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Control of Particle Size of Hollow Silica-alumina Composite Spheres and Their Activity for Hydrolytic Dehydrogenation of Ammonia Borane

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The influence of particle size of hollow silica-alumina composite spheres on their activity for hydrolytic dehydrogenation of ammonia borane (NH_3BH_3) was investigated. A silica-alumina composite shell was coated onto polystyrene (PS) template particles, before the removal of PS template particle by calcination. The diameter of the PS template particles decreased with an increase in the amount of poly (vinyl pyrrolidone) and the centrifugation speed, and the diameter of the obtained PS template particles was controlled between 150 and 400 nm. Hollow silica-alumina composite spheres with diameters of 180, 230, and 430 nm were prepared using these PS template particles; the shell thickness was controlled 15 nm by adjusting the amount of PS suspension and coating time. The hydrolytic dehydrogenation of NH_3BH_3 evolved 9.5, 9.0, and 7.0 mL hydrogen in the presence of hollow spheres with diameters of 180, 230, and 430 nm, respectively; the molar ratios of the generated hydrogen to the initial NH_3BH_3 in the presence of the hollow spheres were 2.5, 2.3, and 1.8, respectively. The results indicate that the activity increases with a decrease in the diameter of hollow spheres.

本研究では、球状中空シリカ-アルミナの粒径制御を行い、得られた試料がアンモニアボラン加水分解活性におよぼす影響について検討した。球状中空シリカ-アルミナは、犠牲層であるポリスチレン(PS)粒子上にゾル-ゲル法によってコートされた後、焼成によってPS粒子を除去することで調製した。ポリビニルピロリドン量および遠心分離の回転数を調整することによって、PS粒子の粒径は150-400 nmの範囲で制御できた。これらの粒径のPS粒子を用いて調製した球状中空シリカ-アルミナの壁厚は15 nmであることが確認できた。これらの得られた試料を用いて、アンモニアボラン加水分解活性を評価した。それぞれの水素発生量は、9.5, 9.0 および 7.0 mLであり、水素発生量より算出した水素/アンモニアボランモル比(理論値:3.0)は、2.5, 2.3 および 1.8であった。この結果から、球状中空シリカ-アルミナの粒径の減少に伴い、アンモニアボラン加水分解活性は増大することが確認できた。また、アンモニア昇温脱離の結果から、活性は試料の酸点量に依存することが示唆された。

Key Words

Hollow silica-alumina composite spheres, Particle size control, Ammonia borane,
Hydrolytic dehydrogenation

1. Introduction

One of the most critical issues in the development of clean, hydrogen-based energy sources is the storage and release of hydrogen under ambient conditions^{1)~5)}. Ammonia borane (NH_3BH_3) has attracted increased attention in the recent years as an efficient hydrogen storage material

because of its high hydrogen content (19.6 wt.%) and low molecular weight ($30.9 \text{ g}\cdot\text{mol}^{-1}$)^{4)~18)} and high solubility/stability in water. Conversely, in the presence of suitable catalyst, NH_3BH_3 releases hydrogen gas via the hydrolysis reaction shown below (Eq. 1)^{12) 13) 17) 18)}.

A number of effective catalysts for the hydrolysis of NH_3BH_3 have been reported^{6)~14) 16)~22)}; the continued development of efficient and inexpensive catalysts to improve the hydrolysis of NH_3BH_3 under moderate conditions is important for potential future applications

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in hydrogen economy. It has been reported that solid acids such as zeolites (H-BEA and H-MOR) are active for hydrolysis of NH_3BH_3 ⁷⁾. However, there are few reports about solid acids, and the relationship between the activity and the structural properties such as material size and pore size has not been fully elucidated. To systematically investigate the effect of particle morphology on activity, we have focused on hollow spheres because of their intrinsic features such as easily controllable structures and pore size. In recent years, micro-sized, monodisperse, hollow silica^{23) 24)} and titania²⁵⁾ spheres have been fabricated via a one-step process, in which the formation of the inorganic shells and the dissolution of core particles occur in the same medium. The one-step method entails, the preparation of micro-sized, monodisperse, positively charged polystyrene (PS) particles by dispersion polymerization using the cationic monomer, 2-(methacryloyl)-ethyltrimethylammonium chloride (MTC), as the co-monomer²⁶⁾, or by emulsifier-free emulsion polymerization using α, α' -azodiisobutyramidine dihydrochloride (AIBA) as the initiator and poly(vinyl pyrrolidone) (PVP) as the stabilizer^{27) 28)}. Such PS template particles without a positively charged co-monomer could conceivably be dissolved in the same medium. However, the PS template particles are generally incompletely dissolved in the same medium. In a previous study, our group reported the fabrication of hollow metal oxide - nickel composite spheres prepared by the PS template method, and their catalytic activity for the hydrolytic dehydrogenation of NH_3BH_3 ^{29) 30)}. In this study, we investigate the influence of the particle size of hollow silica-alumina composite spheres on their activity for hydrolytic dehydrogenation of NH_3BH_3 .

2. Experiment

2.1 Composite spheres preparation

The hollow silica-alumina composite spheres were fabricated by the PS template method as described previously²⁴⁾. The monodisperse PS particles were prepared by emulsifier-free emulsion polymerization as follows: 9.0 mL of styrene (Kanto Chem. Co.), 0.5–4.5 g of PVP (K30 grade $M_w \approx 40000$, Fluka), 0.26 g of cationic initiator AIBA (Kanto Chem. Co.), and 100 mL of deionized water were charged into a 250-mL three-neck flask equipped with a mechanical stirrer, a thermometer with a temperature controller, a N_2 inlet, a Graham condenser, and a heating oil bath. 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 washed three times with ethanol, and

the content of the PS suspension could be tailored through the addition of ethanol. 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 5–15 g of the PS suspension, before 155.1 μL of tetraethoxysilane (TEOS, Kanto Chem. Co., >99.9%) was added. The sol-gel reaction was carried out at 323 K for 1.5–90 h, and the as-prepared samples could be obtained. After drying in a desiccator overnight, the hollow silica-alumina composite spheres were obtained by calcination in air at 873 K for 0 h at a heating rate of 0.5 $\text{K}\cdot\text{min}^{-1}$. The white powders obtained in this fashion were used without further treatment.

2.2 Characterization

The morphologies of the hollow silica-alumina composite spheres were observed using a Hitachi S-4500 scanning electron microscope (SEM) operating at an acceleration voltage of 15 kV, and a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. Specific surface areas of the obtained samples were measured by N_2 adsorption at 77 K with an ASAP 2010 Automatic Physical Adsorption Instrument. Temperature-programmed desorption of ammonia (NH_3 -TPD) were carried out on a BELCAT-B instrument. The analysis was performed by loading 50 mg of the sample into a quartz reactor and drying it in a pure He flow at 783 K for 1 h followed by purging with pure He at the same temperature for 1 h. After the sample had cooled to 373 K under the He flow, the NH_3 adsorption was carried out by exposing the sample to an NH_3 -He gas mixture (95 vol.% He), which was maintained at 373 K for 1 h. The sample was then purged using pure He, allowing the accurate detection of the desorbed NH_3 . The NH_3 -TPD measurements were conducted using a pure He flow by heating the sample from 373 K to 873 K at a rate of 10 $\text{K}\cdot\text{min}^{-1}$, the desorbed NH_3 molecules were detected by a thermal conductivity detector (TCD). The amount of acid sites within the recycled hollow spheres after reaction was measured by neutralization titration with *n*-butyl amine (Kanto Chem. Co.). 0.2 g of the recycled hollow spheres was dispersed in 20 mL of deionized water under sonication. The suspension was titrated with a 0.1 M *n*-butylamine using methyl red (Kanto Chem. Co.) as an indicator.

2.3 Experimental procedure for the hydrolysis of NH_3BH_3

The 0.8 g of hollow silica-alumina composite 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 NH_3BH_3 solution (0.14 wt.%, 3.5 mL, Aldrich, 90%) was added from the addition funnel, the evolution of gas was monitored using the gas burette.

3. Result and discussion

Fig. 1 shows the SEM images of the PS template particles. From these SEM images, the diameters of the PS template particles were determined as 150, 200, and 400 nm, respectively, according to the varied reaction conditions listed in the figure caption. The results indicate that the diameter of the PS template particles decreases as the amount of PVP and the centrifugation speed increase. Then, hollow silica-alumina composite spheres with various diameters were prepared using PS template particles with diameter of 150, 200, and 400 nm, respectively.

Fig. 2 shows the SEM images of hollow silica-alumina composite spheres prepared using PS template with a diameter of 150 nm at various coating times. From the SEM images in Fig. 2 (a), it is evident that the hollow spheres with a coating time of 1.5 h formed agglomerations because the hydrolysis and condensation of TEOS was incomplete under these conditions; the result suggests that the coating time was probably too short to allow the formation of homogeneous hollow spheres. The SEM images in Fig. 2 (b) demonstrate that homogeneous hollow spheres were obtained with a coating time of 19.0 h. While silica and/or alumina agglomerations were observed for the hollow spheres with a coating time of 48.0 h, parts of the hollow spheres were observed to collapse with a coating time

of 90.0 h, as shown in Figs 2 (c) and (d), respectively. The SEM results indicate that the hydrolysis and condensation of TEOS promoted by NH_3 , and the decomposition of silica and/or alumina particles caused by pH effects occur competitively, and that silica and/or alumina are removed from the shell of the hollow spheres via the decomposition for longer coating time. Fig. 3 shows TEM morphology images of hollow silica-alumina composite spheres with diameters of 180, 230, and 430 nm, respectively. From the TEM images, it can be seen that homogeneous hollow spheres are prepared. Additionally, the hollow spheres with a shell thickness of 15 nm could be reliably prepared by adjusting the amount of PS suspension and coating time during the preparation.

Fig. 2 SEM images of hollow silica-alumina composite sphere with diameter of 180 nm prepared for (a):1.5, (b):19, (c):48, and (d):90 h. Amount of PS suspension: 15 g

Fig. 1 SEM images of PS template particles with diameters of (a):150, (b):200, and (c):400 nm. Centrifugation speed: (a):8000, (b): 6000, and (c):3500 rpm. Amount of PVP used: (a):4.5, (b):1.5, and (c):0.5 g

Fig. 3 TEM images of hollow silica-alumina composite spheres with diameter of (a):180, (b):230, and (c):430 nm. Amount of PS suspension: (a):15, (b):7.5, and (c):5 g. Coating time: (a):19, (b):15, and (c):6 h

Fig. 4 The $\text{H}_2/\text{NH}_3\text{BH}_3$ molar ratio of hydrogen generated from aqueous NH_3BH_3 solution (0.14 wt%, 3.5 mL) versus reaction time catalyzed by hollow silica-alumina composite spheres with diameter of (a):180, (b):230, and (c):430 nm

Fig. 4 shows the molar ratio of the hydrolytically generated hydrogen to the initial NH_3BH_3 in the presence of hollow silica-alumina composite spheres with diameters of 180, 230, and 430 nm versus reaction time. From the hydrolytic dehydrogenation reaction, 9.5, 9.0, and 7.0 mL of hydrogen was released in the presence of hollow silica-alumina composite spheres with 180, 230, and 430 nm, respectively. The molar ratio of the hydrolytically generated hydrogen to the initial NH_3BH_3 in the presence of hollow silica-alumina composite spheres with diameters of 180, 230, and 430 nm is 2.5, 2.3, and 1.8, respectively. The result indicates that the dehydrogenation activity in the presence of the hollow spheres with a smaller diameter is higher than those with larger diameter. The specific surface area of hollow spheres with diameters of 180, 230, and 430 nm were determined as 220, 188, and 152 $\text{m}^2\cdot\text{g}^{-1}$, respectively, indicating that the specific surface area of the hollow spheres increases as the diameter of the hollow spheres decreases. Conversely, the average pore size of the hollow spheres calculated from the results of N_2 adsorption-desorption measurements was about 4–5 nm. The results of the specific surface area and average pore size suggest that the specific surface area increases with a decrease in the size of the primary particles in the hollow spheres.

Fig. 5 shows the molar ratio of the hydrolytically generated hydrogen to the initial NH_3BH_3 in the presence of hollow silica-alumina composite spheres with diameters of 180, 230, and 430 nm versus specific surface area; the results of this study demonstrate that the higher specific surface area of the hollow spheres, the higher the activity.

Fig. 6 shows the NH_3 -TPD profiles of hollow silica-alumina composite spheres with diameters of 180, 230, and 430 nm, respectively. The TCD signal in this figure shows the amount of desorption of adsorbed NH_3 on the surface

Fig. 5 The $\text{H}_2/\text{NH}_3\text{BH}_3$ molar ratio of hydrogen generated from aqueous NH_3BH_3 solution (0.14 wt%, 3.5 mL) versus specific surface area of hollow silica-alumina composite spheres with diameters of (a):180, (b):230, and (c):430 nm Amount of sample: 0.8 g

Fig. 6 NH_3 -TPD profile of hollow silica-alumina composite spheres with diameters of (a):180, (b):230, and (c):430 nm

Fig. 7 The $\text{H}_2/\text{NH}_3\text{BH}_3$ molar ratio of hydrogen generated from aqueous NH_3BH_3 solution (0.14 wt%, 3.5 mL) versus the number of acid sites in hollow silica-alumina composite spheres with a diameter of (a):180, (b):230, and (c):430 nm

of the hollow spheres. In the NH_3 desorption profiles of all the hollow spheres, one peak was observed at about 423 K, reflecting the presence of surface acid sites. The amount of acid sites calculated in the peak area in the temperature range of 373–523 K of the hollow spheres with diameter of 180, 230, and 430 nm were 0.15, 0.13, and 0.09 $\text{mmol}\cdot\text{g}^{-1}$, respectively.

Fig. 7 shows the molar ratios of the hydrolytically generated hydrogen to the initial NH_3BH_3 in the presence of hollow silica-alumina composite spheres with diameters

of 180, 230, and 430 nm versus the amount of acid sites. The results of these experiments reveal that the activity increases with an increase in the number of acid sites within the hollow spheres.

Furthermore, 0 mL hydrogen was released in the presence of recycled hollow spheres; the amount of acid sites present in the recycled hollow spheres was measured by the neutralization titrations. From the results, the amount of acid sites of the recycled all hollow spheres was 0 mmol·g⁻¹, i.e. all acid sites were consumed for the recycled hollow spheres.

4. Conclusion

In this study, we investigated the influence of the particle size of hollow silica-alumina composite spheres on their activity for the hydrolytic dehydrogenation of ammonia borane. A silica-alumina composite shell was coated onto PS template particles, and the PS template particles were completely removed by calcination. The diameter of the obtained PS template particles were 150, 200, and 400 nm, respectively. The results indicate that the diameter of the PS template particles decreases with an increase in the amount of PVP and the centrifugation speed. Hollow silica-alumina composite spheres with diameters of 180, 230, and 430 nm were obtained by using these PS template particles; the hollow spheres were prepared with a shell thickness of 15 nm by adjusting the amount of PS suspension and the coating time during the preparation. The evolution of 9.5, 9.0, and 7.0 mL hydrogen via hydrolytic dehydrogenation of NH₃BH₃ were released in the presence of the hollow spheres with diameters of 180, 230, and 430, respectively; the molar ratio of the generated hydrogen to the initial NH₃BH₃ in the presence of these hollow spheres was 2.5, 2.3, and 1.8, respectively. The specific surface area of the hollow spheres with diameters of 180, 230, and 430 nm were 220, 188, and 152 m²·g⁻¹, respectively, and the amount of acid sites in the hollow spheres with 180, 230, and 430 nm were 0.15, 0.13, and 0.09 mmol·g⁻¹, respectively. The results indicate that the activity increases with increases in the specific surface area and number of acid sites within the hollow spheres.

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