted at 60.0 °C for 100 min. 42.6 mmol of H₂ was produced and the turnover frequency of Pt-PVP reached 43.8 h⁻¹.

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Introduction

Currently, the share of fossil fuels such as oil, coal and natural gas in global primary energy is still as high as 82%.¹ Thus, environmental problems such as the phenomenon of global warming, caused by CO₂ emission after using fossil fuels, have been caused.¹ In contrast, H₂ has long been attracting attention as an alternative energy source to fossil fuels because it emits no CO₂ when burned and can be produced by electrolysis of water using renewable energy sources such as sunlight. H₂ is the lightest and lowest density gas on earth. In order to utilize H₂ as an energy source, it must be stored in large quantities. The key to the realization of a hydrogen society lies in how much H₂ can be stored in a small volume, and H₂ storage methods are being vigorously studied.² To solve these problems, technologies to safely store and transport H₂ have been actively studied in recent years, using substances (hydrogen

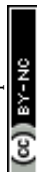
carrier) that contain hydrogen atoms in their molecules and readily and reversibly release and uptake hydrogen through chemical reactions.³ A variety of molecules have been studied as hydrogen carriers, including ammonia,^{4,5} organic hydrides such as methylcyclohexane,^{6,7} metal hydrides,^{8–10} and formic acid.^{11–15} Among these molecules, we focused on formic acid for its molecular properties and H₂ storage function. Formic acid has low toxicity and is liquid at atmospheric pressure and room temperature. Furthermore, pure formic acid contains 4.3 wt% (53 g L⁻¹) of hydrogen,¹⁶ making formic acid a prime candidate as a hydrogen energy carrier. To decompose formic acid into H₂ and CO₂ selectively, various heterogeneous catalysts containing metals have been investigated.¹⁷ Pd metal-containing materials have been widely studied as heterogeneous catalysts for H₂ production based on formic acid decomposition.^{18–23}

Homogeneous molecular catalysts based on complexes containing metals such as Ir, Rh, and Ru have also been widely studied as highly active catalysts for H₂ production based on formic acid decomposition.^{24–31} On the other hand, we focused on colloidal Pt nanoparticles with the H₂ production catalytic function as homogenous catalysts. Colloidal Pt nanoparticles have attracted a lot of attention due to their simple preparation *via* the chemical reduction of chloroplatinic acid.³² Dispersants such as hydrophilic polymers and surfactants are needed to

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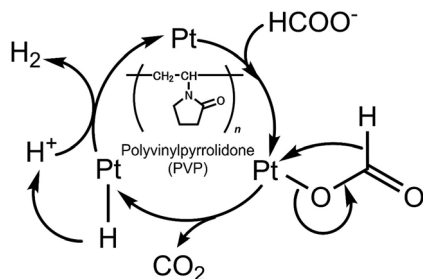


Fig. 1 Suggested mechanism of formic acid decomposition into H₂ and CO₂ with Pt-PVP and the chemical structure of polyvinylpyrrolidone (PVP).

maintain colloidal Pt particle size on the nanoscale. Thus, the catalytic activity of platinum nanoparticles is controlled by the dispersing agent. It has already been reported that the catalytic activity of colloidal platinum nanoparticles for the decomposition of formic acid to H₂ and CO₂ is controlled by the difference in hydrophilic polymers as dispersants.³³ We found that only colloidal platinum nanoparticles dispersed in polyvinylpyrrolidone (Pt-PVP) catalyse H₂ production based on formic acid decomposition.³⁴ In the decomposition of formic acid to H₂ and CO₂ using Pt-PVP, we have found that the catalytic activity increases near the pK_a = 3.75 of formic acid.^{33,34} Moreover, the H₂ production mechanism based on formic acid decomposition with Pt-PVP, as shown in Fig. 1, was clarified using TEM, IR, and X-ray absorption fine structure (XAFS) analysis (detailed data are shown in the ESI,† Fig. S1–S3)^{33,34} and the kinetic isotope effect (KIE) on H₂ production using isotope-labelled formic acid.³⁵

Another property of formic acid making it beneficial as a hydrogen energy carrier is that it can be produced from CO₂ using a photoredox system of an electron donor, a photosensitizer and a catalyst.^{36–42} Fig. 2 shows the H₂ storage and release cycle *via* formate with the linked photoredox system and thermal catalyst.

In previous reports of H₂ production based on formic acid decomposition catalysed by Pt-PVP conducted in an isochoric process system, cessation of H₂ production due to reaching equilibrium pressure with incubation time was observed.³⁴ While high-pressure H₂ gas can be obtained by using an isochoric process system, the H₂ production rate saturates in a short period time and the decomposition efficiency to H₂ for the initial concentration of formic acid is low. Especially at high reaction temperature (60.0 °C), the H₂ production rate saturates

in a remarkably short period of time. A system capable of completely decomposing formic acid into H₂ using Pt-PVP is desired. It is predicted that the improvement of H₂ production efficiency with Pt-PVP can be achieved by controlling the pressure in the reactor to a constant level. Thus, an isobaric process system with both a variable volume and a constant internal pressure (maintained to atmospheric pressure) in reaction vessel is proposed. Furthermore, the catalytic activity of Pt-PVP can be maximized by optimizing temperature and pH for H₂ production using an isobaric process system.

In this study, an isobaric process system with internal pressure maintained at atmospheric pressure (= 101.3 kPa) was proposed to improve H₂ production based on the formic acid decomposition using the Pt-PVP catalyst. In addition, a scale-up system with an isobaric process for H₂ production based on Pt-PVP-catalysed formic acid decomposition was also proposed.

Experimental

Materials

The colloidal platinum nanoparticles dispersed in PVP (Pt-PVP) were purchased from TANAKA HOLDINGS Company Limited. The Pt concentration in Pt-PVP was estimated to be 4.0 wt%. The average particle size of Pt nanoparticles in the Pt-PVP was estimated to be 2.3 nm from a size distribution based on the TEM image measurement.^{33,34} Formic acid was purchased from FUJIFILM Wako Pure Chemical Corporation.

Internal pressure changes during H₂ production from formic acid with Pt-PVP in an isochoric process

3.0 mmol of formic acid aqueous solution (3 mL) adjusted to pH 3.5 by NaOH was added to a vial (13 mL), then the gas phase was removed by bubbling nitrogen gas for 15 min. Pt-PVP (0.15 mL; Pt 0.8 wt%) was added to a vial with a syringe and reacted with a thermostatic chamber. The reaction temperature was adjusted from 30.5 to 60.0 °C. The internal pressure during the reaction was measured with a digital pressure gauge (KDM30 KRONE CORPORATION).

Pt-PVP catalysed H₂ production from formic acid in an isobaric process system

The isobaric process system is a vial equipped with a syringe, as shown in Fig. 3.

The operating principle of the isobaric process system is as follows. The plunger rises by the volume of the gas produced in the vial, and the pressure of the entire system is maintained at atmospheric pressure. 3.0 mmol of formic acid aqueous solution (3 mL) adjusted to pH 3.5 by NaOH was added to a vial (13 mL), then the gas phase was removed by bubbling nitrogen gas for 15 min. Pt-PVP (0.15 mL; Pt 0.8 wt%) was added to a vial with a syringe and then the stopcock was opened to allow gas to flow into the syringe. The reaction temperature was adjusted from 30.5 to 60.0 °C. The H₂ production was determined by gas chromatography (GC-2014, SHIMADZU Corporation) with a TCD detector. An activation charcoal column (column length:

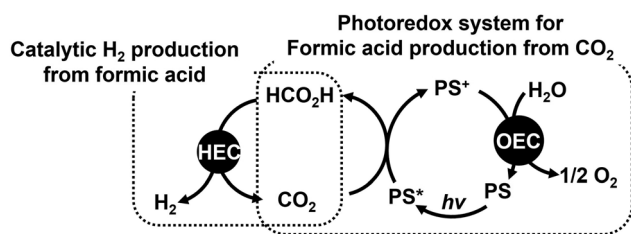


Fig. 2 Hydrogen storage and production cycle *via* formic acid with the catalytic and photoredox system. HEC: Hydrogen evolution catalyst, OEC: Oxygen evolution catalyst, PS: Photosensitizer.



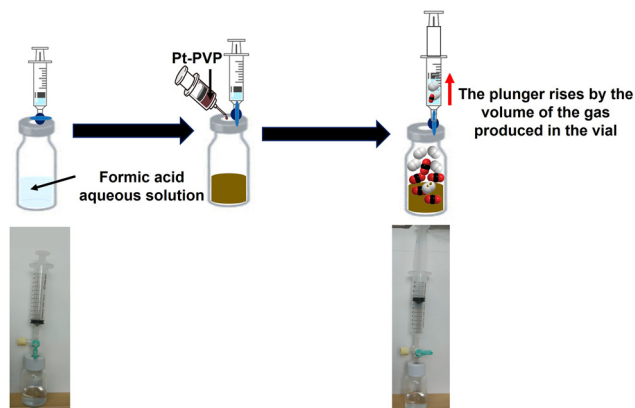


Fig. 3 Schematic representation for the Pt-PVP catalysed H_2 production from formic acid in an isobaric process system.

3 mm I.D. $\times$ 2 m) was equipped for detecting those gasses. The temperature of injection, column and detector were 100.0, 70.0 and 100.0 $^{\circ}C$ respectively. Argon gas was used as the carrier gas and the flow rate was 30.0 mL min^{-1} . The chromatogram of the standard sample of H_2 for measuring the calibration line is shown in Fig. S4 (ESI †). The calibration line for the determination of the amount of H_2 produced by gas chromatography is shown in Fig. S5 (ESI †), and eqn (S1) (ESI †), respectively.

pH dependence of the Pt-PVP catalysed H_2 production from formic acid in an isobaric process system

3.0 mmol of formic acid aqueous solution (3 mL) adjusted to pH 1.9–5.7 by NaOH was added to a vial (13 mL), then the gas phase was removed by bubbling nitrogen gas for 15 min. Pt-PVP (0.15 mL; Pt 0.8 wt%) was added to a vial with a syringe, then the stopcock was opened to allow gas to flow into the syringe and reacted at 30.0 $^{\circ}C$ with a thermostatic chamber. The H_2 production was determined by gas chromatography.

Scale-up for Pt-PVP catalysed H_2 production from formic acid in an isobaric process system

90 mmol of formic acid aqueous solution (30 mL) adjusted to pH 2.7 or 3.5 by NaOH was added to a vial (110 mL), then the gas phase was removed by bubbling nitrogen gas for 30 min. Pt-PVP (3.0 mL; Pt 4.0 wt%) was added to a vial with a syringe, then the stopcock was opened to allow gas to flow into the syringe and reacted at 60.0 $^{\circ}C$ with a thermostatic chamber. The H_2 production was determined by gas chromatography.

Results and discussion

Internal pressure changes during H_2 production from formic acid with Pt-PVP in an isochoric process

Fig. 4 shows the time dependence of the internal pressure changes during H_2 production from formic acid with Pt-PVP in an isochoric process under various reaction temperatures. The amount of H_2 production from formic acid (3.0 mmol, pH 3.5) with Pt-PVP after 5 h incubation at the reaction temperatures of 30.5, 40.0, 50.0 and 60.0 $^{\circ}C$ was reported to be 91.9, 121.5, 133.1

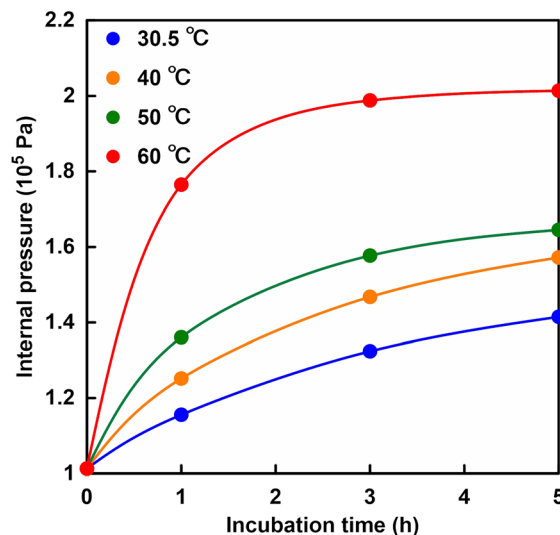


Fig. 4 The internal pressure changes during Pt-PVP-catalysed H_2 production from formic acid aqueous solution (3.0 mmol, pH 3.5) in an isochoric process under various reaction temperatures with incubation time.

and 130.2 μ mol, respectively. However, the reported hydrogen production did not account for internal pressure changes in an isochoric process. When considering H_2 as an ideal gas and taking into account internal pressure changes, the amount of H_2 production after 5 h incubation at the reaction temperatures of 30.5, 40.0, 50.0 and 60.0 $^{\circ}C$ was estimated to be 130.0, 191.0, 219.1 and 262.2 μ mol, respectively. After 5 h incubation, the yield for formic acid to H_2 gas at the reaction temperature of 30.5, 40.0, 50.0 and 60.0 $^{\circ}C$ was estimated to be 4.3, 6.4, 7.3 and 8.4%, respectively. In particular, at a reaction temperature of 60.0 $^{\circ}C$, the internal pressure in a vial reaches a constant level of about 2.0×10^5 Pa. It is predicted that the internal pressure of 2.0×10^5 Pa is the equilibrium pressure of Pt-PVP-catalysed H_2 production from formic acid in an isochoric process. Based on these results, Pt-PVP-catalysed H_2 production from formic acid in an isobaric process system was investigated.

Pt-PVP-catalysed H_2 production from formic acid in an isobaric process system

First, the accuracy of the isobaric system shown in Fig. 3 was checked under the following conditions. 3.0 mmol of formic acid aqueous solution (3 mL) adjusted to pH 3.5 by NaOH was added to a vial (13 mL), then the gas phase was removed by bubbling nitrogen gas. Pt-PVP (0.15 mL; Pt 0.8 wt%) was added to a vial with a syringe and then the stopcock was opened to allow gas to flow into the syringe. The reaction temperature was adjusted to be 30.5 $^{\circ}C$.

Fig. S3 (ESI †) shows the relationship among the incubation time, volume changes of the syringe (ΔV) and internal pressure changes. As shown in Fig. S6 (ESI †), the volume of the syringe increased with increasing incubation time. In contrast, no change in the internal pressure was observed with increasing incubation time. Thus, the system shown in Fig. 3 ensured that the internal pressure was maintained at atmospheric pressure.



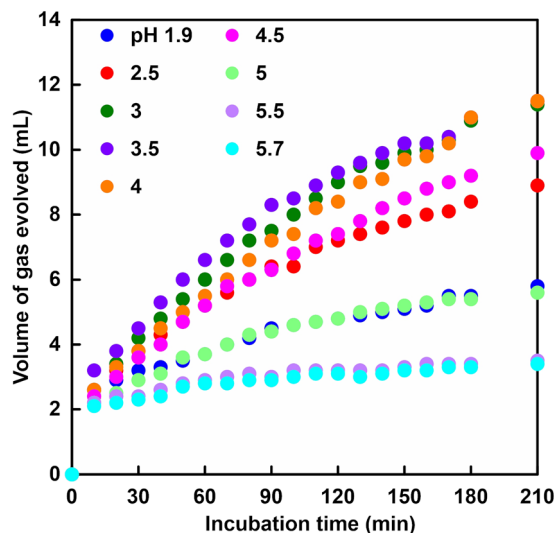


Fig. 5 Time dependence of the volume changes of gas evolved in an isobaric process system of Pt-PVP-catalysed H_2 production from various pH formic acid aqueous solutions at a reaction temperature of 50.0 °C.

Fig. 5 shows the time dependence of the volume changes of gas evolved in an isobaric process system of Pt-PVP-catalysed H_2 production from various pH formic acid aqueous solutions at a reaction temperature of 50.0 °C as an example. As shown in Fig. 5, the volume of gas evolved was increased with incubation time in all pH formic acid aqueous solutions. Since the initial gas phase volume of the vial was 10.0 mL, the total volume doubled at pH 3.0, 3.5 or 4.0 conditions. The amount of H_2 production from formic acid (pH 3.5) with Pt-PVP after 3 h incubation at the reaction temperature of 50.0 °C was estimated to be 259.4 μmol . The yield for formic acid to H_2 gas was estimated to be 8.6%. On the other hand, the amount of H_2 production with Pt-PVP after 3 h incubation at the reaction temperature of 50 °C in an isochoric process was estimated to be 186.1 μmol and the yield for formic acid to H_2 gas was estimated to be 6.2%. By using an isobaric process system, thus, the amount of H_2 produced was improved 1.4 times as much as that of an isochoric process system.

Fig. 6 shows the time dependence of H_2 production from formic acid with Pt-PVP in an isobaric process under various reaction temperatures.

As shown in Fig. 6, the amount of H_2 production from formic acid by Pt-PVP was increased with increasing the reaction temperature in an isobaric process system. As a reference, the time dependence of the amount of H_2 production from formic acid by Pt-PVP in an isochoric process system at the reaction temperature of 60.0 °C is also shown in Fig. 6. By using an isochoric process system, the amount of H_2 produced was estimated to be 251.7 μmol . On the other hand, by using the isobaric process system, the amount of H_2 produced increased steadily at any reaction temperature. By using an isobaric process system, the amount of H_2 produced was improved 1.1 times as much as that of an isochoric process system at any reaction temperature. Fig. 7 shows the reaction temperature dependence of the amount of H_2 production from formic acid with Pt-PVP

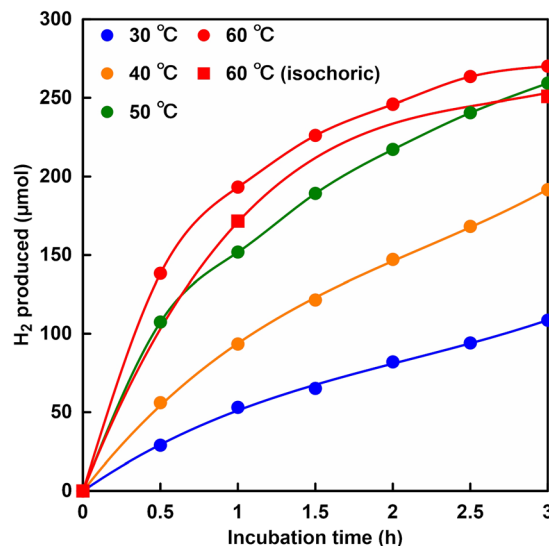


Fig. 6 Time dependence of Pt-PVP-catalysed H_2 production from formic acid aqueous solution (0.3 mmol, pH 3.5) in an isobaric process under various reaction temperatures with incubation time. ■: an isochoric process system.

under the pH 3.5 condition in the isobaric and the isochoric process systems. The amount of H_2 production from formic acid with Pt-PVP after 1 h incubation increased with increasing reaction temperature in both isobaric and isochoric process systems. However, the temperature-dependence of the H_2 production rate was remarkably increased in the isobaric process system, compared with that in the isochoric system. Let us now discuss the difference in activation energy for the H_2 production with Pt-PVP between the isobaric and the isochoric process systems.

In the isochoric process system, when the reaction temperature was increased from 50.0 to 60.0 °C, the amount of H_2 produced

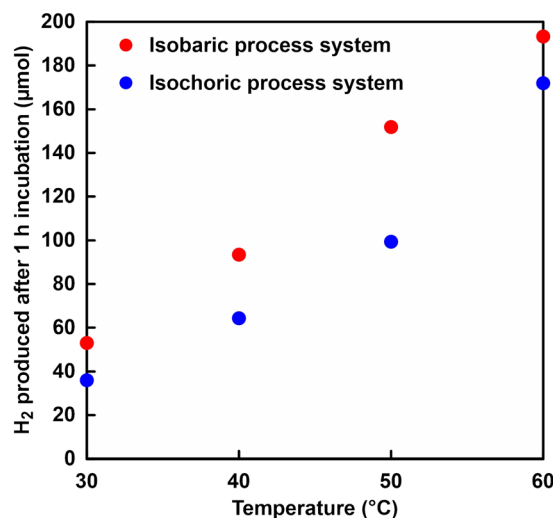


Fig. 7 The reaction temperature dependence of H_2 production from formic acid with Pt-PVP under the pH 3.5 condition in the isobaric (red) and the isochoric (blue) process systems.



after 1 hour of incubation increased significantly as shown in Fig. 7. As shown in Fig. 4, under the condition of a reaction temperature of 60.0 °C with the isochoric process system, the time until the internal pressure became constant was shorter than under other conditions, and it is predicted that the equilibrium pressure was reached. Therefore, the validity of these values was examined using Arrhenius plots.

Arrhenius plots between reaction temperature and H₂ production rate (ν) for formic acid decomposition with Pt-PVP in the isobaric and the isochoric process systems are shown in Fig. 8.

The activation energy (E_a) and the pre-exponential factor were obtained according to the H₂ production after 1 h incubation. The ν value ($\mu\text{mol h}^{-1}$) was determined to be the amount of H₂ production under various temperature conditions after 1 h incubation. The slope of the Arrhenius plots gave the E_a of H₂ production due to the formic acid decomposition with Pt-PVP, and it was calculated to be 41.0 kJ mol⁻¹ in an isobaric process system. On the other hand, the E_a of H₂ production in an isochoric process system was estimated to be 52.0 kJ mol⁻¹. Moreover, the activation energy for the formic acid decomposition without a catalyst has been reported to be 326.6 kJ mol⁻¹.²⁴ Thus, the E_a for H₂ production based on the formic acid decomposition can be significantly reduced by Pt-PVP in both isobaric and isochoric process systems as compared to the system without any catalyst. Pre-exponential factors for the isobaric and the isochoric process systems were estimated to be 50.6 and 56.3 h⁻¹ calculated from the intercept of the plot, respectively. The pre-exponential factor is a measure of the frequency of collisions between reacted molecules. A higher pre-exponential factor means a higher number of collisions of reacted molecules. Therefore, it is predicted that H₂ production based on formic acid decomposition by Pt-PVP was enhanced in the isobaric process system under pH 3.5, even though the pre-exponential factor of the isochoric process system is larger than that of the isobaric system. Moreover, in an isochoric

system, equilibrium pressure is reached and H₂ production is expected to reach a constant level. These results suggest that H₂ production based on the formic acid decomposition with Pt-PVP proceeded predominantly by using the isobaric process.

pH dependence of Pt-PVP-catalysed H₂ production from formic acid in an isobaric process system

Fig. 9 shows the pH dependence of H₂ production after 3 h incubation based on formic acid aqueous solution (3.0 mmol) decomposition with Pt-PVP in an isobaric system at the reaction temperature of 30.0 °C.

As shown in Fig. 9, the amount of H₂ production reached a maximum in isobaric and isochoric systems around pK_a 3.75 of formic acid. Based on these results, it is predicted that H₂ production based on Pt-PVP-catalysed formic acid decomposition in the isobaric process system proceeds by the same mechanism as the isobaric process system shown in Fig. 1. Now let us focus on the difference in activation energies for H₂ production with Pt-PVP in different pH solutions of formic acid in the isobaric system. Fig. 10 shows the reaction temperature dependence of H₂ production with Pt-PVP after 1 h incubation in different pH solutions of formic acid in the isobaric system.

As shown in Fig. 10, the H₂ production with Pt-PVP increased with increasing reaction temperature in the isobaric process system under any pH solutions of formic acid. Even in the isobaric process system, the amount of H₂ production reached a maximum around pK_a 3.75 of formic acid regardless of the reaction temperature. Arrhenius plots between reaction temperature and H₂ production rate for formic acid decomposition with Pt-PVP in the isobaric process system under different pH solutions of formic acid are shown in Fig. 11. As shown in Fig. 11, the E_a of H₂ production in the isobaric process system under pH values of 1.9, 3.5 and 5.5 were estimated to be 32.7, 41.0 and 38.1 kJ mol⁻¹, respectively. There is little difference among these pH conditions in the isobaric process

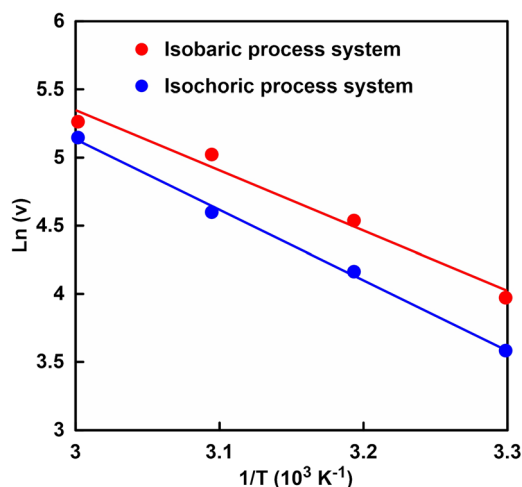


Fig. 8 Relationship between the inverse reaction temperature and logarithm of reaction rate (ν) for H₂ production with Pt-PVP in the isobaric (red) and isochoric (blue) process system.

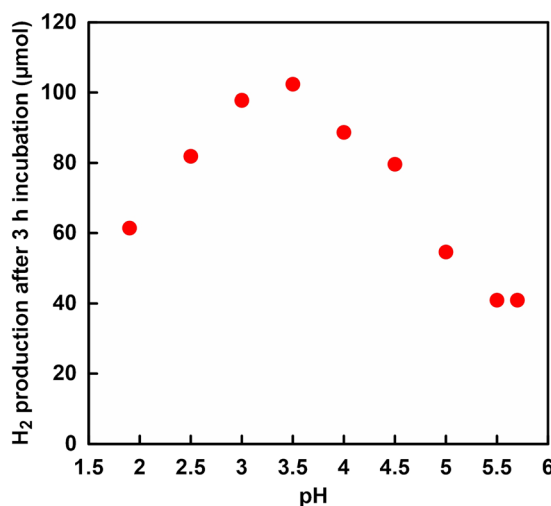


Fig. 9 pH dependence of H₂ production based on formic acid (3.0 mmol) decomposition with Pt-PVP after 3 h incubation in the isobaric process system.



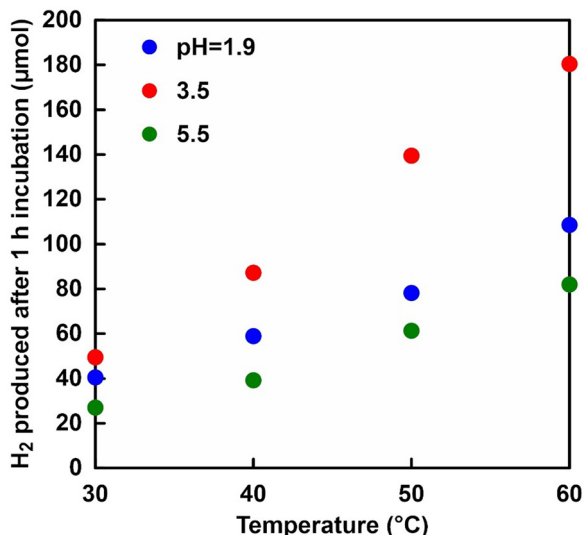


Fig. 10 The temperature-dependence of H₂ production based on formic acid decomposition with Pt-PVP under various pH (1.9, 3.5 and 5.5) after 1 h incubation in the isobaric process system.

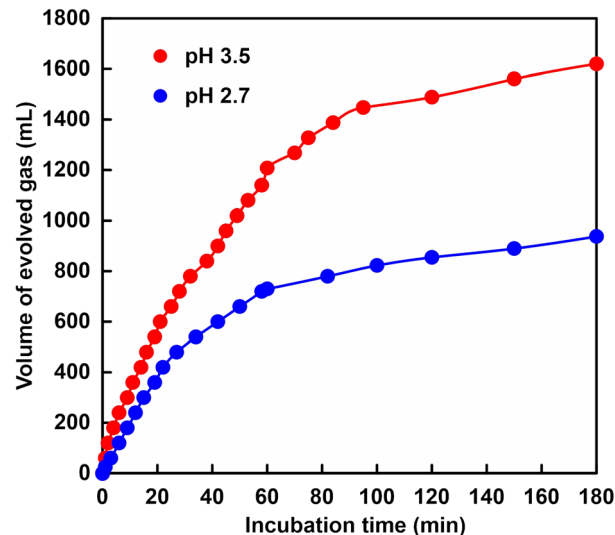


Fig. 12 Time dependence of volume change due to the gas evolution from formic acid with Pt-PVP under various pH (2.7 and 3.5) in the isobaric process with scale-up reaction vessel.

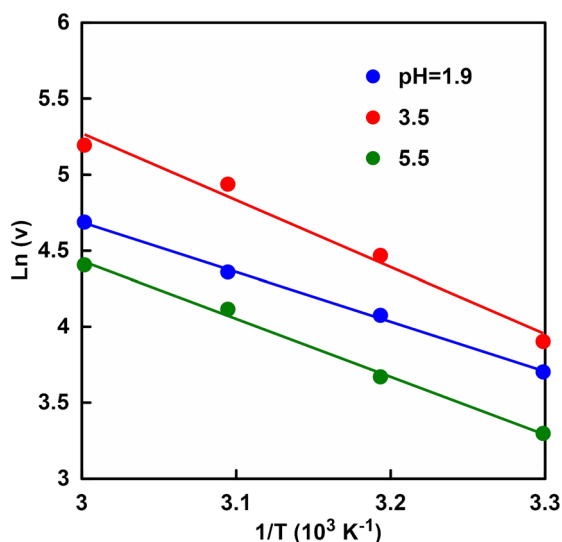


Fig. 11 Relationship between the inverse reaction temperature and logarithm of reaction rate (v) for H₂ production with Pt-PVP under various pH (1.9, 3.5 and 5.5) in the isobaric process system.

system. However, the pre-exponential factor was maximized with the formic acid solution of pH 3.5 and decreased on both sides of the pH 3.5 condition.

Scale-up for Pt-PVP catalysed H₂ production from formic acid in an isobaric process system

By using the isobaric process system, the efficiency of H₂ production based on Pt-PVP-catalysed formic acid decomposition was improved. Therefore, we investigated the amount of Pt-PVP catalyst for scale-up of the reaction system with the aim of further improving the H₂ production efficiency. Fig. 12 shows the time dependence of the volume changes of gas

evolved in an isobaric process system of Pt-PVP-catalysed H₂ production from 90 mmol of formic acid aqueous solution (30 mL; pH 2.7 or 3.5) at a reaction temperature of 60.0 °C.

The total volume of the reaction vial was estimated to be 110 mL. As shown in Fig. 12, the volume of gas evolved was increased with incubation time in both pH formic acid aqueous solutions. After 180 min incubation, the gas evolved from the formic acid aqueous solutions prepared at pH 2.7 and 3.5 was estimated to be about 940 and 1620 mL, respectively. The amount of H₂ produced from formic acid with Pt-PVP after 180 min incubation under the pH 2.7 and 3.5 conditions at the reaction temperature of 60.0 °C was estimated to be 27.1 and 47.4 mmol, respectively. The yields for formic acid to H₂ gas under the pH 2.7 and 3.5 conditions were improved to be 30.1 and 52.7%, respectively. Roughly estimating the amount of platinum in Pt-PVP was determined to be 650 μmol. Thus, the turnover number of Pt-PVP under the pH 2.7 and 3.5 conditions were estimated to be 15.4 and 27.0 h⁻¹, respectively. However, the amount of H₂ production tended to saturate with incubation time under both conditions of pH 2.7 and 3.5. Under both conditions, no change in the pH of the solution after the reaction was observed. The abundance ratios of formate under conditions of pH 2.7 and 3.5 are estimated to be 0.08 and 0.35, respectively. From the amount of formic acid remaining after 180 min of incubation, the amounts of formate were estimated as 5.0 and 15 mmol under pH 2.7 and 3.5 conditions, respectively. In other words, it is predicted that the amount of formate in solution under both pH conditions is reflected in the difference in the amount of H₂ produced. The tendency for the amount of H₂ produced to saturate under both conditions is predicted to be due to the deactivation of the catalyst due to the adsorption of the simultaneously produced CO₂ onto Pt-PVP. This is supported by the fact that H₂ production resumed when the reaction solution was replaced with nitrogen gas after the reaction.



Conclusion

In an isochoric process system, the amount of H₂ produced in formic acid decomposition catalysed by Pt-PVP tends to approach a constant value with the incubation time. It is predicted that the internal pressure increases due to H₂ production and reaches the equilibrium pressure. In this study, improvement of the amount of H₂ produced based on formic acid decomposition catalysed by Pt-PVP by maintaining the internal pressure at atmospheric pressure using the isobaric process system was attempted. As a result, by using the isobaric process system, amount of H₂ produced based on formic acid decomposition catalysed with Pt-PVP was more than double compared with that using the isochoric process system. In addition, we also successfully scaled up H₂ production based on Pt-PVP-catalysed formic acid decomposition using the isobaric process system and it was demonstrated that 52% of the initial formic acid can be selectively decomposed into H₂ with a reaction time of 180 min under the condition of pH 3.5.

Data availability

The authors confirm that the data supporting the findings of this manuscript are available within the article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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