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Fabrication of hollow silica–alumina composite spheres and their activity for hydrolytic dehydrogenation of ammonia borane



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ARTICLE INFO

Article history:

Received 20 May 2014

Received in revised form

28 July 2014

Accepted 10 August 2014

Available online 10 September 2014

Keywords:

Ammonia borane

Hollow silica–alumina composite spheres

Preparation conditions

Hydrolytic dehydrogenation

Acid sites

ABSTRACT

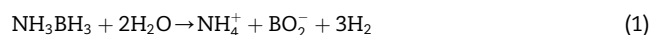
In this study, we investigated the influence of the preparation conditions of hollow silica–alumina composite spheres on their activity for the hydrolytic dehydrogenation of ammonia borane. Hollow silica–alumina composite spheres were prepared by polystyrene template method, and the polystyrene template particles were removed by calcination. The as-prepared hollow spheres were calcined at 523–873 K for 3 h. From the results of elemental analysis, polystyrene templates were completely removed by calcination at 873 K. Small particles around the hollow spheres were observed from the images of transmission electron microscopy. To obtain homogeneous hollow spheres, the as-prepared hollow spheres were calcined at 873 K for 0–12 h. From the results of transmission electron microscopy, homogeneous hollow spheres were obtained by calcination for 0 h. The activity of the hollow spheres was the 2.6 times higher than that of the hollow spheres calcined for 3 h. From the results of activity tests and ammonia temperature-programming desorption, the activity of the hollow spheres depends on amount of acid sites.

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Introduction

Hydrogen has recently attracted much attention as an alternative energy source to satisfy the increasing demand for effective and clean energy because of its abundance, high energy density, and environmental friendliness [1–3]. However, several challenges need to be addressed before transitioning to a hydrogen economy. Therefore, it is necessary to develop new hydrogen storage materials and efficient catalysts for the hydrogen release reaction [4,5]. Among the

various materials that can be used for hydrogen storage, ammonia borane (NH_3BH_3) is an attractive candidate because of its high hydrogen capacity (19.6 wt%), and high stability in the solid state or in solution [3,6–20]. Furthermore, this compound can release highly pure hydrogen in the presence of an appropriate catalysts or acids at room temperature, as shown by Eq. (1) [3,7,14,18,20].



A number of catalysts or acids have been recently utilized for the hydrolysis of NH_3BH_3 [3,6–20]. Among these catalysts

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<http://dx.doi.org/10.1016/j.ijhydene.2014.08.057>

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and acids, it has been reported that solid acids such as H-type zeolites (Beta zeolites and Mordeite) exhibit activity for the hydrolysis of NH_3BH_3 [11]. However, there have been few investigations into solid acids regarding the correlation between their structure and activity. To clarify this correlation, we have focused on hollow spheres.

The most frequently used method to prepare hollow spheres is the template-based route. The template method can be classified into two possible methods [21]: the soft template method [22–24] and the hard template method [25–27]. The hard template method in particular has attracted much interest because it can be used to prepare monodisperse particles and easily control the shell and hollow structures. However, the removal of the core particles by selective dissolution in an appropriate solvent or by calcination at optimal conditions in the air is crucial to obtain hollow spheres.

Microsized, monodisperse, hollow silica [28,29] and titania [30] spheres have been recently fabricated via a one-step process, with the formation of inorganic shells and the dissolution of the core particles occurring within the same medium. Using this method, microsized, monodisperse, positively charged polystyrene (PS) particles were prepared through dispersion polymerization using the cationic monomer 2-(methacryloyl)-ethyltrimethylammonium chloride (MTC) as the co-monomer [31] or through emulsifier-free emulsion polymerization using α,α' -azodiisobutyramidine dihydrochloride (AIBA) as the initiator and poly(vinyl pyrrolidone) (PVP) as the stabilizer [32,33]. These PS template particles, which lacked a positively charged co-monomer could also be dissolved in the same medium subsequently after, or even simultaneously, during the coating of the silica shells to directly form the hollow spheres. In previous study, PS template particle were incompletely dissolved in the same medium although hollow silica-nickel composite spheres were prepared through the PS template method. The amount of PS residues is able to be reduced by increasing aging time and amount of aqueous ammonia solution for the preparation, and the catalytic activity of the hollow spheres increases when the amount of PS residues decreases [12].

In this study, we first investigated the influence of preparation condition of hollow silica–alumina composite spheres using the PS template method and subsequently investigated their activity for the hydrolytic dehydrogenation of NH_3BH_3 .

Experimental

Hollow composite spheres preparation

Hollow silica–alumina spheres were fabricated using the PS template method [31]. Monodisperse PS particles were prepared through emulsifier-free emulsion polymerization as follows: 9.0 mL of styrene (Kanto Chem. Co.), 1.5 g of PVP K30 (Mw \approx 40,000, Fluka), 0.26 g of the cationic initiator AIBA (Kanto Chem. Co.), and 100.0 mL of deionized water were placed in 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 first deoxygenated by bubbling N_2 gas

through the solution at room temperature for 1 h. The reaction was then carried out at 343 K for 24 h at a stirring rate of 250 rpm. The obtained PS suspension was centrifuged at 6000 rpm for 5 min and washed with ethanol 3 times; the contents of the PS suspension could be fine-tuned through the addition of appropriate amount of ethanol. 0.0057 g of aluminum isopropoxide (Kanto Chem. Co., >99.0%), 3 mL of aqueous ammonia solution (Kanto Chem. Co., 28 wt%), and 40 mL of ethanol were added to 15 g of the PS suspension, followed by the addition of 155.1 μL of tetraethoxysilane (Kanto Chem. Co., >99.9%). The sol–gel reaction was then carried out at 323 K for 1.5 h, and the as-prepared hollow spheres were obtained. After drying in a desiccator overnight, hollow silica–alumina spheres were obtained upon calcination under various conditions in air. The obtained white powders were subsequently used in the hydrolysis experiments. After drying in a desiccator overnight, the recycled hollow spheres were obtained. The obtained white powders were also used in the hydrolysis experiments.

Characterization

The morphologies of as-prepared hollow silica–alumina composite spheres and the hollow spheres calcined various conditions were observed by mean of transmission electron microscopy (TEM) using a Hitachi FE2000 microscope operating at an acceleration voltage of 200 kV. Fourier transform infrared (FT-IR) spectra of the as-prepared hollow spheres and the hollow spheres calcined various temperature were recorded using a Perkin–Elmer FT-IR with a resolution of 4 cm^{-1} in the angle attenuated total reflectance (ATR) sampling mode. The hollow spheres powder was placed on the horizon of the internal reflectance crystal where the total internal reflection occurred. A ZnSe crystal with a transmission range of 4000–650 cm^{-1} was used in this experiment. The thermal dissolution temperature of the PS residues within the as-prepared hollow spheres was conducted using thermogravimetric – differential thermal analysis (TG-DTA) using Rigaku Thermo plus TG-8120, operated under air with a heating rate of 24 K min^{-1} from room temperature to 1073 K. The amount of PS residues within the as-prepared hollow spheres and the hollow spheres calcined various conditions was estimated by the elemental analysis of C, H, and N using MICRO CORDER JM10. The amount of acid sites of the hollow spheres was measured by neutralization titration with *n*-butyl amine (Kanto Chem. Co.). About 0.2 g of the hollow spheres was dispersed in 20 mL of ethanol under sonication. The suspension was titrated with a 0.1 M *n*-butylamine using methyl red (Kanto Chem. Co.) as an indicator. The amount of acid sites of the hollow spheres was calculated as follow: The amount of 0.1 M *n*-butylamine was divided by amount of composites. Temperature-programmed desorption of ammonia (NH_3 -TPD) were carried out on BELCAT-B instrument. The analysis was performed by loading 50 mg of the sample into quartz reactor and drying it in a pure He flow at 783 K for 1 h followed by a pure He purge at the same temperature for 1 h. After the sample was cooled to 373 K by a pure He flow, NH_3 adsorption was carried out by exposing the sample to NH_3 –He gas mixture (95 vol.% He) and then keeping it at 373 K for 1 h. The sample was then purged using a pure He purge allowing the

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