



# Preparation of hollow mesoporous silica spheres with immobilized silicomolybdic acid and their catalytic activity for the hydrolytic dehydrogenation of ammonia borane



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## ABSTRACT

In this paper, we report our investigation into the immobilization of silicomolybdic acid on hollow mesoporous silica spheres and the activity of the modified spheres for hydrolytic dehydrogenation of ammonia borane. Silica shells were coated onto polystyrene (PS) template particles by the sol–gel method, followed by calcination. In this process, a surfactant, cetyltrimethylammonium bromide (CTAB), was added to obtain the mesoporous silica shell. The hollow mesoporous spheres have much greater specific surface area and pore volume than the hollow spheres prepared without CTAB. In addition, the pore sizes of the hollow mesoporous spheres were narrowly distributed and the average was centered at around a diameter of 2–3 nm. The pH was controlled during the immobilization process using amino acids (L-aspartic acid or L(+)-arginine), and samples were prepared at pH values of 3.0, 7.0, and 9.0. The morphology of silicomolybdic acid immobilized on the hollow mesoporous spheres did not change with changing the pH of the reaction mixtures, but changed the amount of immobilized silicomolybdic acid on the surface of the spheres. Fourier transform infrared spectroscopy (FTIR) spectra of the prepared spheres showed bands originating from silicomolybdic acid. These bands were identified in the samples prepared in solution with pH values = 3.0 and 7.0, however, at pH 9, these characteristic bands were not observed. We found that hydrogen evolution was dependent on the pH of the solution used during their preparation. Indeed, when solutions of  $\text{NH}_3\text{BH}_3$  containing the mesoporous samples prepared at pH 3.0, 7.0, and 9.0 were used, volumes of 12.0, 10.0, and 5.0 mL of hydrogen gas were evolved, and were completed after approximately 8, 2, and 2 min, respectively. Also, the molar ratios of evolved hydrogen to the initial  $\text{NH}_3\text{BH}_3$  were 2.6, 2.1, and 1.3, respectively. The Mo 3d region of the XPS spectra of the samples was measured after the reaction and these showed that the peak intensities of sample prepared in lower pH had lower intensity than those prepared at higher pH. This indicates that silicomolybdic acid was also immobilized on the inner surface of the hollow mesoporous spheres prepared at lower pH and was highly dispersed. XPS measurements indicate that the valence of the Mo species did not change significantly in the sample prepared at low pH compared to those prepared at higher pH.

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## 1. Introduction

There have been intensive efforts for developing safe and efficient methods for hydrogen storage: this is a key issue for the concept of the hydrogen economy [1–3]. Ammonia borane ( $\text{NH}_3\text{BH}_3$ ) has a low molecular weight (30.9 g mol<sup>-1</sup>) and high hydrogen content (19.6 wt%) [4]; therefore it is an attractive

candidate for chemical hydrogen storage application [4–18].  $\text{NH}_3\text{BH}_3$  is nontoxic, stable, and environmentally benign, and can be handled at room temperature [3]. Hydrolysis of  $\text{NH}_3\text{BH}_3$  occurs at an appreciable rate in the presence of a suitable acid or catalyst at ambient temperature [9–18]. For example, solid acids such as aluminosilicate zeolites have been reported [9,10]. However, there has been limited investigation of the performance of solid acids on hydrogen evolution via the hydrolysis of  $\text{NH}_3\text{BH}_3$ , and there is little information about the factors that affect performance; such as the structure of the solid acids and their elemental compositions, etc.

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We have focused on nano-structured materials to investigate the effect of the structure of the solid acid and its catalytic effect for hydrolysis of  $\text{NH}_3\text{BH}_3$  [10,13–16]. Of various nano-structured materials, we have mainly focused on hollow spheres to investigate the relationship between catalyst structure and activity, especially, for the hydrolytic dehydrogenation of  $\text{NH}_3\text{BH}_3$  [10,15,16]. In recent years, the preparation and study of core–shell solid and hollow microspheres with well-defined structures have attracted substantial interest because of their potential applications in controlled drug delivery system, lightweight fillers, catalysis, chromatography, vessels for confined reactions, and photonic band gap materials [19–25]. A number of efforts to find new methods have been devoted to generating colloids with the core–shell structure such as template-assisted sol–gel process [10,15,16,26,27], layer by layer (LBL) techniques [28–30], micro-emulsion/interfacial polymerization strategies [31–34].

Silicomolybdc acid is a heteropoly acid and a solid acid [35]. Because it is soluble in water, immobilization of the compound is required for its effective use, recovery and reuse. We have investigated the immobilization of silicomolybdc acid using hollow spheres as a support. We have reported that the amount of silicomolybdc acid immobilized on hollow spheres of silica and their activity for hydrolysis of ammonia borane depend on the pH of the reaction mixture during the immobilization process. Silicomolybdc acid immobilized at low pH shows higher activity with subsequent hydrogen evolution [36]. However, stoichiometric amount of the hydrogen evolution did not occur in the presence of hollow spheres with immobilized silicomolybdc acid. This is probably due to pore structure of the hollow spheres of silica, which was not controlled during their synthesis, and the low concentration of silicomolybdc acid on the inner surface of the spheres. In the present study, we fabricated a mesoporous silica support of hollow spheres with a controlled pore structure using cetyltrimethylammonium bromide (CTAB), and we investigated the influence of the reaction pH on immobilization of silicomolybdc acid on the hollow mesoporous spheres and their subsequent activity for hydrolytic dehydrogenation of  $\text{NH}_3\text{BH}_3$ .

## 2. Experimental

### 2.1. Preparation of hollow silica spheres

Hollow spheres of mesoporous silica were prepared using polystyrene bead templates as follows [37]. Monodisperse PS particles were prepared by emulsifier-free emulsion polymerization as follows: styrene (54.0 mL, Kanto Chem. Co.), poly(vinyl pyrrolidone) (PVP) K30 (9.0 g,  $M_w \approx 40000$ , Fluka), cationic initiator 2,2'-azobis-(isobutyramidine) dihydrochloride (1.56 g, AIBA, Kanto Chem. Co.), and distilled water (600.0 g) were charged into a 1-L three-neck flask equipped with a mechanical stirrer, a thermometer with a temperature controller, a  $\text{N}_2$  inlet, a Graham condenser, and a heating oil bath. The reaction solution was deoxygenated by bubbling nitrogen gas at room temperature for 1 h. Then, at a stirring rate of 150 rpm, the reaction was carried out at 343 K for 24 h.

The PS template suspension was then centrifuged (6000 rpm, 5 min) and washed with ethyl alcohol three times. The content of the PS template suspension could be tailored through the addition of ethyl alcohol. Then, the PS template suspension (50.0 g), aqueous ammonia solution (1.0 mL, 28 wt%, Kanto Chem. Co.), and distilled water (165 mL) were added to ethyl alcohol (50.0 mL). Then tetraethoxysilane (0.1 mL, Kanto Chem. Co., >99.9%) was added to the mixed solution. The sol–gel reaction was carried out at room temperature for 16 h. The hollow silica spheres were obtained directly from this reaction mixture. The spheres were dried

overnight in a desiccator, the resulting fine powder was calcined at 873 K at heating rate of  $0.5 \text{ K min}^{-1}$ .

The resulting hollow silica spheres (0.06 g) were immersed in an aqueous solution of silicomolybdc acid (20 mL, 0.06 g, Nippon Inorg. Colour Chem. Co. Ltd.), and the slurry was stirred for 1 h. The solution was then heated at 373 K until dryness.

### 2.2. Characterization

The specific surface area and porosity of the hollow silica spheres were measured by  $\text{N}_2$  adsorption–desorption isotherms at 77 K using a Micromeritics Model ASAP 2010 MC analyzer. The morphologies of the samples were examined using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. FTIR spectra of silicomolybdc acid immobilized on hollow silica spheres were recorded using a Fourier transform infrared spectrophotometer (FTIR-8400S, Shimadzu Co. Ltd.) with a resolution of  $4 \text{ cm}^{-1}$ . The valence state of the surface Mo species was determined by X-ray photoelectron spectroscopy using a Kratos ESCA-3400.

### 2.3. Experimental procedures for hydrolysis of ammonia borane

Each catalyst (0.12 g) was placed in a two-necked round-bottom flask. One neck was connected to a gas burette and the other was fitted with a septum inlet to allow the introduction of aqueous ammonia borane (1.5 mL,  $\text{NH}_3\text{BH}_3$ , 0.0055 g, Aldrich, 90%) solution. The evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature.

## 3. Results and discussion

For the samples prepared with and without CTAB, the specific surface area was determined by BET, and the average pore size and pore volumes were determined by the BJH method (Table 1). The pore size distribution, average pore diameter and pore volume were calculated by using the adsorption branch of the isotherm. The specific surface area and pore volume of the hollow spheres support prepared with CTAB were larger than those of the hollow spheres support prepared without CTAB. The average pore size of the hollow spheres supports prepared with CTAB was lower than that of the hollow spheres prepared without CTAB. Fig. 1 shows the  $\text{N}_2$  adsorption–desorption isotherms and pore size distributions of the hollow spheres prepared with and without CTAB. In all pressure region, the amount of  $\text{N}_2$  sorption by the hollow spheres prepared with CTAB was much greater than that of the hollow spheres prepared without CTAB. The isotherm of the hollow mesoporous spheres is a type IV isotherm, which is typical for mesoporous silica with CTAB as a surfactant. The corresponding hysteresis loop is type H4, which suggests the presence of narrow mesopores in the hollow spheres. This result is reflected in the pore size distribution of the hollow spheres (Fig. 1(b)), which shows a sharp peak centered at around 2.5 nm.

Morphologies of silicomolybdc acid immobilized on hollow mesoporous silica spheres prepared in various pH solutions were examined using TEM. Fig. 2 shows the TEM images of silicomolybdc acid immobilized on the hollow mesoporous spheres at various pH values. From the figure, the spheres have similar particle sizes (200–300 nm) and wall thickness (ca. 6 nm). Considering that the template particle size is approximately 200 nm, the images indicate that PS particles acted as templates and directed the morphology of the samples.

In order to quantify the amount of immobilized silicomolybdc acid on the hollow mesoporous silica spheres prepared at various pH values, the samples were characterized by FTIR spectroscopy, as

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