1. Introduction

Hydrogen is currently considered to be an alternative source energy to fossil fuels, which are the cause of excessive carbon dioxide emissions. Hydrogen has a high energy density and can be easily produced by electrolysis of water using electric energy derived from renewable energy, so has high potential as a renewable energy source. However, hydrogen is a gas at normal temperature and pressure, so presents problems with storage and transportation, and techniques for overcoming these disadvantages are being actively researched. One technology for storing and transporting hydrogen is the hydrogen carrier that contains a hydrogen atom in the molecule which can be released as hydrogen molecules by chemical reaction. Candidate substances that can be used as hydrogen carriers include ammonia, organic hydride, and hydrogen storage alloys. Formate is one of the most promising candidates for a hydrogen carrier material. Formic acid is a liquid at ordinary temperature and pressure, and formic acid with a concentration of 90% or less does not fall under the Poisonous and Deleterious Substances Control Law in Japan. Furthermore, an aqueous solution of formic acid of less than 78% does not fall under the category of dangerous goods under the Fire Service Act of Japanese Law and is easy to handle, is less toxic, and contains 4.3 wt% hydrogen in the formic acid molecule. These characteristics of formic acid as a hydrogen carrier are very suitable for safe storage and transportation of hydrogen energy.

Use of formic acid as a hydrogen carrier requires in-
terconversion between molecular hydrogen and formic acid, and the catalytic reaction for synthesizing formic acid from hydrogen and carbon dioxide has been widely studied. On the other hand, a photocatalytic system capable of synthesizing formic acid based on carbon dioxide reduction using visible light energy has also been studied, and formic acid can be directly synthesized from water and carbon dioxide without requiring molecular hydrogen in this system. Metal complexes or metal nanoparticles-based catalysts for selective hydrogen production based on formic acid decomposition have been widely studied. Such a formate production and decomposition cycle based on catalytic dehydrogenation of formate and photoredox formate production directly from carbon dioxide and water will be very sustainable. Figure 1 shows the hydrogen storage and production cycle via formate using the catalytic and photoredox processes.

We focused on platinum colloidal nanoparticles with efficient hydrogen production catalytic activity to decompose formate into hydrogen and carbon dioxide. Platinum nanoparticles can be simply prepared by the chemical reduction of chloroplatinic acid. Dispersants such as hydrophilic polymers or surfactants are required to maintain the size of platinum nanoparticles, and we have already reported the effect of various polymers for this purpose. Platinum nanoparticles dispersed with polyvinylpyrrolidone (Pt-PVP) efficiently catalyzed selective hydrogen production based on formate decomposition. In addition, we clarified the hydrogen production mechanism based on formate decomposition with Pt-PVP using IR and X-ray absorption fine structure (XAFS) analysis.

The present study further clarified the mechanism of hydrogen production based on formate decomposition catalyzed by Pt-PVP by investigating the kinetic isotope effect (KIE) on hydrogen production using isotope-labelled formate, pH dependence of activation energy for hydrogen production, and CO production based on the dehydrogenation of formate.

2. Experimental

2.1. Materials

Pt-PVP (dispersed in aqueous media) was purchased from TANAKA HOLDINGS Co., Ltd. The Pt concentration in Pt-PVP was estimated to be 4.0 wt%. Formic acid, sodium formate, isotope-labelled formic acid (d1; DCOOH, d2; DCOOD, OD; HCOOD), sodium deuteroxide (40 w/w% solution in D2O) and D2O were purchased from FUJIFILM Wako Pure Chemical Corp.

2.2. Preparation of Isotope-labelled Formic Acid Solution

The 0.9 M formate aqueous solution was prepared as follows. 0.74 mL (19 mmol) of 98 % formic acid (relative density: 1.22 g mL−1) solution was added to a 20 mL volumetric flask, and a 40 % aqueous sodium hydroxide solution was added dropwise to adjust the pH to 1.8 or 3.5.

The 0.9 M d1-formate aqueous solution was prepared as follows. 0.76 mL (19 mmol) of 98 % d1-formic acid (relative density: 1.25 g mL−1) solution was added to a 20 mL volumetric flask, and a 40 % aqueous sodium hydroxide solution was added dropwise to adjust the pH to 1.8 or 3.5.

The 0.9 M OD-formate aqueous solution was prepared as follows. 0.76 mL (19 mmol) of 98 % OD-formic acid (relative density: 1.25 g mL−1) solution was added to a 20 mL volumetric flask, and a 40 % aqueous sodium deuteroxide solution was added dropwise to adjust the pH to 1.8 or 3.5.

The 0.9 M d2-formate aqueous solution was prepared as follows. 0.76 mL (19 mmol) of 98 % d2-formic acid (relative density: 1.27 g mL−1) solution was added to a 20 mL volumetric flask, and a 40 % aqueous sodium deuteroxide in D2O solution was added dropwise to adjust the pH to 1.8 or 3.5.

2.3. Hydrogen Production from Formate with Pt-PVP

0.9 M Formate aqueous solution (3 mL) adjusted to pH 1.8-3.5 was placed in a vial (13 mL), then air in the vial was removed by bubbling argon gas for 15 min. Pt-PVP (0.1 mL) was added with a syringe and reacted.
at 30.0 °C in a thermostatic chamber. The reaction occurred in a closed system and 50 µL of gas phase was sampled with a gastight syringe for product analysis. The amount of hydrogen and carbon dioxide produced was determined by gas chromatography (GC-2014, Shimadzu Corp.) with a thermal conductivity detector (TCD) and an activated charcoal column (column length: 3 mm I.D. × 2 m) for detecting the gas products. The temperatures of injection, column and detector were 100.0, 70.0 and 100.0 °C respectively. The carrier gas was Ar and the flow rate was 30.0 mL min⁻¹. Hydrogen and carbon dioxide in the gas phase can be measured using these gas chromatography conditions²⁵,²⁶. Carbon dioxide in solution can be measured by ion chromatography²⁵,²⁶.

2.4. Estimation of Activation Energy for Hydrogen Production with Pt-PVP

The activation energy for hydrogen production based on the decomposition of formate with Pt-PVP was estimated from the Arrhenius plot of the temperature dependence of hydrogen production. 0.9 M formate solution (3 mL) adjusted to pH 1.8-3.5 was placed in a vial (13 mL), then air in the vial was removed by bubbling argon gas for 15 min. Pt-PVP (0.1 mL) was added with a syringe, and reacted in a thermostatic chamber. The amount of hydrogen produced was determined by gas chromatography with a TCD. The reaction temperature for hydrogen production from formate with Pt-PVP was varied from 30.5 to 60 °C. The reaction system and gas phase sampling for product analysis are the same as those shown in section 2.3.

2.5. Carbon Monoxide Measurement

0.9 M formate solution (3 mL) adjusted to pH 3.5 was placed in a vial (13 mL), then the air in the vial was removed by bubbling argon gas for 15 min. Pt-PVP (0.1 mL) was added with a syringe, and reacted in a thermostatic chamber at 60 °C for 3 h. The reaction system and gas phase sampling for product analysis were the same as those shown in section 2.3. Carbon monoxide production from formate with Pt-PVP was measured by gas chromatography (GC-8A, Shimadzu Corp.) with a hydrogen-flame ionization detector (FID) attached to a methanizer, and a Shincarbon-ST column was equipped for detecting carbon monoxide concentration in the gas phase. The temperatures of injection and column were 200.0 °C and 120.0 °C, respectively. Carbon monoxide adsorption behavior during formate decomposition with Pt-PVP was examined by infrared spectroscopy (IR). IR spectra for before and after formate decomposition with Pt-PVP were obtained with a FT/IR-6600 (JASCO Corp.) by the Attenuated Total Reflection (ATR) method.

3. Results and Discussion

3.1. Hydrogen Production from Isotope-labelled Formic Acid Solution with Pt-PVP

We previously proposed the mechanism for hydrogen production based on formate decomposition with Pt-PVP as shown in Fig. 3⁶.

Formate is monodentate-bonded to the platinum nanoparticles. The C-H bond of the bonded formate is cleaved by the interaction between the catalyst and the hydrogen atom, and carbon dioxide is released (β-hydrogen desorption). Presumably the hydrogen atoms on the platinum nanoparticles combine to produce molecular hydrogen gas. In this reaction mechanism, either absorption of formate ion onto platinum nanoparticles (1), release of carbon dioxide from formate bounded platinum nanoparticles (2), or formation of hydrogen molecules (3) is the rate-determining step. Therefore, we investigated hydrogen production from isotope-labelled formic acid with Pt-PVP.

Figure 4 shows the amount of hydrogen production from d1-(DCOOH), d2-(DCOOD) and OD-(HCOOD) formates with Pt-PVP at pH 3.5 (black) and 1.8 (red) after 3 h incubation.
we discuss the production of hydrogen from iso-
tope-labelled formate with Pt-PVP from the perspective of KIE. The KIE value was estimated by dividing the amount of hydrogen produced with formate by the amount of hydrogen produced with isotope-labelled formate, which indicates the effect of isotope labelling on the reaction rate. Table 1 shows the amounts of hydrogen production from HCOOH, DCOOH, DCOOD or HCOOD with Pt-PVP and the KIE value at pH 3.5 and 1.8 after 3 h incubation.

Figure 5 shows the hydrogen production mechanism from DCOOH, DCOOD or HCOOD with Pt-PVP. In hydrogen production from formate, the rate-determining step is hydrogen formation from hydride species adsorbed on platinum nanoparticles and protons in the solution (process ① in Fig. 3) under the condition that the KIE of HCOOD is higher than that of DCOOH⑵,⑶. Under the opposite condition, the rate-determining step is absorption of formate ion onto platinum nanoparticles or cleaving the C-H bond of formate adsorbed on platinum nanoparticles (process ② or ③ in Fig. 3)⑷,⑸. From Fig. 4 and Table 1, the KIE value of HCOOD is larger than that of DCOOH in the hydrogen production process with Pt-PVP. Thus, the rate-determining step in formate decomposition with Pt-PVP is presumably hydrogen formation from hydride species adsorbed on platinum nanoparticles and protons in the solution⑵,⑶. Next, let us discuss the relationship between the pH of the isotope-labelled formate solution and the KIE values. There was no significant change in KIE values for hydrogen production from DCOOH under conditions of pH 1.8 and 3.5. The pH of the isotope-labelled formate solution is related to the KIE values. KIE values showed no significant change for hydrogen production from DCOOH at pH 1.8 and 3.5. However, KIE values showed a considerable difference for hydrogen production from HCOOD at pH 1.8 and 3.5. The KIE value for hydrogen production from DCOOH at pH 1.8 was about 2.8 times larger than that at pH 3.5, suggesting effects of the adsorption of formate ion on platinum nanoparticles (1) or the process of cleaving the C-H bond of formate adsorbed on platinum nanoparticles (2) at pH 1.8. The difference in KIE values between DCOOH and HCOOD is due to the release rates of H⁺ and D⁺ from these formic acid species in the pH 1.8 region. Therefore, the pKᵦ of formic acid in D₂O and H₂O must be considered. pKᵦ in D₂O is expressed by the following equation⑷.

\[ pKᵦ (D) = pKᵦ (H) + 0.44 \]

Consequently, the concentration of formate ion in D₂O containing HCOOD is lower than that in H₂O containing HCOOH or DCOOH. These facts also suggest that the formate ion concentration affects the overall rate of hydrogen production. Furthermore, the overall reaction rate in Pt-PVP-catalyzed hydrogen production using DCOOD is predicted to decrease with fewer DCOO⁻ species in the solution. The overall rate of hydrogen production will decrease based on the decomposition of DCOOD with Pt-PVP due to the slower bond cleavage between platinum nanoparticles and deu-

| Formate species | Hydrogen production [μmol] | pH 3.5 | pH 1.8 | pH 3.5 | pH 1.8 |
|-----------------|-----------------------------|--------|--------|--------|--------|
| HCOOH           | 50.1                        | 23.4   | -      | -      | -      |
| DCOOH           | 29.4                        | 11.1   | 1.7    | 2.1    |
| HCOOD           | 19.8                        | 3.3    | 2.5    | 7.1    |
| DCOOD           | 11.4                        | 1.1    | 4.4    | 18.0   |

Fig. 5 Hydrogen Production Mechanism Based on DCOOH, DCOOD or HCOOD with Pt-PVP
3.2. Estimation of Activation Energy for Hydrogen Production with Pt-PVP

The activation energy for hydrogen production from decomposition of formate with Pt-PVP was calculated from the Arrhenius plot of the temperature dependence of the hydrogen production rate. In addition, hydrogen production depends on the pH of the formate solution, so the pH dependence of the activation energy was also investigated.

Figure 6 shows the temperature dependence of hydrogen production from the decomposition of formate with Pt-PVP. The pH of the formate solution was adjusted to 1.8, 2.5 and 3.5. Under all pH conditions, the amount of hydrogen produced increased with higher reaction temperature. Especially at pH 3.5, the amount of hydrogen produced had a strong temperature dependence. We have reported that Pt-PVP-catalyzed hydrogen production showed the highest catalytic activity near the pK\textsubscript{a} value of formic acid of 3.75. On the other hand, the amount of hydrogen produced with Pt-PVP decreased in the pH range lower than the pK\textsubscript{a} of formic acid.

The Arrhenius plots for hydrogen production from formate decomposition catalyzed by Pt-PVP in each pH region is shown in Fig. 7. The activation energies (E\textsubscript{a}) for formate decomposition with Pt-PVP at pH 1.8, 2.5 and 3.5 were estimated to be 29, 38 and 40 kJ mol\textsuperscript{-1}, respectively, calculated from the gradient of the plot. In contrast, the E\textsubscript{a} for formate decomposition without catalyst was reported to be 326.6 kJ mol\textsuperscript{-1} [33]. The E\textsubscript{a} for hydrogen production from formate decomposition catalyzed by Pt-PVP decreased with lower pH.

Figure 8 shows the molar concentrations of formic acid, formate and protons in various pH ranges [34]. The concentrations of formate at pH 1.8, 2.5 and 3.5 were estimated to be 9.54, 45.8 and 315 mM, respectively. In contrast, the proton concentrations at pH 1.8, 2.5 and 3.5 were estimated to be 15.8, 3.2 and 0.32 mM, respectively. Proton concentration in the reaction solution increased in the lower pH region \( \text{pH} \leq 2.0 \), so hydrogen production with Pt-PVP is predicted to proceed more easily in process (3) of Fig. 3. E\textsubscript{a} for the hydrogen production with Pt-PVP was predicted to proceed more easily in process (3) of Fig. 3. E\textsubscript{a} for the hydrogen production with Pt-PVP was lower in the lower pH region \( \text{pH} < 2.0 \), so hydrogen production with Pt-PVP is predicted to proceed more easily in process (3) of Fig. 3. However, the amount of hydrogen produced decreased significantly at pH 1.8 compared to pH 2.5 or 3.5. Probably, the rate-determining step of hydrogen and carbon dioxide production based on formate decomposition as shown in Fig. 3 changed with lower pH. This assumption is also supported by the pH dependence of the KIE values for hydrogen production from isotope-labelled formate. In other words, the decrease in E\textsubscript{a} at pH 1.8 compared to higher pH conditions probably resulted from the effects on the adsorption of formate ion on platinum nanoparticles or the process of cleaving C-H of formate adsorbed on platinum nanoparticles. Comparison of
formate decomposition by Pt-PVP at pH 1.8, 2.5 and 3.5 with the pre-exponential factor obtained from the intercept of the plot showed formate decomposition into hydrogen and carbon dioxide with Pt-PVP as a pseudozero-order reaction. The pre-exponential factors of Pt-PVP at pH 1.8, 2.5 and 3.5 were estimated to be 8.25, 11.3 and 12.5, respectively. These values show that the pre-exponential factor at pH 3.5 was relatively large compared with other pH conditions. In other words, the increase in the frequency of adsorption of formate ion on platinum nanoparticles may depend on the amount of hydrogen produced. In our previous study, the catalytic activity of Pt-PVP for formate decomposition was strongly dependent on the concentration of formate, so that the reaction rate was diffusion dependent using the formate buffer with lower pH (less than 3.5). These results indicate that hydrogen production from Pt-PVP-catalyzed formate decomposition is strongly dependent on formate concentration.

3.3. Carbon Monoxide Production from Formate with Pt-PVP

Dehydration of formate is a side reaction of hydrogen production based on formate decomposition, and forms carbon monoxide\(^\text{18}\). Since carbon monoxide is chemically adsorbed on the platinum surface and causes catalyst poisoning, development of a catalyst that is inert to this side reaction is required\(^\text{35,36}\). Carbon monoxide bound to platinum appears as a peak at the position of 2000 to 2100 cm\(^{-1}\) in the IR spectrum\(^\text{37,38}\). Figure 9 shows the IR spectra before formate decomposition by Pt-PVP and after reaction for 3 h. No significant difference was found between the spectra before and after the reaction. In addition, no absorption peak of 2000 to 2100 cm\(^{-1}\) was observed assigned to the adsorption of carbon monoxide on platinum. Therefore, no adsorption of carbon monoxide on the platinum occurred during the formate decomposition reaction by Pt-PVP.

The gas phase during the formate decomposition reaction by Pt-PVP was also analyzed by gas chromatograph with an FID attached to a methanizer. Figure 10 shows the chromatograms for the gas phase during formate decomposition by Pt-PVP and polyacrylic acid dispersed platinum nanoparticles (Pt-PAA). Carbon monoxide production is expected as a peak at 6 min retention time. Pt-PAA catalyst caused carbon monoxide production of 50 nmol as shown in Fig. 10. Hydrogen production from formate with Pt-PAA was also attempted. Amounts of hydrogen produced from 0.3 M of formate at 30.5 °C and 40 °C after 3 h incubation were estimated to be 90.0 nmol and 219 nmol, respectively. In contrast, no peak based on carbon monoxide production using Pt-PVP was observed in the chromatogram as shown in Fig. 10. The catalytic activity of Pt-PAA for hydrogen production based on formate decomposition was significantly lower than that of Pt-PVP. In other words, Pt-PVP catalyzes the selective decomposition of formic acid into hydrogen and carbon dioxide without carbon monoxide production from formate dehydration.

4. Conclusion

The detailed mechanism of hydrogen production based on formate decomposition catalyzed by Pt-PVP was clarified by investigating the KIE of hydrogen production using isotope-labelled formate (DCOOH, DCOOD and HCOOD), and the pH dependence of \(E_a\) for hydrogen production and carbon monoxide production from formate dehydration. The KIE value of HCOOD was larger than that of DCOOH in hydrogen production from formate with Pt-PVP, suggesting that the rate-determining step is hydrogen formation from hydride species adsorbed on platinum nanoparticles and protons in the solution. The Arrhenius plot for hydrogen production by formate decomposition catalyzed by Pt-PVP in various pH regions found no significant difference in \(E_a\) for hydrogen production between pH 2.5
and 3.5. In contrast, the $E_a$ for hydrogen production decreased at pH 1.8, whereas the amount of hydrogen produced decreased significantly, compared with pH 2.5 or 3.5. These results suggest that the rate-determining step for Pt-PVP-catalyzed formate decomposition was hydrogen production from hydride species adsorbed on platinum nanoparticles and protons at pH 2.5 or 3.5, but was adsorption of formate ion on platinum nanoparticles or cleaving C-H of formate adsorbed on platinum nanoparticles at pH 1.8. Finally, Pt-PVP only catalyzed the selective decomposition of formate into hydrogen and carbon dioxide without carbon monoxide production from formate dehydration.

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要 旨

ポリビニルピロリドンで分散した白金微粒子を触媒とするギ酸分解に基づく水素生成機構

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ギ酸は毒性が低く取り扱いが容易なため，水素キャリアとして注目されている。本論文では，ポリビニルピロリドンによって分散された白金微粒子（Pt-PVP）を触媒としたギ酸分解に基づく選択的水素生成機構について，同位体標識したギ酸からの水素生成に対する速度論的同位体効果，水素生成に対する活性化エネルギーの pH 依存性，およびギ酸の脱水に基づく二酸化炭素生成から議論した。同位体標識したギ酸を使用した水素生成に対する速度論的同位体効果の結果から，ギ酸が水素と二酸化炭素とに分解される過程の律速段階は，Pt-PVP に吸着したヒドリド種と溶液中のプロトンからの水素生成であることが示唆された。次に，Pt-PVP を触媒とするギ酸からの水素生成に対する活性化エネルギーの pH 依存性を調べた結果，pH 2.5 と 3.5 では差は見られないものの，pH 1.8 では活性化エネルギーが低減されることが分かった。一方で，pH 1.8 では水素生成量は他の pH 領域と比較して著しく低下したことから，Pt-PVP を触媒とするギ酸分解に基づく水素生成は，ギ酸イオン濃度に強く依存することが示唆された。これは，pH 2.5 と 3.5 では Pt-PVP を触媒とする水素生成の律速段階が，白金微粒子上の水素と溶液中のプロトンからの水素生成であるのに対して，pH 1.8 ではその段階が金微粒子上でのギ酸イオンの吸着あるいは微粒子上でのギ酸塩の C-H 結合開裂であることを示している。さらに，Pt-PVP はギ酸を選択的に水素と二酸化炭素に分解する触媒として作用し，ギ酸の脱水による二酸化炭素生成は進行しないことが分かった。