Original Paper

Fabrication of Spherical Silica Particles from Sodium Silicate and Their Application as Support Materials for Ruthenium-based Catalysts for the Hydrogenation of Supercritical Carbon Dioxide into Formic Acid

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Spherical silica nanoparticles were fabricated from sodium metasilicate solution using urea as a precipitant. Homogeneity of the silica particles was improved by adjusting the ratio of sodium metasilicate to urea, and their size was adjusted between 20 and 1600 nm by adjusting the amount of sodium metasilicate and urea. Supported ruthenium catalysts were prepared by impregnation method using the silica spheres as a support of the catalysts. The amount of supported ruthenium depended on the ruthenium concentration during the impregnation process. The catalytic activity for hydrogenation of carbon dioxide into formic acid increased with increasing their ruthenium contents. The activity did not significantly depend on the particle size of the silica supports; however, the amount of ruthenium deposited on the particles depended on the particle size of the silica supports, with a larger amount of ruthenium being immobilized on the silica supports with a smaller particle size.

本研究では、ルテニウム系触媒の担体として、メタケイ酸ナトリウムを原料とし、尿素を沈殿剤とした方法で球状シリカ粒子の調製を試みた。シリカ粒子の均一性は、メタケイ酸ナトリウムと尿素の比率により調整可能であり、そのサイズは20～1600 nmまで調整可能であることが確認された。ルテニウム担持触媒はこれらのシリカ粒子を担体として含浸法により調製したところ、ルテニウム溶液の濃度により担持されるルテニウム量が増加し、そのルテニウム量によって二酸化炭素水素化からのギ酸合成活性が変化することが確認された。一方、担持されるルテニウム量はシリカ担体の粒径が小さいほど増大するが、活性にはそれほど影響しないことが確認された。

Key Words

Spherical silica particles, Sodium metasilicate, Supported ruthenium catalyst,
Hydrogenation of carbon dioxide into formic acid

1. Introduction

Silica nanoparticles are generally synthesized by tetraethyl orthosilicate (TEOS) as a precursor in alkaline medium¹⁾. Spherical, non-agglomerated silica nanoparticles are usually produced by this method^{2) 3)}, and their particle size increases upon increasing the concentration of both TEOS and ammonia⁴⁾. In addition to TEOS, sodium silicate solution is another low-cost precursor which is used for the synthesis of silica nanoparticles. Sodium silicate solution offers several advantages over TEOS, including its ability to form nanoparticles of uniform size in high yields⁵⁾. The

conventional synthesis of silica from sodium silicate solution is usually performed in acid medium^{6) 7)}, which can often result in agglomeration of the particles²⁾. However, the use of alkaline sodium silicate solutions as precursors for non-agglomerated silica nanoparticles has been less studied. The production of metal oxide particles via homogeneous precipitation with urea has been demonstrated as a promising approach to the successful preparation of powders with controlled particle size and shape^{8) ~10)}.

On heating the aqueous solution of urea (NH_2)₂CO, urea was decomposed via hydrolysis. During the decomposition of urea, NH_4^+ ions are slowly produced homogeneously throughout the solution, avoiding the formation of localized H^+ gradients. Thus, in contrast to

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heterogeneous precipitation with alkali or ammonia, when ureic solutions are applied to the hydrolysis of metal ions the precipitating agent is slowly formed throughout the reaction mixture allowing the slow ripening of particles, resulting in better product crystallinity and uniformity. According to the Arrhenius plot for the decomposition urea, its activation energy is $32.4 \text{ kcal mol}^{-1}$ ¹⁰⁾, and this decomposition can be precisely controlled using the heating temperature. The decomposition constant of urea in water at 298 K is calculated to be $6.65 \times 10^{-8} \text{ s}^{-1}$, which is $\sim 1/15000$ of its value at 363 K. Thus, urea is neither acidic nor alkaline in water under ambient conditions. However, it produces ammonia in water upon heating, which causes the solution to become alkaline. A urea solution at high temperature can dissolve silica in a controlled manner even though silica is sparingly soluble in water ^{11) ~ 21)}, and the weak alkalinity of the urea solution allows it to be used for the uniform deposition of metal precursors.

Using spherical silica particles as a support, we prepared supported catalysts for the hydrogenation of carbon dioxide. Carbon dioxide is an attractive carbon resource to reduce carbon wastes from various industries ^{22) ~ 24)}, and the hydrogenation of carbon dioxide to formic acid ($\text{H}_2 + \text{CO}_2 \rightarrow \text{HCO}_2\text{H}$) has been studied from this view point ^{25) ~ 27)}. Waste gas of fossil fuels directly converts to useful products in this process, and it is also expected as a potential route for hydrogen storage. Homogeneous metal complex catalysts (Ru, Pd, etc.) have been developed for the hydrogenation reaction for some decades, and significant development in catalyst activity has been achieved ^{25) ~ 27)}. Gas phase hydrogenation is thermodynamically unfavorable ²⁸⁾, however, the equilibrium was shifted in favor of product formation under high pressures ²⁹⁾. Under supercritical conditions, the turnover frequency of the reaction increases with increasing the partial pressure of carbon dioxide ³⁰⁾. The catalytic reaction have typically been tested with $\text{H}_2/\text{CO}_2 = 5/8$ (MPa/MPa), at lower total pressure with the same reactant ratio ^{28) 31) 32)}. Although the reasonable conversions and yields of formic acid have been obtained using homogeneous catalysts, the separation of formic acid from the bases and catalysts remains a challenge. Thus, a heterogeneous catalytic system is required to develop. To the best of our knowledge, very few heterogeneous systems with solid (supported) catalysts have been investigated in this reaction ^{28) 33) ~ 37)}.

In the present study, we have investigated the preparation of spherical silica particles using urea, and apply them as supports for ruthenium-based catalysts for the hydrogenation of supercritical carbon dioxide into formic acid.

2. Experimental

2.1 Sample preparation

Spherical silica particles were prepared using a sodium metasilicate solution (SiO_2 35-38 %, Na_2O 17-19 %) and urea under hydrothermal conditions. All reagents were commercially purchased and used without purification. Sodium metasilicate solution (0.24 - 5.0 g) and urea (0.3 - 2.4 g) were dissolved in deionized water (15 mL) in a Teflon-lined stainless steel vessel, and the solution was heated at 393 K for 15 h. The suspension was filtered and washed using deionized water, and the powder product was obtained after drying.

Using these spherical silica particles as supports, supported ruthenium catalysts were prepared. The silica particles (0.384 g) were immersed in 10 mL of aqueous solution of ruthenium chloride *n*-hydrate ($n \approx 1.87$) with 28 wt.% of aqueous ammonia solution (5 mL). The concentration of ruthenium species was adjusted from 2.0×10^{-4} - 8.0×10^{-4} M. The suspension was filtered and washed using deionized water, and the powder product was obtained after drying.

2.2 Characterization

The morphologies of the silica supports and the catalysts were observed using a Hitachi S-450 scanning electron microscope (SEM) (acceleration voltage of 15 kV), and a Hitachi FE2000 transmission electron microscope (TEM) (acceleration voltage of 200 kV). The Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded using an FTIR-8400S spectrophotometer (Shimadzu Co. Ltd.) at a resolution of 4 cm^{-1} . X-ray photoelectron spectra (XPS) was performed using an ESCA-3400 spectrometer (Shimadzu Co. Ltd.) equipped with a $\text{MgK}\alpha$ X-ray source (1253.6 eV) operating at 10 kV and 10 mA. The binding energies (BE) were corrected by reference to the C 1s peak at 285.0 eV.

2.3 Catalytic activity

Hydrogenation of carbon dioxide was carried out in a 120-mL stainless steel autoclave with a magnetic stirrer (Taiatsu Techno). Triethylamine (4 mL) and deionized water (2 mL) were added to the supported ruthenium catalyst suspension including 2 g of the catalyst. The autoclave was heated to 353 K. The reactor was then pressurized to 5 MPa with H_2 , and carbon dioxide was introduced from a cooled (268 K) reservoir using a high pressure liquid chromatography pump until the total pressure was increased to 13.0 MPa. After the reaction for 3 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, $2 \text{ m} \times 3 \text{ mm}$) and a

thermal conductivity detector, and the turnover number (TON) of formic acid, which is the number of moles of formic acid produced per mole of ruthenium, was calculated.

3. Results and discussion

We investigated the effect of the amount of urea on the morphology of silica particles. Fig. 1 shows SEM images of silica particles prepared using different amount of urea, and clearly indicates that the morphology depends on the amount of urea used. When 0.6 g of urea is used, the sample consists of micro-sized rock-like particles (Fig. 1(a)), indicating that the amount of urea is insufficient to react completely with the sodium metasilicate, and unreacted sodium metasilicate precipitates after drying the resulting sample. Conversely, when 1.2 and 2.4 g of urea are used, the resulting samples consist of spherical particles with a diameter of ~1600 nm (Fig. 1(b), (c)), indicating that 1.2 and 2.4 g of urea is sufficient to completely react with the sodium silicate and produce homogeneous particles. In addition, the results of energy-dispersive X-ray spectroscopy (EDX) and XPS reveal that the main components of the particles are silicon and oxygen, indicating that the particles mainly contain silica. We also investigated the effect of amount of sodium metasilicate and urea on morphology of silica particles.

We also investigated the effect of the amount of sodium metasilicate and urea on the morphology of the silica particles. Based on the result shown in Fig. 1, a constant molar ratio of urea to sodium silicate (1.2 g of urea / 5.0 g of sodium metasilicate) was used. Fig. 2 shows SEM images of samples prepared with different amounts of sodium metasilicate and urea, and in the inset of Fig. 2(a), the TEM image of the sample is shown. All the samples contain spherical particles, and the particle size

depends on the amounts of reagents used. The particle size increases from ~20 to ~1600 nm upon increasing the amount of sodium metasilicate and urea, indicating that the concentration of sodium metasilicate and urea significantly influence the silica particle size. Fig. 3 shows relationship between sodium metasilicate concentration and the average particle size. The particle size increases parabolically with increasing sodium metasilicate concentration, indicating that the particle size increases via the aggregation of smaller particles. The tendency reflected their specific surface area, and the surface area of the spherical silica particles prepared with the amount of sodium silicate = 1, 2, 3, 4, and 5 g was 45.3, 15.2, 5.2, 2.2, 3.6 m² g⁻¹, respectively. The results indicate that the specific surface area of the spherical silica particles decrease with increasing their particle size. Explosive nucleation can be achieved at a relative high temperature, usually at temperatures higher than 356 K⁽³⁸⁾⁽³⁹⁾. In the present study, we prepared spherical silica particles over the temperature, thus it is possible that the primary particles of the silica particles homogeneously formed and aggregated to form larger particles.

Using the silica particles as supports for ruthenium-based catalyst, we investigated catalysts prepared by the impregnation method. The morphology of the supported catalysts does not significantly change after impregnation with ruthenium species. Fig. 4 shows XPS spectra of ruthenium species on the spherical silica particles. Samples of spherical silica particles with a diameter of ~1600 nm was used. The peak assigned to Ru³⁺ species at 283.3 eV is shown in Fig. 4(a), indicating that the surface ruthenium species is Ru(OH)₃⁽³⁹⁾. It was also confirmed that there was no significant peak shift assigned to active ruthenium species after hydrogenation of carbon dioxide shown as in Fig. 4(b). Fig. 5 shows the influence of the ruthenium

Fig. 1 Influence of the amount of urea on the morphology of silica particles. Amount of urea: (a) 0.6, (b) 1.2, (c) 2.4, amount of sodium metasilicate: 5.0 g, hydrothermal conditions: 393 K, 15 h

Fig. 2 SEM images of spherical silica particles prepared with different amounts of sodium metasilicate and urea. Amount of sodium metasilicate: (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0, (e) 5.0 g, amount of urea: (a) 0.24, (b) 0.48, (c) 0.72, (d) 0.96, (e) 1.20 g. Inset of (a): TEM image of the spherical silica particles prepared with 1.0 g of sodium metasilicate and 0.24 g of urea. Hydrothermal conditions: 393 K, 15 h

Fig. 3 Influence of the amount of sodium metasilicate on the average particle size of the spherical silica particles

Fig. 4 XPS spectrum of a ruthenium catalyst supported on spherical silica particles prepared by impregnation (a) before and (b) after hydrogenation of carbon dioxide. Ruthenium concentration: 2.0×10^{-2} M, particle size of spherical silica particles: 1600 nm

concentration used for the preparation of supported catalysts on the ruthenium content of the spherical silica particles. The contents were calculated from results by energy dispersion X-ray spectroscopy. The ruthenium content of the supported catalysts increases with increasing ruthenium concentration used during impregnation. Fig. 6 shows the catalytic activity for the hydrogenation of supercritical carbon dioxide into formic acid over silica supported ruthenium catalysts prepared using different ruthenium concentrations during the impregnation process. This result indicates that the activity is significantly influenced by ruthenium concentration during the impregnation process possibly because the ruthenium concentration influences in dispersion of supported ruthenium species.

In order to understand the tendency in Fig. 6, we investigated immobilization efficiency of ruthenium species

Fig. 5 Dependence of ruthenium content calculated from results of energy dispersion X-ray spectroscopy on ruthenium concentration in the preparation of supported catalysts. Size of silica support: 1600 nm

Fig. 6 TON over supported catalysts with different ruthenium contents. Reaction conditions: $\text{H}_2 / \text{CO}_2 = 5 / 8$, 13 MPa, 353 K, 3 h

over the silica supports depending on the particle diameter of the supports. Fig. 7 shows ruthenium content of the supported catalysts. A large amount of ruthenium species (3.9 wt.%) is supported on the smallest sized silica supports. Similar amount of ruthenium species (2.4-2.9 wt.%) are supported on the silica supports with the diameter over 130 nm. This result indicates that small silica supports more efficiently immobilize ruthenium species. Based on this result, the activity of the supported ruthenium catalysts using silica supports with diameters of 20 and 1600 nm were compared. Fig. 8 shows the catalytic activity for hydrogenation of supercritical carbon dioxide to formic acid over the supported catalysts. In the present study, no other products except for formic acid were detected. Both the samples exhibit similar TONs, indicating the size of the silica support does not significantly influence on the activity for the hydrogenation reaction. In order to investigate reusability of the catalyst, the data for the recovery

Fig. 7 Dependence of ruthenium content on the average particle size of the silica support

Fig. 8 Catalytic activity for formic acid formation from supercritical carbon dioxide over a ruthenium catalyst supported using spherical silica particles. Reaction conditions: $\text{H}_2 / \text{CO}_2 = 5 / 8$, 13 MPa, 353 K, 3 h

efficiency of the ruthenium content is also shown. The ruthenium species contained in the supported catalyst with small silica supports is more efficiently recovered compared with that from the catalyst using the larger silica support. From the results shown in Fig. 2(a) and (e), the spherical silica particles with smaller particle size are more closely packed. Void spaces among the particles are small, and the ruthenium content is immobilized in the small void spaces. Thus, the amount of immobilized ruthenium species on the silica support with small particle size after hydrogenation of supercritical carbon dioxide is larger than that on the support with large particle size.

4. Conclusions

Silica nanoparticles with a wide range of particle sizes was fabricated from sodium metasilicate solution with urea as the precipitant, and supported ruthenium catalysts on the silica nanoparticles for the hydrogenation of carbon dioxide into formic acid were investigated. Using urea to precipitate silica, spherical silica particles were obtained, and the homogeneity of the particles was improved by adjusting the ratio of sodium metasilicate to urea. Moreover, adjusting the concentrations of sodium metasilicate and urea, the particle size of the spherical silica particles was adjusted between 20 and 1600 nm, and increase with increasing amount of sodium metasilicate and urea. Using the spherical silica supports, supported ruthenium catalysts were prepared by the impregnation method. The amount of supported ruthenium depended on the concentration of ruthenium used in the impregnation process, and the catalytic activity for the hydrogenation of carbon dioxide into formic acid increased with increasing ruthenium content in the supported catalysts. The activity did not significantly depend on the particle size of silica supports, while the amount of ruthenium supported after the reaction compared to the initial amount of ruthenium depended on the particle size of the silica supports, with a higher amount of ruthenium being immobilized on silica supports with smaller particle size.

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