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Metallic ruthenium nanoparticles for hydrogenation of supercritical carbon dioxide

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Metallic ruthenium nanoparticles prepared in methyl alcohol solution under solvothermal condition showed high activity for hydrogenation of supercritical carbon dioxide to formic acid. The activity of the metallic nanoparticles was drastically improved by addition of an appropriate amount of water to the suspension of methyl alcohol and triethylamide.

The use of carbon dioxide as a carbon resource is an attractive option for increasing the efforts to reduce the carbon footprint of energy and chemical industries.[1] The hydrogenation of carbon dioxide to formic acid ($H_2 + CO_2 \rightarrow HCO_2H$) has been studied intensively in this context.[2] This transformation offers direct access to chemical products from waste material via the energetic use of fossil fuels, opens a possible route to converting carbon dioxide into carbon monoxide, and is a potential option for hydrogen storage. Homogeneous Ru- or Pd-complex catalysts for the hydrogenation of carbon dioxide have been developed since the mid-seventies, and remarkable advancements in catalyst activity has been achieved.[2] The hydrogenation process in gas phase is thermodynamically unfavorable with a standard Gibbs free energy of this reaction of ~32.9 kJ mol^{-1} at 298 K,[3] while use of high pressure can shift the equilibrium in favour of product formation (the equilibrium conversion of CO_2: 0.72×10^{-5} at 3.0 MPa, 373 K, 0.14×10^{-4} at 6.0 MPa, 373 K [4]). Organic or inorganic bases are typically added to the reaction mixture to produce formic acid because formic acid is stabilized by the addition of suitable additives, such as the bases, and the equilibrium can be shifted to the right by trapping formic acid as formate salt.[5] Moreover, solvent systems affect not only the equilibrium but also the activity of the catalyst, and then, reactions in different media such as organic solvents,[6] water,[7] supercritical carbon dioxide,[8] and ionic liquids[9] have shown satisfactory reaction rates.[10] By using supercritical carbon dioxide, turnover frequency of the reaction increases with increasing partial pressure of carbon dioxide,[8b] the catalytic reaction in supercritical carbon dioxide conditions were typically tested with H_2/CO_2 = 8/13 (MPa/MPa) or almost the same ratio with lower total pressure.[3,8] Although the reasonable conversions and yields of formic acid have been obtained using homogeneous catalysts, separation of formic acid from the bases and 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.[11] Ruthenium complex catalysts immobilized on silica and polystyrene resin have been examined.[12] A more attractive heterogeneous system is activated carbon-supported ruthenium prepared by conventional impregnation.[13] BASF recently presented a new process using trihexylamine with a ruthenium catalyst in protic media.[14] The resulting formic acid/trihexylamine adduct could be separated and cleaved into free formic acid and amine by distillation.

In most previous studies using ruthenium catalysts, ruthenium hydride species were found to be active components in the catalytic cycle.[7b, 8-10, 15] However, there are no studies investigating the catalytic effect of metallic ruthenium for the hydrogenation of carbon dioxide to formic acid. This work is the first study of the catalytic effects of metallic ruthenium nanoparticles.

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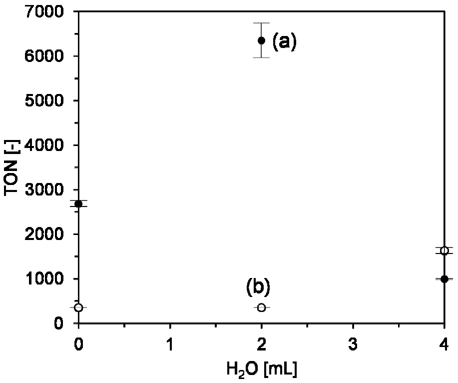

Fig. 1 Effect of H_2O additive on catalytic performance of ruthenium catalyst for hydrogenation of supercritical carbon dioxide to formic acid. Open circle: without pre-reduction procedure of catalyst precursors, closed circle: with pre-reduction procedure of catalyst precursors in methyl alcohol solution at 423 K for 10 h. Reaction conditions:H_2/CO_2 = 5/8 (molar ratio), 353 K, 3 h.

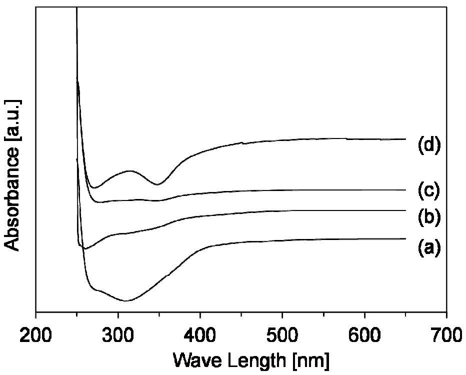

Fig. 2 UV-Vis spectra of reaction mixtures including ruthenium catalysts after hydrogenation of supercritical carbon dioxide. (a) Catalyst without the pre-reduction procedure after the reaction without water added and pre-reduction catalysts after the reaction with water added in the amount of (b) 0, (c) 2, and (d) 4 mL.

Metallic ruthenium nanoparticles were prepared in methyl alcohol solution under solvothermal conditions. Ruthenium chloride hydrate ($RuCl_3$ nH_2O (n ≈ 1.87), 0.022 g) was dissolved in methyl alcohol (15 mL) using Teflon-lined autoclave (Parr Instrument Com.), and was heated at 423 K for 10 h. The resulting metallic ruthenium particles consisted of primary particles with a size of 3-5 nm and secondary particles with a size of 200-240 nm.[16] In addition, ultraviolet and visible spectroscopy (UV-Vis) spectra that the particles confirmed that the particles consisted of metallic ruthenium.[16] The hydrogenation of supercritical carbon dioxide to formic acid was carried out in a 120-mL stainless steel autoclave with a magnetic stirrer (Taiatsu Techno) referred in previous report.[3] Triethylamine (4 mL) and distilled water (0-4 mL) were added to the ruthenium suspension. The autoclave was heated to 353 K, and the reactor was then pressurized to 5 MPa with H_2. 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 13.0 MPa at which point the reaction was considered to have started. After the reaction (3 h), ethyl acetate (2 mL) was added to the mixture as an internal standard for the quantitative analysis of product, and the liquid mixture from the autoclave was analysed with a Shimadzu GC 8A gas chromatograph equipped with a Flusin T column (Shimadzu, 2m×3mm) 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 ruthenium. The mixtures were also measured by UV-Vis (Shimadzu UV-2500PC) to determine the valence state of ruthenium species. The morphologies of Ru nanoparticles were observed using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV.

The effect of reduction procedure and the addition of water to the reaction solutions on the hydrogenation activity for the conversion of supercritical carbon dioxide to formic acid were investigated. Fig. 1 shows the TON of formic acid in the presence of ruthenium catalysts. The pre-reduced catalysts had a much higher TON than the catalysts without the pre-reduction procedure in reaction solutions with up to 2 mL of water added. Comparing between catalysts without and with a pre-reduction procedure, the most active pre-reduced catalyst (water added = 2 mL) had a TON that was about 4 times higher than that of the most active catalyst without a reduction procedure (TON = 1629, water added = 4 mL). We have carried out activity test in the presence of Ru nanoparticles with PPh_3 (PPh_3/Ru = 1/1). The nanoparticles with PPh_3 exhibited negligible activity, indicating that there is negligible amount of Ru ions in the reaction solution. The maximum TON in the present study was 6351. The maximum AAR in this study is 0.02. The value of AAR is expected to increase with increasing reaction time. From the FTIR spectrum of the Ru nanoparticles after the reaction shown in Fig S1 (ESI), From the FTIR spectrum of Ru nanoparticles after the hydrogenation reaction, characteristic bands appeared at around 1590, 1390, and 1350 cm^{-1} were attributed to surface formate species,[17] while the bands appeared at around 1470 and 1430 cm^{-1} were attributed to the monodentate and bidentate carbonate species, respectively.[18] The result suggests that surface carbonate species involve the reaction to form formic acid.

And from the result of ICP, about 15 % Ru in the amount of Ru used under the reaction conditions dissolved in the reaction solution. However, the effect of adding water depends on the reduction procedure. The TON of the catalysts without the pre-reduction procedure increased with an increase in the amount of water added, while the TON of the pre-reduced catalysts reached a maximum with 2 mL of water added. In addition to its bulk solvation effects, water may also participate in the catalytic process on a more intimate, molecular level. For the reaction in this work, the addition of water to the reaction solution may promote the activity for the hydrogenation of supercritical carbon dioxide to formic acid. However, the TON of the pre-reduced catalyst used in a reaction solution with 4 mL of water added (TON = 992) was much lower than that of both the pre-reduced catalyst used in a reaction solution with 2 mL of water added and the unreduced catalyst used in a reaction solution with 4 mL of water added. These results indicate that the performance of the catalyst without the pre-reduction procedure did not significantly depend on the amount of water added, while the performance of the pre-reduction catalysts depend significantly on the amount of water added.

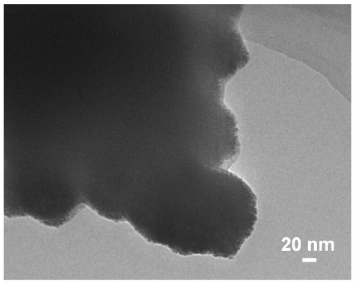

Fig. 3 TEM image of Ru nanoparticles prepared with reduction procedure after the reaction with 2 mL of water.

In order to investigate the effect of the reduction procedure and the addition of water to the reaction solutions, UV-Vis spectra were obtained of the catalysts after the hydrogenation reaction of supercritical carbon dioxide to formic acid. Fig. 2 shows UV-Vis absorption spectra of the ruthenium catalysts after the hydrogenation reaction. In this figure, the spectrum of the ruthenium catalyst without pre-reduction procedure includes a broad peak from 300 to 700 nm, indicating that this catalyst contains Ru(III) species[6,19] after the reaction. However, for pre-reduced catalysts in the reaction solution with up to 2 mL of water added, the peak intensity is negligible in this spectra region, suggesting that the ruthenium species in the pre-reduced catalysts are metallic. These results suggested that ruthenium species with a metallic state was highly active for the hydrogenation of supercritical carbon dioxide to formic acid and that pre-reduction procedure significantly influenced their catalytic activity. However, with the addition of up to 4 mL of water, the spectrum of the pre-reduced catalyst displayed two peaks near 325 and 400 nm (Fig. 2(d)), indicating that the catalyst contained a large amount of Ru(III) species compared to the other pre-reduced catalysts. This result suggested that ruthenium species were probably oxidized in the reaction solution when excess water was added and that an appropriate amount of water promotes the hydrogenation reaction by maintaining ruthenium species in a metallic state. We also confirmed morphology and surface valence state of Ru nanoparticles prepared with the reduction procedure after the reaction with 2 mL of water as shown in Fig. 3 and Fig. S2 (ESI). The TEM image reveals that the catalyst contains grains with primary particles with diameters ca. 5 nm. In the Ru 3d region of the XPS spectrum, a peak at around 280 eV was observed, attributed to metallic Ru.[20]

In summary, metallic ruthenium nanoparticles prepared under solvothermal condition in a methyl alcohol solution displayed a high activity for the hydrogenation of supercritical carbon dioxide to formic acid. The activity of the nanoparticle catalysts was drastically improved by using a pre-reduction procedure and adding the appropriate amount of water to the suspension of methyl alcohol and triethylamide. These nanoparticles maintained metallic state after the reaction.

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