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Fabrication of hollow nickel-silica composite spheres using L(+)-arginine and their catalytic performance for hydrolytic dehydrogenation of ammonia borane

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ABSTRACT

In this paper, we report a facile and effective approach for fabrication of hollow nickel-silica composite spheres. In this approach, when nickel-silica composite shells were coated on polystyrene templates by the sol–gel method using L(+)-arginine as the promoter for the reaction to form nickel-silica composite shell, the polystyrene templates were dissolved subsequently, even synchronously, in the same medium to form hollow spheres. Neither additional dissolution nor a calcination process was needed to remove the polystyrene templates. The as-prepared nickel-silica composite spheres were characterized by transmission electron microscopy and N_2 adsorption/desorption isotherm analysis. The effects of the amount of L(+)-arginine, the existence of hollow structure, and the kinds of promoter for sol–gel reaction on the morphology, porosity and mean pore size, and specific surface areas were systematically evaluated. The catalytic activity of the hollow nickel-silica composite spheres for hydrolytic dehydrogenation of ammonia borane was compared to that of the hollow nickel-silica composite spheres prepared with aqueous ammonia solution and nickel-silica composite spheres without hollow structure. The catalytic activity for the hydrogen evolution over the hollow spheres was higher than those of the hollow spheres prepared with aqueous ammonia solution and the nickel-silica composite spheres without hollow structure. Moreover, the results of diffuse reflectance UV–vis spectra indicate that the amount of hydrogen evolution was correlated with the reduction degree of nickel species after hydrolytic dehydrogenation of ammonia borane.

1. Introduction

There have been intensive efforts for developing safe and efficient methods for hydrogen storage, a key issue of the hydrogen economy [1–4]. Ammonia borane (NH_3BH_3) possesses a low molecular weight (30.9 g mol^{-1}) and high hydrogen content (19.6 wt%) [5,6], and therefore makes it an attractive candidate for chemical hydrogen storage application [5–30]. NH_3BH_3 is nontoxic, stable, and environmentally benign, can be handled at room temperature and can release hydrogen gas upon catalytic hydrolysis under mild conditions [5]. The hydrolysis occurs at appreciable rate in the presence of a suitable acid or a suitable catalyst at ambient temperature [10–22]. From the viewpoint of practical application, the development of efficient, low-cost, and stable catalysts to further improve the kinetic properties under moderate conditions is therefore very important. Nowadays, there is a general interest in searching for more abundant first-row transition-metal-based catalysts, such as Fe, Co, Ni, and so on, to catalyze the hydrolysis of NH_3BH_3 with high efficiency [10,12,15–21]. Studies of catalysts for hydrogen generation from aqueous ammonia borane solution show that dispersion of active metals and/or amorphousness of active phase play important roles in the catalytic performances [12,15–21].

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 material [31–36]. 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 [37–42], layer by layer (LBL) techniques [43–47], microemulsion/interfacial polymerization strategies [48–52]. Microsized, monodisperse, hollow silica [40] and titania [53] spheres were fabricated via a one-step process, which means that the formation of the inorganic shells and the dissolution of core particles occur in the same medium. In that method, microsized, monodisperse, positively charged polystyrene (PS) particles were prepared by dispersion polymerization using the cationic monomer 2-(methacryloyl)-ethyltrimethylammonium chloride (MTC) as the comonomer [54] or by emulsifier-free emulsion polymerization

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using α,α′-azodiisobutyramidine dihydrochloride (AIBA) as the initiator and poly(vinyl pyrrolidone) (PVP) as the stabilizer [40,55,56]. These small PS template particles without a positively charged comonomer could also be dissolved in the same medium subsequently, even simultaneously, during the coating of silica shells to directly form hollow spheres. Neither additional dissolution nor a calcination process was used to remove the PS cores to form hollow spheres.

In the present study, we fabricated hollow nickel-silica composite spheres using PS template method and investigated their activity for hydrolytic dehydrogenation of ammonia borane. In addition, we firstly fabricated the hollow spheres using L(+)-arginine, a kind of basic amino acid, as the promoter for hydrolysis of tetraethoxysilane (TEOS) [57] and for dissolution of PS templates.

2. Experimental

2.1. Catalyst preparation

Hollow nickel-silica composite spheres were prepared by polystyrene beads template method as follows [53]. The 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, 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 at room temperature for 60 min. Then, under a stirring rate of 150 rpm, the reaction was carried out at 343 K for 24 h. The obtained PS suspension was centrifuged (6000 rpm, 5 min) and washed in ethyl alcohol for 3 times, and content of the PS suspension could be tailored through the addition of ethanol. Then, aqueous L(+)-arginine (1.78, 5.34, and 10.68×10^{-3} mol L(+)-arginine/9.0, 27.0, and 54.0 mL of deionized water, Acros Organics Co.) and nickel nitrate hexahydrate (0.03 g, 1.0×10^{-4} mol, Kanto Chem. Co.) mixed solution and tetraethoxysilane (TEOS, 215.2 μL, 9.6×10^{-4} mol, Kanto Chem. Co.) and 160.0 mL of ethyl alcohol were added into 20.0 g of the PS suspension, in which the sol–gel reaction was carried out at 323 K for 0.5–17.0 h, and the hollow nickel-silica composite spheres could be directly obtained.

2.2. Characterization

The morphologies of the catalysts were observed using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. Measurement of specific surface area and analysis of porosity for the nickel-silica composite products were performed through measuring N_2 adsorption–desorption isotherms at 77 K with a Micromeritics Model ASAP 2010MC analyzer. 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. The TPR–TGA (temperature-programmed reduction–thermogravimetric analysis) investigations were performed on a Rigaku TG8120 instrument. TPR profiles were recorded by passing a 10 vol% H_2 in Ar (260 mL min^{-1}) through the sample (≈2 mg) heated at a constant rate of 20 K min^{-1} up to 1173 K.

2.3. Experimental procedures for hydrolysis of ammonia borane

A mixture of sodium borohydride ($NaBH_4$, 5 mg, Kanto Chemical Reagent Co., >98.5%) and ammonia borane (NH_3BH_3, 27.5 mg, Aldrich, 90%) with 28.8 mg of catalyst ($NH_3BH_3/NaBH_4/Ni = 1/0.17/0.06$) was kept in a two-necked round-bottom flask. One neck was connected to a gas buret, and the other was fitted with a septum inlet to introduce distilled water (5 mL). The reaction started when distilled water was introduced to the mixture of $NaBH_4$, NH_3BH_3, and the catalyst, and the evolution of gas was monitored using the gas buret. The reactions were carried out at room temperature in air. All the samples after hydrolysis of NH_3BH_3 were centrifugally separated from the reaction solution, and then dried in desiccator under vacuum condition for characterizations.

3. Results and discussion

The monodisperse PS template beads were prepared by emulsifier free emulsion polymerization using the AIBA as the cationic initiator and PVP as the stabilizer. Fig. 1 illustrates the TEM images of various obtained spheres. The diameter of original PS particles was ca. 200–300 nm (Fig. 1a). Fig. 1b–d shows the TEM images of the solid products formed with L(+)-arginine = 1.78×10^{-3} mol after different times of the coating (1.5, 7.5, and 17.0 h) before hydrolysis of NH_3BH_3. After the aging at 323 K for 1.5 h as shown in Fig. 1b, no particles were observed. After 7.5 h, particles of irregular shape were found, as shown in Fig. 1c. After 17 h, the spherical particles of ca. 200–300 nm in diameter (Fig. 1d) were obtained, and the inset of Fig. 1d demonstrates their hollow feature indicated by the arrows. The morphology and diameters of the hollow spheres were almost the same as the solid products prepared without PS (Fig. 1e) and the solid products prepared with aqueous ammonia solution (Fig. 1f).

Fig. 2a–c shows the TEM images of the solid products formed with L(+)-arginine = 5.34×10^{-3} mol after different times (0.5, 1.5, and 3 h) before the hydrolysis of ammonia borane. After 0.5 h, particles of irregular shape were found, as shown in Fig. 2a. After more than 1.5 h, the spherical particles with the diameter of 200–300 nm (Fig. 2b and c) were obtained. The morphology of the particles is not significantly different from the solid products prepared with L(+)-arginine = 10.68×10^{-3} mol before hydrolytic dehydrogenation of NH_3BH_3 (Fig. 2d). These results indicate that L(+)-arginine has promoting effect on the formation of nickel-silica shell, and the formation rate of the shell increases with the increase in the amount of L(+)-arginine.

The specific surface area, average pore size, and pore volume of the as-samples were determined by BET and BJH method (listed in Table 1). The pore size distribution, the average pore diameter and the pore volume were calculated by using the desorption branch of the isotherm. It could be seen that the BET surface area and pore volume of the solid products prepared with L(+)-arginine do not depend on the amount of L(+)-arginine, while the solid products prepared with higher amount of L(+)-arginine (5.34 and 10.68×10^{-3} mol) has larger average pore size than the solid products prepared with lower amount of L(+)-arginine (1.78×10^{-3} mol). The surface area of the solid sample prepared without PS is about four times lower than that of the solid products prepared with PS, while the average pore size and the pore volume of the solid products prepared without PS are almost the same as those of the solid products prepared with PS, suggesting the existence of hollow structure in the solid product prepared with PS. The specific surface area, average pore size, and pore volume of the solid product prepared with aqueous ammonia solution are almost the same as those of the solid products prepared with L(+)-arginine = 1.78×10^{-3} mol.

Fig. 3 shows the time course of hydrogen evolution from aqueous $NaBH_4/NH_3BH_3$ solution in the presence of hollow nickel-silica composite spheres prepared with PS (L(+)-arginine = 1.78, 5.34, and 10.68×10^{-3} mol), nickel-silica composite spheres prepared without PS (L(+)-arginine = 1.78×10^{-3} mol), and hollow nickel-silica