Influence of Nitrilotriacetic Acid (NTA) Addition on the Activity of Spherical Silica-nickel Particles for Hydrolytic Dehydrogenation of Ammonia Borane

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In this work, we investigated the influence of adding a chelating agent, nitrilotriacetic acid (NTA), on the morphology and activity of spherical silica-nickel composite particles for hydrolytic dehydrogenation of ammonia borane. Their particle sizes prepared with NTA decreased with increasing pH value of the solution used to form the composite particles. The homogeneity of the composite particles prepared with NTA increased with increasing pH value. The hydrogen evolution rate and amount from the aqueous solution containing sodium borohydride (NaBH₄) and ammonia borane (NH₃BH₃) in the presence of the composite particles prepared with NTA did not significantly depend on the pH value. On the other hand, the size and homogeneity of the composite particles depended on the ratio of nickel to NTA. The nickel content of the composite particles increased with increasing the ratio of nickel to NTA, and the composite particles with high ratio of nickel to NTA showed high activity for hydrogen evolution from the aqueous solution containing NaBH₄ and NH₃BH₃. From this and energy-dispersive X-ray spectroscopy (EDX) results, it is suggested that the spherical silica-nickel composite particles prepared with NTA included highly dispersed active nickel species, and showed high activity for hydrogen evolution from aqueous solution containing NH₃BH₃.

Key Words
Spherical silica-nickel composite particles, Chelating agent, Ammonia borane, Hydrogen evolution, Nitrilotriacetic acid

1. Introduction
The development of safe and efficient methods for hydrogen storage is a key issue in realizing the hydrogen economy1) 2). Ammonia borane (NH₃BH₃) possesses a low molecular weight (30.9) and high hydrogen content (19.6 wt%)3), and has attracted much attention as a candidate material for chemical hydrogen storage4) ~ 20). NH₃BH₃ is nontoxic, stable, environmentally benign, and can be handled at around 298 K4). The compound hydrolytically decomposes into hydrogen at an appreciable rate in the presence of a suitable acid or catalyst even at ambient temperature6) ~ 15). For the practical application, efficient,
low-cost, and stable catalysts have been required to further improve the kinetic properties under moderate conditions. Nickel-based catalysts are one of the most highly-active catalysts for this reaction \(^{10} 13 14 21 22 26\), and several reports have also investigated the composite effect of nickel species with metal oxides on the catalysts \(^{10} 13 14 21 24 26\).

We previously reported that additives for the catalyst preparation influenced the reducibility of the active nickel species and subsequently their activity for hydrogen evolution from the aqueous NH₃BH₃ solution \(^{27}\). For controlling the reducibility, we focused a chelating agent as additive for preparation of spherical silica-nickel composite particles for hydrolytic dehydrogenation of NH₃BH₃ in the present study. For some catalytic reactions, modification with chelating agents increases the number of surface metallic sites after the reduction due to modify interaction between support or matrix materials such as silica and improve dispersion of active species, and significantly improve catalytic activity of some metal based catalysts \(^{29} 30\). It was reported that dispersion of nickel species and metal-support interaction was controlled by adding nitritotriacetic acid (NTA) in supported catalyst including nickel, and activity of the supported catalyst for various reactions improved compared with the supported catalyst without these chelating agents \(^{31} 32\). On the other hand, there have been few reports to investigate the effect of the chelating agents on morphology and catalytic activity of composite catalysts. In order to identify the effect of adding the chelating agent on morphology and catalytic activity of composite catalysts, we investigated the influence of adding a chelating reagent, nitirotriacetic acid (NTA) on the activity of spherical silica-nickel composite particles for hydrolytic dehydrogenation of NH₃BH₃ in the present study.

2. Experiments

Spherical silica-nickel composite particles were prepared by the following sol-gel based techniques. Nickel nitrate hexahydrate (Ni(NO₃)₂ · 6H₂O, 0.0462 g, Kanto Chem. Co., > 99.0%) and nitrilotriacetic acid (NTA, 0.0064-0.1911 g, Kanto Chem. Co., > 97%) were dissolved in 4.14 mL of deionized water with varying pH achieved through the addition of aqueous ammonia solution (ca. 28.0 wt.%, Kanto Chem. Co.). Subsequently, 16.9 mL of ethyl alcohol (Kanto Chem. Co., > 99.5%) and 1.1081 mL of tetraethoxysilane (TEOS) were added into the mixture, and the solution was stirred at 343 K for 1 h. The resulting product was filtrated and dried in a desiccator at room temperature, and was used without calcination procedure.

The obtained powder (82.7 mg) was mixed with sodium borohydride (NaBH₄, 5 mg, Kanto Chemical Co., > 98.5%) and ammonia borane (NH₃BH₃, 17.4 mg, Aldrich, 90%) in a two-necked round-bottomed flask. One neck was connected to a gas burette, and the other was fitted with a septum inlet to introduce deionized water (5 mL). The reaction was started by adding the deionized water into the mixture of the sample, NaBH₄, and NH₃BH₃, and the evolution of gas was monitored using the gas burette. The reactions (in-situ activation process of spherical silica-nickel composite particles) were carried out at 323 K. Additional aqueous ammonia borane solution (17.4 mg of NH₃BH₃ in 5 mL of deionized water) was added into the suspension after stopping hydrogen evolution via the above in-situ activation process of the catalyst, and the hydrolytic dehydrogenation reactions were carried out at 323 K.

The morphologies of spherical silica-nickel composite spheres were observed using a Hitachi S-3000N scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX) operating at an acceleration voltage of 15 kV. Diffuse reflectance ultraviolet and visible (DRUV-VIS) spectra were recorded on a V-670 (JASCO) UV-Vis-NIR spectrophotometer with barium sulfate as standard spectra over the range of 250-800 nm.

3. Results and Discussion

We firstly investigated the influence of adding NTA on the morphology of spherical silica-nickel composite particles. Fig. 1 shows the SEM images of the composite particles prepared with NTA in the solution of various pH values. In this figure, the SEM images of the composite particles prepared without NTA are also shown.

![SEM images of spherical silica-nickel composite particles prepared (a-c) with and (d) without nitritotriacetic acid (NTA). pH: (a) 9.88, (b) 10.93, (c,d) 11.80. Ni/NTA = 1/6](image-url)
this figure, all the samples consisted of spherical particles. The size of the composite particles prepared with NTA decreased with increasing pH value, and the homogeneity of the composite particles improved with increasing pH value. In sol-gel based method, silica based particles form via hydrolysis step of TEOS and condensation step of silicate into silica nuclei \(^\text{34\,35}\). With increasing pH value, the rate of condensation is slower than that of hydrolysis, and the size of the formed composite particles decreases. The result in Fig. 1 reflected the dependence of the particle size on pH values. On the other hand, the size and homogeneity depended on pH values. Fig. 2 shows particle size distribution of the samples prepared in the solution with various pH values. The distribution was calculated from the result in Fig. 1. From Fig. 2, the homogeneity of the composite particles prepared with NTA increased with increasing pH values for the preparation process. On the other hand, the distribution of the composite particles prepared with NTA in the solution of pH value = 11.80 was narrower than that of the composite particles prepared without NTA in the solution of pH value = 11.80, suggesting that the chelating agent possessed promoting effect of controlling the size and homogeneity of the composite particles.

Hydrogen evolution from aqueous solution containing NaBH\(_4\) and NH\(_3\)BH\(_3\) in the presence of the composite particles was evaluated. Fig. 3 shows the time course of hydrogen evolution from the aqueous solution in the presence of the composite particles prepared with NTA in the solution of various pH values. The hydrogen evolution rate and amount in the presence of the composite particles prepared with NTA did not significantly depend on the pH values. Evolutions of 20.0, 21.0, and 19.0 mL of hydrogen from the aqueous NH\(_3\)BH\(_3\) solution were completed within approximately 13, 29, and 13 min in the presence of the composite particles prepared at pH = 9.88, 10.93, and 11.80, respectively. The effect of NaBH\(_4\) on nickel-based catalysts for the hydrolysis of NH\(_3\)BH\(_3\) has been reported \(^\text{13\,22\,23}\). In the present reaction system, NaBH\(_4\) was mixed with H\(_2\)O, NH\(_3\)BH\(_3\), and the catalyst. Hydrogen was evolved via reactions (2) and (3):

\[
\begin{align*}
4\text{Ni}^{2+} + \text{BH}_4^- + 2\text{H}_2\text{O} &\rightarrow 4\text{Ni} + \text{BO}_2^- + 8\text{H}^+ \quad (1) \\
\text{NaBH}_4 + 2\text{H}_2\text{O} &\rightarrow \text{Na}^+ + \text{BO}_2^- + 4\text{H}_2 \quad (2) \\
\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} &\rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2 \quad (3)
\end{align*}
\]

Under the present reaction condition, about 13 mL of hydrogen (5.2×10\(^{-4}\) mol) was experimentally generated via reactions (2) from the residual amount of NaBH\(_4\), consumed via reaction (1) (1.4×10\(^{-4}\) total amount of NaBH\(_4\)) - 0.1×10\(^{-4}\) (amount of NaBH\(_4\) consumed via reaction (1)) = 1.3×10\(^{-4}\) mol), and about 40 mL of hydrogen (16.5×10\(^{-4}\) mol) was generated via reaction (3). The molar ratios of the hydrolytically generated hydrogen to the initial NH\(_3\)BH\(_3\) in the presence of the composite particles prepared at pH = 9.88, 10.93, and 11.80 were 0.6, 0.6, and 0.5, respectively. From the result in Fig 1 (a)-(c), it is evident that the size of the composite particles did not significantly depend on the pH of the solution used to prepare the composite particles. These results suggest that the composite particles in the range of the particle size showed similar catalytic activity for hydrogen evolution from the aqueous solution containing NaBH\(_4\) and NH\(_3\)BH\(_3\). Hydrogen evolution of 4.0 mL from the aqueous NH\(_3\)BH\(_3\) solution was completed.
within approximately 6 min in the presence of the particles prepared at pH = 11.80. The molar ratios of the hydrolytically generated hydrogen to the initial NH₃BH₃ in the presence of the particles prepared at pH = 11.80 were less than 0.1. From that and the result in Fig. 1 (d), its inhomogeneity caused the low catalytic activity of the composite particles prepared without NTA for hydrogen evolution from the aqueous solution containing NaBH₄ and NH₃BH₃.

We also investigated the influence of the ratio of nickel content to the chelating agent on the morphology of the composite particles. For the investigation, the samples were prepared under the pH condition in which relatively homogeneous composite particles were obtained, thus, the samples were prepared with pH = 11.80. Fig. 4 shows the SEM images of the silica-nickel composite particles prepared with various ratios of nickel to NTA. All the samples consisted of spherical particles, while, their size and homogeneity depended on the ratios. The size of the composite particles prepared with NTA tended to increase with increasing the ratio, and the homogeneity of the composite particles improved with decreasing the ratio. NTA formed the six-coordinated complexes with nickel species. A Ni-NTA complex has two vacant coordination positions and nickel species can interact with silicate anion on the positions, resulting that highly condensed silica based particles were formed by addition of NTA and their homogeneity was high with even small size of the particles.

Hydrogen evolution from the aqueous solution containing NaBH₄ and NH₃BH₃ in the presence of the composite particles was evaluated. Fig. 5 shows the time course of hydrogen evolution from the aqueous solution in the presence of the particles prepared with various ratios of nickel to NTA. The amount of hydrogen evolution in the presence of the particles prepared with NTA depended on the catalyst. The amount of hydrogen evolution slightly increased with increasing ratio of nickel to NTA. On the other hand, the particles prepared with Ni/NTA = 5/1 showed high hydrogen evolution compared to the other samples prepared with NTA. Hydrogen evolutions of 33.0, 36.0, 41.0, and 57.0 mL from the aqueous NH₃BH₃ solution were completed within approximately 13, 9, 19, and 24 min in the presence of the composite particles prepared with Ni/NTA = 1/6, 1/2, 1/1, and 5/1, respectively. The molar ratios of the hydrolytically generated hydrogen to the initial NH₃BH₃ in the presence of the particles prepared with Ni/NTA = 1/6, 1/2, 1/1, and 5/1 were 1.5, 1.7, 2.1, and 3.3, respectively. In the presence of the particles with Ni/NTA = 5/1, excess amount of gas evolution compared with the stoichiometric amount of hydrogen evolution was observed, probably because part of NH₄⁺ byproduct was vaporized during the reaction. Table 1 lists the composition of nickel and silicon in the composite particles prepared with NTA. The result indicates that the nickel content in the particles prepared with Ni/NTA = 5/1 was relatively high compared

![Fig. 4 SEM images of spherical silica-nickel particles prepared with NTA. Ni/NTA = (a) 1/2, (b) 1/1, (c) 5/1, pH for the preparation: 11.80](image)

![Fig. 5 Hydrogen evolution from aqueous solution containing sodium borohydride (NaBH₄) and ammonia borane (NH₃BH₃) in the presence of spherical silica-nickel particles prepared using NTA with Ni/NTA = (a) 1/6, (b) 1/4, (c) 1/2, (d) 5/1, pH for the preparation: 11.80](image)

| Ni/NTA (molar ratio) | 1/6 | 1/2 | 1/1 | 5/1 |
|----------------------|-----|-----|-----|-----|
| Ni / At%*            | 0.7 | 1.3 | 1.5 | 6.0 |
| Si / At%*            | 99.3| 98.7| 98.5| 94.0|

* Calculated from results of energy dispersive X-ray analysis
with the other samples prepared with NTA. Otherwise, there were not clear trends of hydrogen evolution rate depending on the samples, while, the hydrogen evolution rate in the presence of the particles prepared with Ni/NTA = 5/1 was relatively low compared with the other samples. From this and the result in Fig. 4, it is suggested that the homogeneity of the composite particles significantly influenced the diffusion rate of the reactant (ammonia borane) to the active nickel site in the composite particles.

Fig. 6 shows the diffuse reflectance of UV-Vis (DRUV-Vis) absorption spectra of the spherical silica-nickel composite particles prepared with Ni/NTA = 5/1. Transitions assigned as $^3T_1g(P) \leftrightarrow ^3A_2g(F)$ are located at 300 - 350 and 350 - 450 nm for Ni$^{2+}$ in the spectra of the samples before and after the in-situ activation process, respectively. The result indicates that all the samples before the reaction include octahedral coordination of Ni(II). During the in-situ activation process, the sample was grayish color, and then, its color changed greenish color when the sample was exposed in air after filtration. Consequently, the result in Fig. 6 suggests that metallic nickel species was active for the reaction in our previous study. The result suggests that metallic nickel species was formed via the in-situ activation process, and then, the air sensitive nickel species was oxidized by exposure of the sample in air.

Hydrolytic dehydrogenation reaction was conducted by adding aqueous ammonia borane solution with same concentration of ammonia borane as the in-situ activation process (17.4 mg of ammonia borane in 5 mL of deionized water) into the suspension including the catalyst prepared with Ni/NTA = 5/1. As shown in Fig. 7, hydrogen evolutions of 31.0 mL from the aqueous NH$_3$BH$_3$ solution were completed within approximately 23 min in the presence of the catalyst. The molar ratios of the hydrolytically generated hydrogen to the initial NH$_3$BH$_3$ in the presence of the composite particles were 2.3. The result indicates that the catalyst can use recyclable for the reaction.

### 4. Conclusions

The present work studied the influence of NTA addition on the morphology and activity of spherical silica-nickel composite particles for hydrolytic dehydrogenation of ammonia borane. The size of the composite particles prepared with NTA decreased with increasing pH value of the solution used to form the composite particles. Homogeneity of the composite particles prepared with NTA increased with increasing pH value. The hydrogen evolution amount and rate from aqueous solution containing NaBH$_4$ and NH$_3$BH$_3$ in the presence of the composite particles prepared with NTA did not significantly depend on the pH value. The size and homogeneity of the composite particles also depended on the ratio of nickel to NTA, and the composite particles prepared with a high nickel to NTA ratio included high nickel content and showed high activity for hydrogen evolution from the aqueous solution containing NaBH$_4$ and NH$_3$BH$_3$. From this and EDX results, it is suggested that the spherical silica-nickel composite particles prepared with NTA included highly dispersed active nickel species, and showed high activity and recycling ability for hydrogen evolution from the aqueous solution containing NH$_3$BH$_3$.
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