Control of particle size of hollow silica-alumina composite spheres prepared using L(+)-arginine and their activity for hydrolytic dehydrogenation of ammonia borane

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In this study, we investigated control of particle size of hollow silica-alumina composite spheres prepared using L(+)-arginine and their activity of these hollow spheres for hydrolytic dehydrogenation of ammonia borane. The hollow spheres were prepared by polystyrene templates method, and the polystyrene templates were completely removed by calcination. In this method, silica-alumina composite shell were coated onto polystyrene particles via a sol-gel reaction using L(+)-arginine as a promoter of this reaction. Hollow spheres with average diameter of 206, 277, and 366 nm were prepared using polystyrene particles with average diameter of 150, 200, and 340 nm, respectively. Activities of hollow spheres with various diameter for hydrolytic dehydrogenation of ammonia borane were compared. The evolution of 8, 7.5, and 5 mL of hydrogen was released in the presence of the hollow spheres with the diameter of 210, 260, and 400 nm, respectively. From the results, the activity increase with decrease of diameter of the hollow spheres. The result of neutralization titration and solid state 27 Al MAS NMR indicates that the activity for hydrolytic dehydrogenation of ammonia borane increase with increase of amount of Bronsted acid sites.

Key words: Ammonia borane, Hydrolytic dehydrogenation, Particle size, hollow spheres, Bronsted acid sites

1. INTRODUCTION

Hydrogen has attracted interest as a clean and sustainable energy carrier [1]. Effective release of hydrogen is the limiting factors in the application of hydrogen energy [2]. Due to the significant challenges associated with storing hydrogen securely, much attention has been paid to solid hydrogen storage materials such as metal hydrides and sorbent materials [3-5]. Among the chemical hydrides, ammonia borane \((\text{NH}_3\text{BH}_3)\) is an attractive candidate because of its high hydrogen content (19.6 wt%), high stability under ambient conditions, and environmentally benign properties [6, 7]. More importantly, \(\text{NH}_3\text{BH}_3\) is able to release its hydrogen upon hydrolysis in the presence of suitable acids or catalysts (Eq. (1)) [8-13].

\[
\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ \text{BO}_2^- + 3\text{H}_2
\]  \hspace{1cm} (1)

Acids and catalysts were needed to provide the efficiency, low-cost, and stability required for practical use. Among the acids and catalysts, it has been reported that solid acids such as H-zeolites (H-BEA and H-MOR) were high activities for this reaction [8]. However, there are few reports that explain the activity of solid acids for hydrogen via hydrolysis of \(\text{NH}_3\text{BH}\). In addition, there is little information about the important factors to show the activity such as the structures of the solid acids and elemental compositions of the solid acids. To clarify the relationship between structure and activity, our group has focused on hollow spheres. Hollow spheres have the potential to be used in a wide range of applications, such as thermal insulators, optical devices, chromatography-related components, shields for enzymes and proteins, drug-delivery vehicles, dyes, inks, photonic crystals, artificial cells, waste treatment, and large biomolecular release systems [14, 15]. Many methods to prepare hollow spheres are the template-based route. The template-methods can be classified into two possible methods [16]: the soft template method [17-19] and the hard template method [20-22]. The hard templates are widely used to fabricate homogeneous hollow spheres. This method has been mainly utilized polystyrene (PS) particles as template because it is easy to control the distribution of their size [19, 23].

Our recent studies have reported that hollow
silica-alumina composite spheres can be prepared by the PS template method [24-26]. We have previously prepared the hollow silica-alumina composite spheres using L(+)-arginine as promoter for hydrolysis of tetraethoxysilane (TEOS) [27]. In this study, we investigated control of particle size of hollow silica-alumina composite spheres and their activity for hydrolytic dehydrogenation of NH3BH3.

2. EXPERIMENTS

Hollow silica-alumina composite spheres were fabricated by the PS template method as described previously [24]. The monodisperse PS particles with various diameters were prepared by emulsifier-free emulsion polymerization as follows: 9.0 mL of styrene (Kanto Chem. Co.), 0.5-4.5 g of polyvinylpyrrolidone (PVP) (K30 grade Mw ≈ 40000, Fluka), 0.26 g of cationic initiator 2,2'-azobis(2-methylpropion amide) dihydrochloride (AlB), (Kanto Chem. Co.), and 100 mL of deionized water were charged into a 250-mL three-neck flask. The reaction solution was deoxygenated by bubbling nitrogen gas through the solution at room temperature for 1 h. The reaction solution was then stirred at a rate of 250 rpm, and the reaction solution was heated to 343 K for 24 h. The obtained PS suspension was centrifuged at 3500-8000 rpm for 5 min and then washed three times with ethanol, and the content of the PS suspension could be tailored through the addition of ethanol. To achieve this, 0.0057 g of aluminum isopropoxide (Kanto Chem. Co., >99.0%), 3 mL of aqueous ammonia solution (28 wt.%, Kanto Chem. Co.), and 40 mL of ethanol were added to 10-50 g of the PS suspension, before 155.1 μL of TEOS (Kanto Chem. Co., >99.9%) was added. The sol-gel reaction was carried out at 323 K for 8-22 h, and the as-prepared hollow silica-alumina composite spheres could be obtained. After drying in a desiccator overnight, the hollow spheres were obtained by calcination in air at 873 K for 0 h at a heating rate of 0.5 K · min⁻¹. The 0.8 g of hollow spheres was placed in a two-necked round-bottomed flask in air at room temperature, one neck was connected to a gas burette, and the other was connected to an addition funnel. The reaction was started by stirring the mixture of the hollow spheres, and aqueous NH3BH3 solution (0.14 wt.%, 3.5 mL, Aldrich, 90%) was added from the addition funnel, while the evolution of gas was monitored using the gas burette. The morphologies of the hollow silica-alumina composite spheres were observed using a transmission electron microscope (TEM, Hitachi FE2000). Specific surface areas of the obtained samples were measured by N2 adsorption at 77 K. Amount of acid sites of the obtained hollow spheres were measured by neutralization titration with n-butyl amine (Kanto Chem. Co.) using methyl red (Kanto Chem. Co.) as an indicator. The coordination of aluminum of the hollow spheres was measured by solid state 27Al magic angle spinning (MAS) NMR spectroscopy (JEOL ECA-500 MHz).

3. RESULTS and DISCUSSION

To obtain hollow silica-alumina composite spheres with various diameters, diameter of the PS template particles were controlled by adjusting the amount of PVP and the centrifugation speed. From the SEM images, the diameter of obtained PS template particles was approximately 150, 200, and 340 nm, respectively. Then, hollow silica-alumina composite spheres were prepared using the PS template particle with diameters of 150, 200, and 340 nm, respectively.

Figure 1 shows TEM images of hollow silica-alumina composite spheres prepared using PS template particle with various diameters. Diameter of hollow spheres prepared using PS template particle with 150, 200, and 340 nm was approximately 173-231, 244-314, and 333-423 nm, respectively. From the result, average diameter of the hollow spheres prepared using were 206, 277, and 366 nm, respectively. The result indicates that diameter of the hollow spheres were controlled by using various PS template particles. Additionally, we reported that the shell thickness of the hollow spheres can be controlled by adjusting the optimal coating time and the amount of PS suspension. Based on the results, homogeneous hollow spheres with average diameters of 206, 277, and 366 nm were prepared by coating time of 22, 17, and 8 h and amount of PS suspension of 30, 25, and 10 g, respectively. Moreover, shell thickness of the hollow spheres with average diameters of 206, 277, and 366 nm was 28-36, 26-31, and 22-29 nm, respectively. From the result, average shell thickness of the hollow spheres with average diameters of 206, 277, and 366 nm were 32, 28, and 25 nm, respectively. The result indicates that shell thickness of all of the hollow spheres were same level. Activities were determined for the hydrolytic dehydrogenation of NH3BH3 in the presence of the hollow spheres with average diameters of 206, 277, and 366 nm, respectively.

Figure 2 shows the molar ratios of the hydrolytically generated hydrogen to the initial NH3BH3 in the presence of hollow silica-alumina composite spheres with average diameters of 206, 277, and 366 nm, respectively. From the results, the evolution of 8, 7.5, and 5 mL hydrogen was finished in 13, 17, and 11 min, respectively. The molar ratios of the hydrolytically generated hydrogen to the initial NH3BH3 in the presence of the hollow spheres with diameters of 206, 277, and 366 nm are 2.0, 1.9, and 1.3, respectively. The results indicate that the activity increase with decrease of diameter of the hollow spheres.

Specific surface area and amount of acid site of the hollow spheres with diameters of 206, 277, and 366 nm were measured as shown in Table 1. The specific surface area of the hollow spheres with diameters of 206, 277, and 366 nm were 466, 469, and 506 m² g⁻¹, respectively. The results show that specific surface areas of all the hollow spheres were approximately the same level. Additionally, average pore size of all the hollow spheres was the amount of acid sites of the hollow spheres with
Figure 1 TEM images of hollow silica-alumina composite spheres with average diameters of (a): 206, (b): 277, and (c): 366 nm, respectively.

Figure 2 The H₂/NH₃BH₃ molar ratios of hydrogen generated from aqueous NH₃BH₃ solution (0.14 wt.%, 3.5 mL) in the presence of hollow silica-alumina composite spheres with average diameters of (a): 206, (b): 277, and (c): 366 nm, respectively.

average diameters of 206, 277, and 366 nm about 3 nm. The results probably suggest that all the hollow spheres were similar morphologies.

The amount of acid sites of the hollow spheres with average diameters of 206, 277, and 366 nm were measured by neutralization titration with n-butyl amine using methyl red as an indicator. Amount of 0.1 M n-butyl amine of the hollow spheres have 4-, 5-, and 6- coordinated aluminum species were reported that 4-coordinated aluminum species were separated 27 Al signals at about 52, 30, and 0 ppm, respectively. As is evident from the results, all the hollow spheres have 4-, 5-, and 6- coordinated aluminum species, as evidenced by three spectra with separated 27 Al signals at about 52, 30, and 0 ppm in the 27 Al MAS NMR spectra. Additionally, it has been reported that 4-coordinated aluminum species and 5/6-coordinated aluminum species were

<table>
<thead>
<tr>
<th>Average diameter (nm)</th>
<th>Activity / -</th>
<th>Specific Surface area / m² g⁻¹</th>
<th>Acid sites / mmol g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>206</td>
<td>2.0</td>
<td>466</td>
<td>0.21</td>
</tr>
<tr>
<td>277</td>
<td>1.9</td>
<td>469</td>
<td>0.20</td>
</tr>
<tr>
<td>366</td>
<td>1.3</td>
<td>506</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Figure 3 The H₂/NH₃BH₃ molar ratios of hydrogen generated from aqueous NH₃BH₃ solution (0.14 wt.%, 3.5 mL) versus amount of acid sites of hollow silica-alumina composite spheres with average diameters of (a): 206, (b): 277, and (c): 366 nm, respectively.

Figure 4 Solid state 27 Al MAS NMR spectra of hollow silica-alumina composite spheres with average diameters of (a): 206, (b): 277, and (c): 366 nm, respectively.
typical associated with Bronsted and Lewis acid sites, respectively [28-30], and the activity probably depends on amount of Bronsted acid sites [8, 26]. We calculated the peak area of 4-, 5-, and 6-coordinated aluminum species of the hollow spheres with average diameters of 206, 277, and 366 nm by using Gaussian function. Based on the results, ratio of the peak area of 4-coordinated aluminum species to the total peak area of 4-, 5-, and 6-coordinated aluminum species (I4 / I4u) of the hollow spheres with average diameters of 206, 277, and 366 nm were 0.32, 0.28, and 0.22, respectively. The results indicate that amount of Bronsted acid sites increase with decrease of diameter of the hollow spheres.

4. CONCLUSIONS
In this study, we successfully prepared hollow silica-alumina composite spheres with various diameters using L(+)-arginine, and revealed effect diameter of the hollow spheres on their activity for hydrolytic dehydrogenation of NH3BH3. The hollow spheres were prepared by PS templates method, and the PS templates were completely removed by calcination. In this method, silica-alumina composite shell were coated on PS particles via a sol-gel reaction using L(+)-arginine as promoter of this reaction. The hollow spheres with average diameter of 206, 277, and 366 nm were prepared using PS particles with the diameter of 150, 200, and 340 nm, respectively. The activity of hollow spheres with average diameter of 206, 277, and 366 nm for hydrolytic dehydrogenation of NH3BH3 were compared. From the results, the activity increase with decrease of the diameter of the hollow spheres. From the result of neutralization titration, the activity increase with increase of amount of acid sites. From the result of 27Al MAS NMR spectra, amount of Bronsted acid sites increase with decrease of diameter of the hollow spheres.

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