Catalytic Properties of Palladium Nanoparticles for Hydrogenation of Carbon Dioxide into Formic Acid

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The present study investigated catalytic properties of palladium nanoparticles for hydrogenation of carbon dioxide into formic acid and effect of silica-coating on the palladium nanoparticles to maintain stability of the nanoparticles. The nanoparticles were obtained from palladium nitrate dissolved in methyl alcohol solvent under solvothermal conditions, and the activity for the hydrogenation reaction was evaluated under various reaction conditions. Reaction pressure influenced turnover number (TON) of the nanoparticles for hydrogenation of carbon dioxide into formic acid, and the TON significantly decreased with increasing reaction time under high reaction pressure. UV-Vis spectra of the solution after the hydrogenation reaction indicated that larger amount of active palladium species dissolved in the reaction solution under higher reaction pressure. In order to prevent the active palladium species from dissolving into the reaction solution, we investigated effect of silica coating on the palladium nanoparticles. Thicknesses of silica coated on the nanoparticles by sol-gel based method were controlled by adjusting amount of tetraethoxysilane (TEOS) using as the silica source, and addition of appropriate amount of silica was effective to prevent the active palladium species from dissolving into the reaction solution during the hydrogenation reaction. In addition, the silica coated catalyst possessed good recycle ability for the hydrogenation reaction.

Key Words
Palladium nanoparticles, Hydrogenation of carbon dioxide, Formic acid, Silica coating

1. Introduction
The usage and storage of carbon dioxide is of fundamental interest for chemistry and energy technologies, and it already constitutes an important C1-source for the chemical industry, for example, for the production of urea. It is likely that its use in the future will significantly increase because it is an abundant, inexpensive, and nontoxic compound compared with the widely employed carbon monoxide. Catalytic hydrogenation is considered to be one of the most promising ways to convert carbon dioxide because it can provide a variety of useful compounds. Among them, formic acid is one of the chemicals that has received attention because of its numerous applications, including food technology, agriculture, and the industries of leather and rubber. The compound is also used as a raw material and intermediate for many chemical industries. Moreover,
it has been recently considered to be a promising candidate material for hydrogen storage. Since pioneering works, various organometallic catalysts for hydrogenation of carbon dioxide into formic acid have been developed in the past decade. Although the reasonable conversions and yields of formic acid have been obtained using homogeneous catalysts, separation of formic acid from the solution including the catalysts remains a challenge. Therefore, the development of a heterogeneous catalytic system is highly desirable. To the best of our knowledge, very few heterogeneous systems with solid (supported) catalysts have been investigated. In our previous study, we firstly reported that metallic ruthenium nanoparticles prepared in methyl alcohol solution under solvothermal conditions showed high activity for hydrogenation of supercritical carbon dioxide to formic acid. Otherwise, the metallic ruthenium nanoparticles dissolved in the reaction solution during the hydrogenation reaction and the activity in the presence of the nanoparticles decreased with increasing the amount of dissolved ruthenium species.

In the present study, we investigated catalytic properties of the palladium nanoparticles for hydrogenation of carbon dioxide into formic acid. The lower costed metallic palladium nanoparticles were also prepared by same method for the preparation of the metallic ruthenium nanoparticles. We also investigated effect of silica-coating on the palladium nanoparticles in the present study. Silica coating is one of the most popular techniques for nanoparticle surface modification. This coating method can introduce a cross-linked silica shell to protect the core nanoparticles from the external environment. The method can be used for synthesis of hydrophilic and hydrophobic nanoparticles of metals, metal oxides, and quantum dots in a size range of 1-100 nm. In the present study, we investigated influence of silica-coating on stability of the palladium nanoparticle catalysts for hydrogenation of carbon dioxide into formic acid.

2. Experiments

Metallic palladium nanoparticles were prepared in methyl alcohol solutions under solvothermal conditions. Palladium nitrite (Pd(NO₃)₂, Nacalai Tesque, 0.115 g) was dissolved in methyl alcohol (15 mL) using Teflon-lined autoclave (Parr Instrument Co.), and was heated at 423 K for 10 h. Silica coated palladium nanoparticles were prepared by sol-gel based method. An aqueous solution of L(+) arginine (Wako Chemical Co., Osaka, Japan, >99.0%) was mixed with the suspension including the palladium nanoparticles in methyl alcohol, then tetraethoxysilane (Wako Pure Chem. Co., Osaka, Japan, >99.0%) was added to the solution, followed by stirring at room temperature for 24 h and centrifuging at a rotation speed of 6000 rpm for 5 min. The hydrogenation of carbon dioxide to formic acid was carried out in a 120-mL stainless steel autoclave (Taiatsu Techno) with a magnetic stirrer referred in the previous report. Triethylamine (5 mL) and distilled water (2 mL) were added to the palladium suspension. The autoclave was heated to 323-393 K, and the reactor was then pressurized to 1.9-5.0 MPa with H₂. Subsequently, carbon dioxide was introduced from a cooled (268 K) reservoir by a high pressure liquid chromatography pump and the total pressure was increased to 5.0-13.0 MPa at which point the reaction was considered to have started. After the reaction (1.6 h), the liquid mixture from the autoclave was analyzed with a Shimadzu GC 8A gas chromatograph equipped with a 15% TSG-1 on SHINCARBON A column (Shimadzu, 2 m × 3 mm) and a thermal conductivity detector. The yield is expressed in terms of the turnover number (TON) of formic acid, which is the number of moles of formic acid produced per mole of palladium. The mixtures were also measured by UV-Vis spectrophotometer (Shimadzu UV-3600) to determine the valence state of palladium species. The morphologies of the palladium nanoparticles were observed using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV.

3. Results and Discussion

We firstly investigated dependence of reaction time on the hydrogenation activity of the palladium nanoparticles for the conversion of carbon dioxide to formic acid. Fig. 1 shows the TON of formic acid in the presence of the palladium catalysts. This figure, the activity under reaction pressure
= 5.0, 9.0, and 13.0 MPa was shown. From this figure, the TON did not significantly depend on the reaction time, indicating that formation of formic acid did not increase for more than 1 h, and the activity of the catalyst significantly decreases with increase with the reaction time. In order to identify deactivation of the catalyst, the amount of the dissolved palladium species in the solution after the hydrogenation reaction was evaluated. Fig. 2 shows UV-Vis spectra of the solution after the hydrogenation reaction for various reaction time at 13 MPa. From this figure, the intensity of the peak assigned to Pd²⁺ species increased with increasing reaction time, indicating that amount of dissolved active palladium species increase with increasing the reaction time. Compared with the intensity of the peak assigned as the dissolved palladium species in the solution after the hydrogenation reaction for 1 h, the peak intensities in the solution after the hydrogenation reaction for 3 and 6 h were about 2.53 and 6.64 times higher, respectively. The result indicates that the amount of the dissolved palladium species gradually increase with increasing the reaction time. On the other hand, the peak intensity of the dissolved palladium species was significantly high in the solution after the hydrogenation reaction for 6 h compared with the intensity after the hydrogenation reaction for 1 and 3 h, while TON after the hydrogenation reaction for 6 h decreased compared with TONs after the hydrogenation reaction for 1 and 3 h. The results indicate that the dissolved palladium species possessed negligible activity for the hydrogenation reaction. The tendency was also identified from the UV-Vis spectra of the solution after the reaction under various reaction pressure shown in Fig. 3. The peak intensity of the solutions after the reaction at 9.0 and 13.0 MPa was significantly higher than that after the reaction at 5.0 MPa, and the intensity of the peak assigned as the dissolved palladium species in the solution after the hydrogenation reaction at 9.0 and 13.0 MPa were about 7.36 and 8.30 times higher than that in the solution after the hydrogenation reaction at 5 MPa. Partial pressures of carbon dioxide during the reaction at 9.0 and 13.0 MPa were 5.6 and 8.0 MPa, respectively. Carbon dioxide was liquid and supercritical state under each condition. While, partial pressure of carbon dioxide during the reaction at 5.0 MPa was 3.1 MPa, and carbon dioxide was gas state under the condition. Thus, the results suggested that the palladium nanoparticles easily dissolved in liquid and supercritical phase under the conditions.

In order to suppress dissolution of the active palladium species during the hydrogenation reaction, we investigated effect of silica-coating on the activity of the palladium nanoparticle catalyst. Fig. 4 shows TEM images of the silica coated palladium nanoparticles prepared with various amount of TEOS. The palladium nanoparticles prepared without TEOS consists of particles with diameter of ca. 2-50 nm. On the other hand, the palladium nanoparticles prepared with amount of TEOS = 0.056 and 0.111 mL consists of core-shell like particles with shell thickness of 8.0 and 20.0 nm, respectively. The result indicates that palladium nanoparticles were effectively coated with silica by the method used in the present study. Table 1 listed palladium and silicon content in the silica coated palladium nanoparticles. With increasing amount of TEOS, amount of silicon linearly increased. Activity of the catalysts for hydrogenation of carbon dioxide into formic acid was evaluated. Fig. 5 shows dependence of the catalytic
Fig. 6 UV-Vis spectra of solutions after hydrogenation of carbon dioxide in the presence of silica coated palladium nanoparticle catalysts prepared with amount of tetraethoxysilane = (a) 0, (b) 0.056, and (c) 0.111 mL.

Table 1 Contents of palladium and silicon in silica coated palladium nanoparticles prepared with various amount of TEOS

| TEOS [mL] | Pd [mol%]* | Si [mol%]* |
|-----------|------------|------------|
| 0.056     | 77.8       | 22.2       |
| 0.111     | 40.7       | 59.3       |

* Calculated from results of energy dispersive X-ray analysis

Fig. 5 TON in the presence of silica coated palladium nanoparticles prepared with various amount of tetraethoxysilane. Reaction conditions: H₂/CO₂ = 5/8, 13 MPa, 353 K

activity on silica content of the silica coated catalysts. Formation of formic acid was identified in the presence of both the silica coated catalysts, indicating the silica coated on the palladium nanoparticles consisted of pores, and hydrogen and carbon dioxide were diffused in the silica shells. The silica coated catalyst prepared with amount of TEOS = 0.056 mL showed higher TON than catalyst without silica, while the silica coated catalyst prepared with amount of TEOS = 0.111 g showed lower TON than catalyst without silica. The result indicated that appropriate amount of silica coated on palladium nanoparticles was effective to improve activity, and the thickness of the coated silica influenced on the diffusion of hydrogen and carbon dioxide into the active palladium species. In order to evaluate suppression ability of dissolution of active palladium species, we investigated UV-Vis spectra of the solution after hydrogenation of carbon dioxide into formic acid in the presence of silica coated palladium nanoparticle catalysts. Fig. 6 shows the spectra of the solution after
the hydrogenation reaction in the presence of palladium nanoparticle catalyst coated with various amount of silica. Except for the spectrum of the solution after the hydrogenation reaction in the presence of palladium nanoparticle catalyst without silica, there is no obvious peak assigned to Pd\nobreak\textsuperscript{2+} species in the spectra of the solution after the reaction in the presence of the silica coated catalysts. The result indicated that silica coating was effective to suppress dissolution of the active palladium species. The silica coated catalyst prepared with amount of TEOS = 0.056 mL showed recycle ability for 5 cycles, and TON of 5th cycle in the presence of the catalyst was 549 mol-HCOOH (mol-Pd\nobreak\textsuperscript{-1})\nobreak\textsuperscript{1}, indicating that the silica coated catalyst possessed good recycle ability for hydrogenation of carbon dioxide into formic acid.

4. Conclusion

The present study investigated catalytic properties of palladium nanoparticles for hydrogenation of carbon dioxide into formic acid and effect of silica-coating on the palladium nanoparticles to maintain stability of the nanoparticles. The nanoparticles were obtained from palladium nitrate in methyl alcohol solvent under solvothermal conditions, and the activity for the hydrogenation reaction was evaluated under various reaction conditions. Turnover number (TON) under higher reaction pressure decreases more significantly with increasing reaction time than that under lower reaction pressure. The UV-Vis spectra of the solution after the reaction indicated that higher amount of active palladium species dissolved in the reaction solution under higher reaction pressure. In order to prevent dissolution of the active species, we investigated effect of silica-coating on the palladium nanoparticles. Thicknesses of silica coated on the nanoparticles by sol-gel based method were controlled by adjusting amount of tetraethoxysilane (TEOS) using as the silica source, and appropriate amount of silica was effective to prevent of dissolution of the active palladium species after the hydrogenation reaction.

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