Influence of pH on immobilization of molybdosilicic acid on hollow silica spheres and promotion of hydrolytic dehydrogenation of ammonia borane

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In this work, we investigated the influence of the pH condition during the impregnation process on the immobilization of molybdosilicic acid on hollow silica spheres and their activity for hydrolytic dehydrogenation of ammonia borane. To adjust the pH, amino acids such as L-aspartic acid and L(+)-arginine were added to the impregnating solution. Transmission and scanning electron microscopy showed that samples prepared at lower pH consist of homogeneous hollow silica spheres while those prepared at higher pH include collapsed hollow spheres. The activity for hydrogen evolution from aqueous NH_3BH_3 solution depends on the catalyst; the molar ratios of the hydrolytically generated hydrogen to the initial NH_3BH_3 were 2.0, 1.3, 1.3, and 1.0 at pH = 4.0, 6.0, 8.0, and 9.7, respectively. After the reaction, the sample prepared at lower pH had a higher valence value of Mo species according to results from X-ray photoelectron spectroscopy, and the corresponding amount of Mo species in the reaction solution was also lower. The results indicated that the molybdosilicic acid supported on homogeneous hollow silica spheres had a higher valence value of Mo species and the effectively immobilized acid had a higher activity for hydrogen evolution from aqueous NH_3BH_3 solution.

Key words: Molybdosilicic acid, Hollow spheres of silica, Ammonia borane, Hydrolytic dehydrogenation, pH

1. INTRODUCTION

There have been intensive efforts to develop safe and efficient methods for hydrogen storage, which is a key issue of 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], which therefore makes it an attractive candidate for chemical hydrogen storage application [3-20]. NH_3BH_3 is nontoxic, stable, environmentally benign, and can be handled at room temperature [3]. Hydrolysis of NH_3BH_3 occurs at an appreciable rate in the presence of a suitable acid or catalyst at ambient temperature [6-15]. Solid acids such as aluminosilicate zeolites have been reported [6-9], although only a few have been investigated for their performance in hydrogen evolution via hydrolysis of NH_3BH_3 . Moreover, there is limited information on the important factors that determine the performance such as the structure and elemental composition of solid acids.

We have studied nanostructured materials, especially hollow spheres, to reveal the correlation between the structure of the solid acid and its catalytic activity for the hydrolysis of NH_3BH_3 [7-9, 13, 15]. 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 use as lightweight fillers, vessels for confined reactions, and photonic band gap materials and applications in controlled drug delivery systems, catalysis, and chromatography

[21-26]. A number of efforts to find new methods have been devoted to generating colloids with a core-shell structure, such as template-assisted sol-gel process [7-9, 13, 15, 27-30], layer-by-layer (LBL) techniques [31-33], and microemulsion/interfacial polymerization strategies [34-36].

Molybdosilicic acid is a heteropoly acid and was reported as a solid [37]. The compound is soluble in water, and immobilization of the compound is then required for recovery and/or reuse as an effective solid acid. In the present study, we investigated the influence of pH on the immobilization of molybdosilicic acid on hollow silica spheres and the activity of the acid for hydrolytic dehydrogenation of NH_3BH_3 .

2. EXPERIMENTS

Hollow silica spheres were prepared through the polystyrene (PS) beads template method as previously described [29]. The monodisperse PS particles were prepared through emulsifier-free emulsion polymerization as follows: 54.0 mL of styrene (Kanto Chemical Co.), 9.0 g of poly(vinyl pyrrolidone) (PVP K30, $M_w \approx 40000$, Fluka), 1.56 g of the cationic initiator 2,2'-azobis(isobutyramidine) dihydrochloride (Kanto Chemical Co.), and 600.0 g of distilled water were loaded into a 1-L 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. The reaction was then carried out at 343 K for 24 h, at a stirring rate of 150 rpm.

The obtained PS template suspension was centrifuged (6000 rpm, 5 min) and washed in ethyl alcohol three times, and its content could be adjusted through the addition of ethanol. Subsequently, 100.0 g of the PS template suspension and 60 mL of 28 wt% aqueous ammonia solution (Kanto Chemical Co.) were added to 800 mL of ethyl alcohol, after which 103.4 μL of tetraethoxysilane (>99.9%, Kanto Chemical Co.) was added to the mixture. The sol-gel reaction was carried out at 323 K for 1.5 h, and the hollow silica spheres were directly obtained. After drying in a desiccator overnight, the obtained fine powders were calcined at 873 K at a heating rate of 0.5 K min^{-1} .

The obtained hollow silica spheres (0.06 g) were immersed in an aqueous solution of molybdosilicic acid (Nippon Inorganic Colour & Chemical Co., Ltd.), and the slurry solution was stirred for 1 h and subsequently heated at 373 K until dryness.

The morphologies of hollow silica spheres with immobilized molybdosilicic acid were observed using a Hitachi S-450 scanning electron microscope (SEM) operating at an acceleration voltage of 15 kV and Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. The Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded using an FTIR-8400S spectrophotometer (Shimadzu Co. Ltd.) with a resolution of 4 cm^{-1} . The valence state of the surface Mo species was determined by X-ray photoelectron spectroscopy (XPS) using a Kratos ESCA-3400 spectrometer. Elements in the filtrated solution after the hydrolysis reaction were analyzed by inductively coupled plasma spectrometry.

Each catalyst (0.3 g) was kept 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 introduce 1.5 mL of aqueous ammonia borane (NH_3BH_3 , 0.0055 g, 90%, Aldrich) solution. The evolution of gas was monitored using the gas burette. The reactions were

Figure 1 FTIR spectra of hollow silica spheres supported molybdosilicic acid prepared in the solution with pH = (a) 4.0, (b) 6.0, (c) 8.0, and (d) 9.7.

carried out at room temperature.

3. RESULTS AND DISCUSSION

Molybdosilicic acid supported on as-prepared hollow silica spheres prepared at various pH conditions were characterized by FTIR spectroscopy to confirm the immobilization of the acid. Figure 1 shows the FTIR spectra for molybdosilicic acid supported on hollow silica spheres prepared in the solution with pH = 4.0, 6.0, 8.0, and 9.7. All samples display the bands of the terminal Mo-O bond at around 990 cm^{-1} and those of the Si-O-Mo bond at around 930 cm^{-1} [37], accompanied by those of the Si-O-Si bond at around 1077 cm^{-1} [38]. The band intensity of the terminal Mo-O bond and Si-O-Mo bond in the spectra of the samples prepared at pH conditions below 6.0 is higher than that in the spectra of the samples prepared at pH conditions above 8.0. These results indicate that molybdosilicic acid was effectively immobilized on hollow silica spheres at pH conditions above 8.0.

The morphologies of hollow silica spheres supporting molybdosilicic acid, prepared at various pH conditions, were examined using TEM and SEM. As can be seen from Figure 1, all samples include spherical particles with a hollow structure and diameters of approximately 200–300 nm. The homogeneity of the hollow spheres depended on the pH conditions during the preparation process. From the results shown Figure 1 (e)–(h), it can be seen that the sample prepared at lower pH consists of relatively homogeneous hollow spheres while that prepared at higher pH includes collapsed hollow spheres. The results indicate that the molybdosilicic acid supported hollow spheres were collapsed at higher pH and homogeneous molybdosilicic acid supported hollow spheres were obtained at lower pH, especially at pH = 4.0, under the

Figure 2 TEM (a–d) and SEM (e–i) images of hollow silica spheres supported molybdosilicic acid prepared in the solution with pH = 4.0 (a,e), 6.0 (b,f), 8.0 (c,g), and 9.7 (d,i).

Figure 3 Hydrogen evolution from aqueous NH_3BH_3 solution in the presence of hollow silica spheres supported molybdsilicic acid prepared in the solution with pH = (a) 4.0, (b) 6.0, (c) 8.0, and (d) 9.7.

impregnation condition in this study.

The activity for hydrolytic dehydrogenation of NH_3BH_3 in the presence of molybdsilicic acid supported on hollow spheres was evaluated. Figure 3 shows the time course of hydrogen evolution from aqueous NH_3BH_3 solution in the presence of the supported molybdsilicic acid prepared in the solution with pH = 4.0, 6.0, 8.0, and 9.7. The reaction rate and amount of hydrogen evolved significantly depended on the catalyst. The evolution of 8.0, 5.0, 5.0, and 8.0 mL hydrogen from aqueous NH_3BH_3 solution were completed within approximately 3, 4, 11, and 10 min, respectively, in the presence of the solid acid prepared at pH = 4.0, 6.0, 8.0, and 9.7, respectively. Under the present reaction condition, about 12 mL of hydrogen (4.9×10^{-4} mol) was generated via reaction (1).

The molar ratios of the hydrolytically generated hydrogen to the initial NH_3BH_3 are 1.0, 1.3, 1.3, and 2.0 for catalysts prepared at pH = 4.0, 6.0, 8.0, and 9.7, respectively, as shown in Figure 3. The results indicate that catalytic activity for hydrolytic dehydrogenation of NH_3BH_3 increased with a decrease in pH.

To confirm the effect of the pH condition of the

Figure 4 Relation between the molar ratios of $\text{H}_2/\text{NH}_3\text{BH}_3$ and the amount of molybdsilicic acid in the filtrated solution of the reacted solution in the presence of hollow silica spheres supported molybdsilicic acid prepared in the solution with pH = (a) 4.0, (b) 6.0, (c) 8.0, and (d) 9.7.

preparation process on the immobilization of molybdsilicic acid on hollow silica spheres, the amount of molybdsilicic acid in the reaction solution after hydrolysis of NH_3BH_3 was determined. Figure 4 shows the correlation between the molar ratio of H_2 to NH_3BH_3 and amount of molybdsilicic acid in the reaction solution. With the exception of the reaction solution containing the catalyst prepared at pH 9.7, the amount of molybdsilicic acid in the reaction solutions was the same. This result indicates that molybdsilicic acid was effectively immobilized on hollow silica spheres when prepared at pH = 8.0.

The valence state of the molybdenum species after the reaction in the samples prepared at various pH conditions was investigated. Figure 4 shows the XPS spectra in the Mo 3d region of molybdsilicic acid supported on hollow silica spheres. The figure shows that the binding energy of the peaks assigned to Mo species in the supported molybdsilicic acid prepared at higher pH is around 231 eV, indicating that this sample mainly includes Mo^{4+} (230.4 eV [39]) and Mo^{5+} (232.1 eV [39]) species. On the other hand, the binding energy of the peaks assigned to Mo species in the supported molybdsilicic acid prepared at lower pH is around 233 eV, indicating that this sample mainly includes Mo^{5+} (232.1 eV) and Mo^{6+} (233.7 eV [39]) species. Consequently, the results shown in Figures 3 and 4 suggest that the supported molybdsilicic acid consists of higher valence states of Mo species after hydrolytic dehydrogenation of ammonia borane, showing high activity for the reaction.

4. CONCLUSIONS

In this study, we investigated the influence of the pH condition during the impregnation process

Figure 5 XPS spectra in Mo 3d region of hollow silica spheres supported molybdsilicic acid prepared in the solution with pH = (a) 4.0, (b) 6.0, (c) 8.0, and (d) 9.7.

on the immobilization of molybdosilicic acid on hollow silica spheres and activity of the acid for hydrolytic dehydrogenation of ammonia borane. To adjust the pH, amino acids such as L-aspartic acid and L(+)-arginine were added to the impregnating solution. The intensity of bands in the FTIR spectra originating from molybdosilicic acid decreased with pH, indicating that the amount of acid immobilized on hollow silica spheres decreased. The TEM and SEM images showed that the samples prepared at lower pH (especially at the lowest, pH 4.0) consist of homogeneous hollow silica spheres supporting molybdosilicic acid, while the samples prepared at higher pH include collapsed hollow spheres. The reaction rate and amount of hydrogen evolved increased with a decrease in the pH of the impregnation process. After the reaction, the sample prepared at lower pH consisted of a higher valence value of Mo species according to XPS results and the corresponding amount of Mo species in the reaction solution was also lower. The results indicate that molybdosilicic acid supported on homogeneous hollow silica spheres had a higher valence value of Mo species and the effectively immobilized acid had a higher reaction rate and amount of hydrogen evolved from aqueous ammonia borane solution.

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