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Influence of preparation conditions on the morphology of hollow silica–alumina composite spheres and their activity for hydrolytic dehydrogenation of ammonia borane

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ABSTRACT

We investigated the influence that preparation conditions have on the morphology of hollow silica–alumina composite spheres and their ability for hydrolytic dehydrogenation of ammonia borane (NH_3BH_3). Silica–alumina composite shells were coated on polystyrene (PS) template particles by the sol–gel method using L(+)-arginine as a promoter for the reaction, followed by calcination. The hollow silica–alumina composite spheres were characterized by transmission electron microscopy, N_2 adsorption/desorption isotherm analysis, and X-ray diffraction. Compared with the hollow spheres prepared with ammonia, hollow spheres prepared using L(+)-arginine showed higher surface area and narrower pore size distribution. The hollow spheres prepared using L(+)-arginine showed a higher rate of hydrogen evolution from aqueous NH_3BH_3 solution. To control the wall thickness of the hollow spheres prepared using L(+)-arginine, we adjusted the amount of PS suspension used during coating process. The time required to obtain homogeneously coated hollow spheres depends on the amount of PS suspension. Hollow spheres with the wall thickness of 20, 30, and 50 nm were obtained using 30.0, 15.0, and 7.5 g of PS suspension, respectively. The hydrogen evolution activity in the presence of the hollow spheres prepared using L(+)-arginine with the wall thickness of 20, 30, and 50 nm was higher than those of the hollow spheres prepared using ammonia.

1. Introduction

Developing safe and efficient methods for hydrogen storage is a key issue for the hydrogen economy [1,2]. Ammonia borane (NH_3BH_3) possesses a low molecular weight (30.9 g mol^{-1}) and high hydrogen content (19.6 wt.%) [3], making it an attractive candidate for chemical hydrogen storage [3–23]. NH_3BH_3 is nontoxic, stable, and environmentally benign; it can be handled at room temperature and releases hydrogen under mild catalytic hydrolysis. Hydrolysis occurs at an appreciable rate in the presence of a suitable acid or catalyst at ambient temperature [7–22], but for practical applications, the development of efficient, low-cost, and stable acids or catalysts to further improve kinetic properties under moderate conditions is very important. Solid acids such as aluminosilicate zeolites have been reported [7,8]; however, their performance for NH_3BH_3 hydrolysis has not been quantified and there is little information about the importance of solid acid structure and elemental compositions on the performance.

We have focused our attention on nano-structured materials to reveal the relation between the structure of solid acids or catalysts and the catalytic activity toward NH_3BH_3 hydrolysis [8,11,12–16]. In various nano structured materials, we have used on hollow spheres to reveal the relationship between the catalyst structure and catalytic activity, especially, for hydrolytic dehydrogenation of NH_3BH_3 [8,15,16]. In recent years, the preparation and study of core–shell solid and hollow microspheres with well-defined structures has attracted substantial interest because of potential applications in controlled drug delivery system, lightweight fillers, catalysis, chromatography, vessels for confined reactions, and photonic band gap materials [24–29]. Attempts at finding new methods have been devoted to generating colloids with core–shell structures, such as template-assisted sol–gel processes [8,15,16,30–35], layer by layer (LBL) techniques [36–38], and microemulsion/interfacial polymerization strategies [39–43].

We have fabricated hollow silica–alumina composite spheres by a sol–gel method using ammonia as a conventional promoter

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of the sol–gel reaction [8]. In the present study, we investigated methods for controlling the wall thickness of hollow silica–alumina composite spheres using L(+)-arginine as the promoter, and then studied their activity for hydrolytic dehydrogenation of NH_3BH_3.

2. Experimental

2.1. Catalyst preparation

Hollow silica–alumina composite spheres were prepared by a polystyrene bead template method [35]. Monodisperse PS particles were prepared by emulsifier-free emulsion polymerization as follows: 10.0 g of styrene (Kanto Chem. Co.), 1.5 g of poly(vinyl pyrrolidone) (PVP) K30 ($M_w \approx 40{,}000$, Fluka), 0.26 g of cationic initiator 2,2′-azobis-(isobutyramidine) dihydrochloride (AIBA, Kanto Chem. Co.), and 100.0 g of distilled water were charged into a 250-mL three-neck flask equipped with a mechanical stirrer, thermometer with a temperature controller, N_2 inlet, Graham condenser, and heating oil bath. The reaction solution was deoxygenated by bubbling nitrogen gas at room temperature for 60 min. Then, while stirring at 150 rpm, the reaction was carried out at 343 K for 24 h. The resulting PS suspension was centrifuged (6000 rpm, 5 min) and washed with ethyl alcohol 3 times; the content of the PS suspension could be tailored by adding ethanol. The PS template suspension (7.5–30.0 g depending on the desired layer thickness) and 6.75 mL of aqueous L(+)-arginine (0.2325 g, Kanto Chem. Co.) solution were added to 40 mL of ethyl alcohol. Next, 20 mL of aluminium(IV) iso-propoxide (0.0057 g, Aldrich)/ethyl alcohol solution was added, followed by addition of 0.1551 mL of tetraethoxysilane (Kanto Chem. Co., >99.9%). The sol–gel reaction was carried out at 323 K for 8–24 h, after which hollow silica–alumina composite spheres could be obtained. After drying in a desiccator overnight, the fine powder was calcined at 873 K for 0 h at a rate of 0.5 K min^{-1}.

2.2. Characterization

Catalysts morphology was observed using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. The specific surface area and porosity of the hollow silica–alumina spheres were measured by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics Model ASAP 2010MC analyzer. The crystalline phase and the average crystallite size were determined by X-ray powder diffraction using a Rigaku MultiFlex X-ray diffractometer.

2.3. Experimental procedure for hydrolysis of ammonia borane

Each catalyst (0.8 g) was added to a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was fitted with a septum inlet to introduce 3.5 mL of aqueous ammonia borane (NH_3BH_3, 0.0055 g, Aldrich, 90%) solution. The reaction was carried out at room temperature in air, and the evolution of gas was monitored using the gas burette.

3. Results and discussion

The morphology of the hollow silica–alumina composite spheres was examined using TEM. In the present study, the wall thickness of the hollow composite spheres was controlled by adjusting the amount of PS templates without changing the amount of Si and Al. The number of PS template particles increased with the amount of PS templates, and the amount of Si and Al coated on each template particle increased with the decrease of the number of the template particles. Fig. 1 shows TEM images of the hollow spheres using 7.5, 15.0, and 30.0 g of PS template suspension. The TEM image of the hollow spheres prepared using ammonia is also shown. In order to obtain homogeneous hollow spheres, the coating time was adjusted depending on the amount of PS template suspension. All the samples consist of spherical

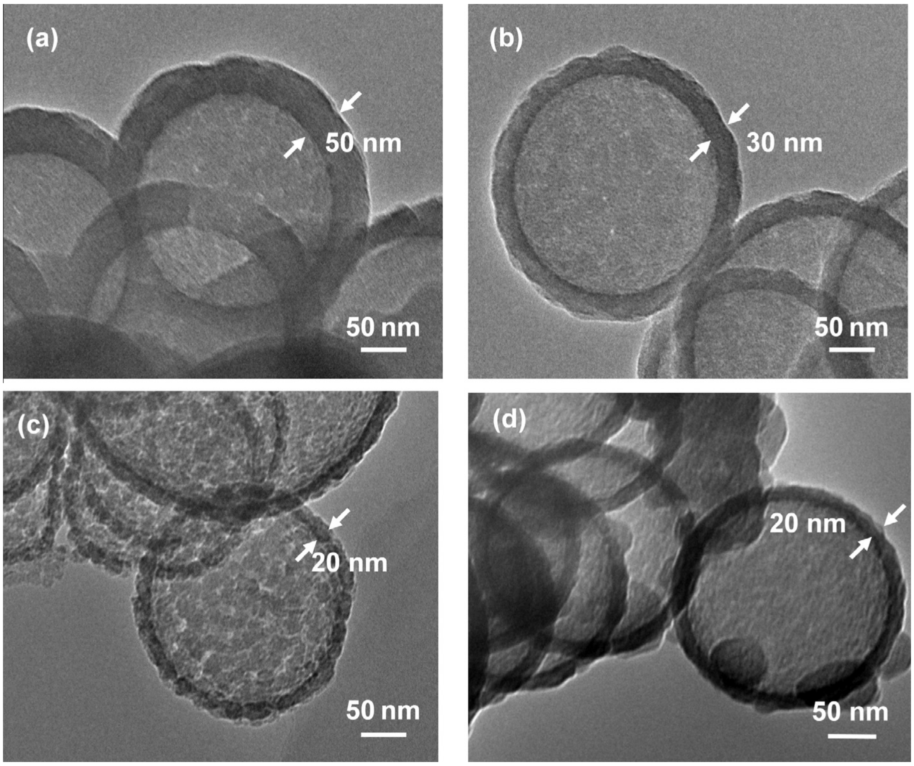

Fig. 1. TEM images of hollow silica–alumina composite spheres prepared using L(+)-arginine with the amount of PS template suspension = (a) 7.5, (b) 15.0, (c) 30.0 g, and (d) prepared using ammonia. The samples were prepared for stirring time = (a) 24, (b) 17, (c) 8, and (d) 24 h.