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Influence of preparation conditions of hollow silica-nickel composite spheres on their catalytic activity for hydrolytic dehydrogenation of ammonia borane

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Abstract

In this paper, we investigated influence of preparation conditions of hollow silica-nickel composite spheres on their morphology and catalytic activity for hydrolytic dehydrogenation of ammonia borane. In the preparation method of this study, when silica-nickel composite shells were coated on polystyrene templates by the sol-gel

method using L(+)-arginine as the promoter for the reaction to form silica-nickel composite shell, the polystyrene templates were dissolved subsequently, even synchronously, in the same medium to form hollow spheres. The as-prepared silica-nickel composite spheres were characterized by transmission electron microscopy and scanning electron microscopy. The effects of Si+Ni content on the morphology were systematically evaluated. All the as-prepared hollow silica-nickel composite spheres have the similar morphology as identified by SEM and TEM measurement. Homogeneity of the hollow silica-nickel composite spheres increases with the increase in the Si+Ni content as shown by the laser diffraction particle size analysis. The catalytic activities of the hollow silica-nickel composite spheres for hydrolytic dehydrogenation of ammonia borane prepared with different Si+Ni contents were compared. The catalytic activity for the hydrogen evolution in the presence of the hollow spheres increases with the increase of Si+Ni content. The results of FTIR spectra of the hollow silica-nickel composite spheres indicate that a certain amount of residual PS templates exists in hollow silica-nickel composite spheres. The residual PS templates was able to be reduced by procedure of as-prepared samples with toluene solvent. The catalytic activity of hollow silica-nickel composite spheres increases with decrease in the amount of residual PS templates.

Keywords: Hollow silica-nickel composite spheres; L(+)-arginine; Hydrolytic dehydrogenation; Ammonia borane

1. Introduction

There have been intensive efforts for developing safe and efficient methods for controlled storage and release of hydrogen, a key issue of a fuel-cell-based hydrogen economy [1-3]. Owing to its low molecular weight (30.9 g mol^{-1}), high hydrogen content (19.6 wt%), high stability at room temperature, and nontoxicity, ammonia borane (NH_3BH_3) is has been identified as an attractive candidate for chemical hydrogen storage application [4-25]. Moreover, NH_3BH_3 can be handled at room temperature and can release hydrogen gas upon catalytic hydrolysis under mild conditions [4]. The hydrolysis occurs at appreciable rate in the presence of a suitable acid or a suitable catalyst at ambient temperature [12-25]. For 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. It is reported that nickel based catalyst is one of highly active catalysts for this reaction [14, 17, 19-25], and several reports have studied supported or composite effect with

metal oxides on nickel based catalysts [14, 17, 21, 22, 24, 25].

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 [26-29]. 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 [30-35], layer by layer (LBL) techniques [36-40], microemulsion/interfacial polymerization strategies [41-45]. Microsized, monodisperse, hollow silica [32] and titania [46] 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 [47] or by emulsifier-free emulsion polymerization using α,α' -azodiisobutyramidine dihydrochloride (AIBA) as the initiator and poly(vinyl pyrrolidone) (PVP) as the stabilizer [32, 48]. 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.

Our recent studies reveal that hollow metal oxide-nickel composite spheres have been able to be fabricated by the similar method [49, 50]. We firstly fabricated the hollow silica-nickel composite spheres using L(+)-arginine, a kind of basic amino acid, as the promoter for hydrolysis of tetraethoxysilane (TEOS) [51] and for dissolution of PS templates [50]. The hollow spheres shows higher catalytic activity for hydrolytic dehydrogenation of ammonia borane than the hollow spheres prepared using aqueous ammonia solution as the promoter for hydrolysis of tetraethoxysilane (TEOS) and for dissolution of PS templates [50].

In the present study, we investigated the influence of preparation conditions, such as Si+Ni content, aging temperature, and procedure for reduction of residual PS templates, of the hollow silica-nickel composite spheres by PS template method using L(+)-arginine on their morphology and catalytic activity for hydrolytic dehydrogenation of ammonia borane.

2. Experimental

2.1 Catalyst preparation

Hollow silica-nickel composite spheres were prepared by polystyrene beads template method as follows [50]. 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. The mixed aqueous solution of 0.03, 0.09, 0.15, and 0.30 g of $Ni(NO_3)_2 \cdot 6H_2O$ (Kanto Chem. Co., > 99.0 %), 0.3093 g of L(+)-arginine (Kanto Chem. Co.), and 160 mL of ethyl alcohol were added into 20.0 g of the PS suspension, to which added was 0.215, 0.646, 1.076, and 2.152 mL of tetraethoxysilane (Kanto Chem. Co., > 99.9 %). The sol-gel reaction was carried out at 323 K, and the hollow silica-nickel composite spheres could

be directly obtained. After drying in a desiccator overnight, the obtained light blue fine powders were used as catalysts.

2.2. Characterization

The morphologies of hollow silica-nickel composite spheres were observed using a Hitachi S-450 scanning electron microscope (SEM) operating at an acceleration voltage of 15 kV and a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. The particle size distribution of the hollow silica-nickel composite spheres dispersed in water was analyzed by laser diffraction method using a Shimadzu SALD-2000A analyzer. 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% H₂ in Ar (260 mL min⁻¹) through the sample (≈ 2 mg) heated at a constant rate of 5 K min⁻¹ up to 1173 K. FTIR spectra of hollow metal oxide-nickel composite spheres were recorded using a Fourier transform infrared spectrophotometer (FTIR-8400S, Shimadzu Co., Ltd.) with a resolution of 4 cm⁻¹.

2.3. Experimental procedures for hydrolysis of ammonia borane

A mixture of sodium borohydride (NaBH₄, 5 mg, Kanto Chemical Reagent Co., > 98.5 %), ammonia borane (NH₃BH₃, 27.5 mg, Aldrich, 90 %), and catalyst

($\text{NH}_3\text{BH}_3/\text{NaBH}_4/\text{Ni} = 1/0.17/0.05$) 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 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 burette. 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. For obtaining the activation energy, we carried out the hydrogen generation reaction at 298, 323 and 343 K.

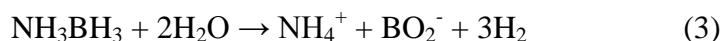
3. Results and discussion

The morphologies of hollow silica-nickel composite spheres with different Si+Ni contents before hydrolysis of NH_3BH_3 were examined using TEM and SEM. From the TEM image of hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06×10^{-3} mol (Figure 1(a)), the spherical particles with their hollow feature indicated by the arrows were obtained. All the SEM images of the hollow silica-nickel composite spheres reveal that the samples prepared with Si+Ni content = 1.06, 3.19, 5.32, and 10.64×10^{-3} mol consist of spherical particles (Figure 1(b)-(e)). Figure 2 shows laser

diffraction size distribution profile of the hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06, 3.19, 5.32, and 10.64×10^{-3} mol. There are two main peaks at around 300 and 680 nm in the particle size distribution profile of the hollow spheres prepared with Si+Ni content = 1.06×10^{-3} mol (Figure 2(a)). The peak at around 300 nm in the profile of the hollow spheres prepared Si+Ni content = 3.19, 5.32, and 10.64×10^{-3} mol is narrower and larger than that in the profile of the hollow spheres prepared with Si+Ni content = 1.06×10^{-3} mol, while the number of the particle of around 680 nm in diameter drastically decreases with increase of Si+Ni content. The results indicate that homogeneity of the hollow silica-nickel composite spheres increases with the increase of Si+Ni content.

Figure 3 shows the time course of the hydrogen evolution from aqueous $\text{NaBH}_4/\text{NH}_3\text{BH}_3$ solution in the presence of hollow silica-nickel composite spheres. The reaction rate and the amount of hydrogen evolution significantly depend on the catalysts. The evolution of 54, 55, 56, and 56 mL hydrogen from aqueous NaBH_4 solution were finished in 32, 30, 22, and 18 min in the presence of hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06, 3.19, 5.32, and 10.64×10^{-3} mol, respectively. In the present reaction system, NaBH_4 was mixed with H_2O , NH_3BH_3 , and catalyst. Hydrogen is evolved via following two reactions (reactions (2) and (3)) besides

reaction (1);



Under the present reaction condition, about 12 mL of hydrogen (4.8×10^{-4} mol) is generated via reactions (2) from residual amount of NaBH_4 consumed via the reaction (1) (1.3×10^{-4} (total amount of NaBH_4) - 0.1×10^{-4} (amount of NaBH_4 consumed via the reaction (1)) = 1.2×10^{-4} mol), and about 59 mL of hydrogen (24.0×10^{-4} mol) is generated via reaction (3), experimentally. The molar ratios of the hydrolytically generated hydrogen to the initial NH_3BH_3 in the presence of hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06, 3.19, 5.32, and 10.64×10^{-3} mol are 2.3, 2.3, 2.4, and 2.4, respectively. These results indicate that hydrogen evolution rate from aqueous $\text{NaBH}_4/\text{NH}_3\text{BH}_3$ solution in the presence of hollow silica-nickel composite spheres increases with the increase of Si+Ni content.

In order to obtain information about reducibility of active nickel species, the temperature programmed reduction (TPR) profiles observed upon treatment of the as-prepared samples in H_2 are obtained by TGA. Figure 4 shows the DTG curves of the as-prepared samples. The curves involved three main domains that point to the presence

of different kinds of nickel species with diverse reducibility: one reduced at the lower temperature (T_{\max} at about 550 K) and another reduced at higher temperatures (T_{\max} at about 724 K). From the reduction profile of hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06×10^{-3} mol (Figure 4(a)), the clearly defined peaks at around 724 K appear in the DTG curve. This peak is assigned to nickel species contacting with silica matrix [52-54]. Contrary to the sample, a low temperature peak at about 550 K which is ascribed to the presence of clustered nickel species [53] appears in the reduction profiles of silica-nickel composite spheres prepared with Si+Ni content = 3.19 and 5.32×10^{-3} mol in addition to the high temperature peak at around 724 K. With increase of Si+Ni content, the intensity of the low temperature peak increases and the intensity of the high temperature peak decreases, and then only low temperature peak appears in the reduction profiles of silica-nickel composite spheres prepared with Si+Ni content = 10.64×10^{-3} mol. These results indicate that clustered nickel species in hollow silica-nickel composite spheres increase with increase of Si+Ni content, and more reducible nickel species exist in the hollow spheres prepared with higher Si+Ni content.

The as-prepared hollow silica-nickel composite spheres were characterized by using FTIR spectroscopic methods to confirm that the difference in the catalytic activity depends on the amount of residual PS templates. Figure 5(a) shows FTIR spectra for

hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06×10^{-3} mol at 323 K. These hollow spheres display the characteristic bands of PS at around 1600, 1492, 1449, 754, and 698 cm^{-1} [55]. These bands indicate that the PS segments are included in the shell of hollow spheres. In order to reduce the amount of residual PS templates in the hollow silica-nickel composite spheres, we investigate the effect of the various conditions of procedures during or after preparation. Figure 5(b) and (c) show the spectra of the hollow silica-nickel composite spheres prepared at 343 K and treated in toluene after preparation of the hollow spheres. In addition to the characteristic bands of PS described above, these samples display the stretch vibration bands of the Si-O-Si bond at around 1077 cm^{-1} [55]. These bands indicate that the shell of hollow spheres is composed of both silica and PS segments. The ratio of the peak intensity for the characteristic band of PS at around 698 cm^{-1} to the peak intensity for the Si-O-Si band depends on the procedure. The ratios, $I_{\text{PS}}/I_{\text{SiO}_2}$, of the hollow silica-nickel composite spheres prepared at 323 and 343 K, and treated in toluene after preparation of the hollow spheres are 1.34, 1.12, and 0.43, respectively, indicating that the stirring procedure in toluene is effective for reducing the amount of residual PS templates.

The morphologies of hollow silica-nickel composite spheres prepared at 323 and 343 K, and treated in toluene after preparation of the hollow spheres were examined using

SEM (Figure 6). All the SEM images reveal that all the samples consist of homogeneous spherical particles and that the morphology of hollow silica-nickel composite spheres was not significantly different with the preparation conditions or treatment procedure of as-prepared sample.

Figure 7 shows the catalytic activity over the hollow silica-nickel composite spheres prepared or treated in various conditions. The reaction rate does not depend on the catalysts, however, the amount of hydrogen evolution depend on the catalysts. The evolution of 54, 53, and 57 mL hydrogen were finished in 32, 36, and 34 min in the presence of the hollow silica-nickel composite spheres prepared at 323 and 343 K, and treated in toluene after preparation of the hollow spheres, respectively. The molar ratios of the hydrolytically generated hydrogen to the initial NH_3BH_3 in the presence of the hollow silica-nickel composite spheres prepared at 323 and 343 K, and treated in toluene after preparation of the hollow spheres are 2.3, 2.2, and 2.4, respectively. The results indicate that the catalytic activity of hollow silica-nickel composite spheres increases when the amount of residual PS templates decreases.

Figure 8 shows FTIR spectra of hollow silica-nickel composite spheres prepared with various amount of silica-nickel composite following the treatment in toluene. The results indicate that all the spectra consist of the characteristic bands of PS at around

698 cm^{-1} with negligible intensity, thus, all the samples treated in toluene include negligible amount of residual PS templates.

The morphologies of hollow silica-nickel composite spheres prepared with various amount of silica-nickel composite following treatment in toluene were examined using SEM (Figure 9). All the SEM images reveal that all the samples consist of homogeneous spherical particles and that the morphology of all the hollow spheres were not significantly changes compared with the sample without the treatment in toluene.

Figure 10 shows the catalytic activity over the hollow silica-nickel composite spheres prepared with various amount of silica-nickel composite following treatment in toluene. The reaction rate depends on the catalysts. The evolution of 57, 58, 60, and 61 mL hydrogen from aqueous NaBH_4 solution were finished in 31, 30, 29, and 22 min in the presence of hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06, 3.19, 5.32, and 10.64×10^{-3} mol, respectively. The molar ratios of the hydrolytically generated hydrogen to the initial NH_3BH_3 in the presence of hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06, 3.19, 5.32, and 10.64×10^{-3} mol are 2.4, 2.5, 2.6, and 2.6, respectively. These results indicate that the amount and rate of hydrogen evolution from aqueous $\text{NaBH}_4/\text{NH}_3\text{BH}_3$ solution in the presence of hollow silica-nickel composite spheres increases with the increase of Si+Ni content. The results

in Figure 4 indicate that clustered nickel species in hollow silica-nickel composite spheres increase with increase of Si+Ni content, and more reducible nickel species exist in the hollow spheres prepared with higher Si+Ni content. The results in Figure 4 and 10 suggest that the amount of clustered nickel species in the hollow spheres increases with increase of Si+Ni content, and then, the catalytic activity increases with increase of Si+Ni content.

The hollow silica-nickel composite spheres catalyzed hydrolysis of NH_3BH_3 was carried out at various temperatures in the range of 298-343 K.

$$-3d[\text{NH}_3\text{BH}_3]/dt = d[\text{H}_2]/dt = k \quad (4)$$

Under our experimental conditions, the reaction rate constant, k , is constant for a given temperature, implying zero order kinetics for the NH_3BH_3 hydrolysis reaction. This suggests that the hydrogen generation rate is controlled within a surface reaction. The reaction rate equation can be written as follows:

$$k = k_0 \exp(-E_a/RT) \quad (5)$$

where k_0 is the reaction constant (ml min^{-1}), E_a the activation energy for the reaction, R the gas constant and T is the reaction temperature. Following the above mentioned equation, the values of rate constant k at different temperatures for hydrolysis of NH_3BH_3 catalyzed by the hollow spheres were calculated from the linear part of time

courses of the hydrogen evolution in the presence of the hollow spheres with various Si+Ni contents at various temperatures in the range of 298-343 K. The Arrhenius plots are shown in Fig. 11. They were also used to calculate the activation parameters: $E_a = 44, 54, 49, \text{ and } 45 \text{ kJ mol}^{-1}$ for the hollow spheres with Si+Ni content = 1.06, 3.19, 5.32, and 10.64×10^{-3} mol, respectively. The activation energies obtained for the hydrolysis of NH_3BH_3 catalyzed hollow silica-nickel composite spheres do not significantly depend on the Si+Ni contents.

4. Conclusion

In this paper, we investigated influence of preparation conditions of hollow silica-nickel composite spheres in their morphology and catalytic activity for hydrolytic dehydrogenation of ammonia borane. In the preparation method of this study, when silica-nickel composite shells were coated on polystyrene templates by the sol-gel method using L(+)-arginine as the promoter for the reaction to form silica-nickel composite shell, the polystyrene templates were dissolved subsequently, even synchronously, in the same medium to form hollow spheres. All the as-prepared hollow silica-nickel composite spheres have the similar morphology identified by SEM and TEM measurement. Homogeneity of the hollow silica-nickel composite spheres

increases with the increase of Si+Ni content as observed by laser diffraction particle size analysis. The catalytic activity for the hydrogen evolution in the presence of the hollow spheres increases with the increase of Si+Ni content. The results of FTIR spectra of the hollow silica-nickel composite spheres indicate that a certain amount of residual PS templates exists in hollow silica-nickel composite spheres. The residual PS templates was able to be reduced by procedure of as-prepared samples with toluene solvent. The catalytic activity of hollow silica-nickel composite spheres increases when the amount of residual PS templates decreases.

References

- [1] Basic research needs for the hydrogen economy, report of the basic energy sciences workshop on hydrogen production, storage and use, May 13-15, 2003, Office of Science, U.S. Department of Energy, www.sc.doe.gov/bes/hydrogen.pdf.
- [2] J. Turner, G. Sverdrup, M.K. Mann, P.G. Maness, B. Kroposki, M. Ghirardi, R. J. Evans, D. Blake, *Int. J. Energy Res.* 32(5) (2008) 379-407.
- [3] A.W.C.V. Berg, C.O. Areán, *Chem. Commun.* 27 (2008) 668-681.
- [4] Basic research needs catalysis for energy, report from the U.S. Department of Energy, basic energy sciences workshop report, August 6-8, 2007, <<http://www.sc.doe.gov/bes/reports/list.html>>.
- [5] A. Gutowska, L.Y. Li, Y.S. Shin, C.M.M. Wang, X.H.S. Li, J.C. Linehan, et al. , *Angew. Chem. Int. Ed.* 44(23) (2005) 3578-3582.
- [6] V. Sit, R.A. Geanangel, W.W. Wendlandt, *Thermochim. Acta* 113 (1987) 379-382.
- [7] M.E. Bluhm, M.G. Bradley, R. Butterick III, U. Kusari, L.G. Sneddon, *J. Am. Chem. Soc.* 128(24)(2006) 7748-7749.
- [8] M.C. Denney, V. Pons, T.J. Hebden, D.M. Heinekey, K.I. Goldberg, *J. Am. Chem. Soc.* 128(37) (2006) 12048-12049.
- [9] F.H. Stephens, R. Tom Baker, M.H. Matus, D.J. Grant, D.A. Dixon, *Angew. Chem.*

- Int. Ed. 46(5) (2007) 746-749.
- [10] A. Paul, C.B. Musgrave, *Angew. Chem. Int. Ed.* 46(43) (2007) 8153-8156.
- [11] R.J. Keaton, J.M. Blacquiere, R.T. Baker, *J. Am. Chem. Soc.* 129(7) (2007) 1844-1845.
- [12] M. Chandra, Q. Xu, *J. Power Sources* 156(2) (2006) 190-194.
- [13] M. Chandra, Q. Xu, *J. Power Sources* 159(2) (2006) 855-860.
- [14] Q. Xu, M. Chandra, *J Power Sources* 163(1) (2006) 364-370.
- [15] M. Chandra, Q. Xu, *J. Power Sources* 168(1) (2007) 135-142.
- [16] J.M. Yan, X.B. Zhang, S. Han, H. Shioyama, Q. Xu, *Angew. Chem. Int. Ed.* 47(12) (2008) 2287-2289.
- [17] S.B. Kalidindi, M. Indirani, B.R. Jagirdar, *Inorg. Chem.* 47(16) (2008) 7424-7429.
- [18] S.B. Kalidindi, U. Sanyal, J B.R. Jagirdar, *Phys. Chem. Chem. Phys.* 10(38) (2008) 5870-5874.
- [19] J.M. Yan, X.B. Zhang, S. Han, H. Shioyama, Q. Xu, *Inorg. Chem.* 48(15) (2009) 7389-7393.
- [20] T. Umegaki, J.M. Yan, X.B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, *Int. J. Hydrogen Energy* 34(9) (2009) 3816-3822.
- [21] T. Umegaki, J.M. Yan, X.B. Zhang, Shioyama, N. Kuriyama, Q. Xu, *J. Power*

- Sources 191(2) (2009) 209-216.
- [22] H.L. Jiang, T. Umegaki, T. Akita, X.B. Zhang, M. Haruta, Q. Xu, *Chem. Eur. J.* 16(10) (2010) 3132-3137.
- [23] O. Metin, V. Mazumder, S. Ozkar, S. Sun, *J. Am. Chem. Soc.* 132(5) (2010) 1468–1469.
- [24] O. Metin, S. Ozkar, S. Sun, *Nano Res.* 3(9) (2010) 676-684.
- [25] P.Z. Li, K. Aranishi, Q. Xu, *Chem. Commun.* 48(26) (2012) 3173-3175.
- [26] M. M. Ren, R. Ravikrishna, K. T. Valsaraj, *Environ. Sci. Technol.* 40(22) (2006) 7029-7033.
- [27] P. Jiang, J. F. Bertone, V. L. Colvin, *Science* 291 (2001) 453-457.
- [28] Y. Li, J. Shi, Z. Hua, H. Chen, M. Ruan, D. Yan, *Nano Lett.* 3(5) (2003) 609-612.
- [29] U. Jeong, Y. L. Wang, M. Ibisate, Y. N. Xia, *Adv. Funct. Mater.* 15(12) (2005) 1907-1921.
- [30] P. Wang, D. Chen, F. Q. Tang, *Langmuir* 22(10) (2006) 4832-4835.
- [31] A. Imhof, *Langmuir* 17(12) (2001) 3579-3585.
- [32] Z. Z. Yong, Z. W. Niu, Y. F. Lu, Z. B. Hu, C. C. Han, *Angew. Chem. Int. Ed.* 42(17) (2003) 1943–1945.
- [33] M. Chen, L. M. Wu, S. X. Zhou, B. You, *Adv. Mater.* 18(6) (2006) 801-806.

- [34] Y. N. Xia, B. Gates, Y. D. Yin, Y. Lu, *Adv. Mater.* 12(10) (2000) 693-713.
- [35] Z. Y. Zhong, Y. D. Yin, B. Gates, Y. N. Xia, *Adv. Mater.* 12(3) (2000) 206-209.
- [36] H. Nakamura, M. Ishii, A. Tsukigase, M. Harada, H. Nakano, *Langmuir* 21(19) (2005) 8918-8922.
- [37] F. Caruso, R. A. Caruso, H. Möhwald, *Science* 282 (1998) 1111-1114.
- [38] D. Y. Wang, F. Caruso, *Chem. Mater.* 14(5) (2002) 1909-1913.
- [39] A. Yu, Y. Wang, E. Barlow, F. Caruso, *Adv. Mater.* 17(14) (2005) 1737-1741.
- [40] H. W. Duan, D. Y. Wang, N.S. Sobal, M. Giersig, D. G. Kurth, H. Mohwald, *Nano Lett.* 5(5) (2005) 949-952.
- [41] K. Zhang, X. H. Zhang, H. T. Chen, X. Chen, L. L. Zheng, J. H. Zhang, B. Yang, *Langmuir* 20(26) (2004) 11312-11314.
- [42] M. Zhang, G. Gao, D. C. Zhao, Z. Y. Li, F. Q. Lu, *J. Phys. Chem. B* 109(19) (2005) 9411-9415.
- [43] W. J. Li, M. O. Coppens, *Chem. Mater.* 17(9) (2005) 2241-2246.
- [44] I. Csetneki, G. Filipcsei, M. Zrinyi, *Macromolecules* 39(5) (2006) 1939-1942.
- [45] T. Nakashima, N. Kimizuka, *J. Am. Chem. Soc.* 125(21) (2003) 6386-6387.
- [46] X. Cheng, M. Chen, L. Wu, G. Gu, *Langmuir* 22(8) (2006) 3858-3863.
- [47] M. Chen, S. Zhou, B. You, L. Wu, *Macromolecules* 38(15) (2005) 6411-6417.

- [48] Z. Deng, M. Chen, S. Zhou, B. You, L. Wu, *Langmuir* 22(14) (2006) 6403-6407.
- [49] T. Umegaki, C. Takei, Q. Xu, Y. Kojima, *Int. J. Hydrogen Energy* 38(3) (2013) 1397-1404.
- [50] T. Umegaki, C. Takei, Y. Watanuki, Q. Xu, Y. Kojima, *J. Mol. Catal. A*, 371 (2013) 1-7.
- [51] T. Yokoi, Y. Sakamoto, O. Terasaki, Y. Kubota, T. Okubo, T. Tatsumi, *J. Am. Chem. Soc.* 128(42) (2006) 13664-13665.
- [52] K.-Q. Sun, E. Marceau, M. Che, *Phys. Chem. Chem. Phys.* 8(14) (2006) 1731-1738.
- [53] V. Mavrodinova, M. Popova, Ch. Minchev, R. Nickolov, M. Linden, *J. Porous Mater.* 14(2) (2007) 213-218.
- [54] J. Li, G. Lu, *Appl. Catal. A: Gen.* 273(1-2) (2004) 163-170.
- [55] W. Leng, M. Chen, S. Zhou, L. Wu, *Langmuir* 26(17) (2010) 14271–14275.

Figure captions

Figure 1 (a) TEM image of as-prepared hollow silica-nickel composite spheres prepared with Si+Ni content = 1.06×10^{-3} mol (aging time = 17 h) and SEM images of as-prepared hollow silica-nickel composite spheres prepared with Si+Ni content = (b) 1.06, (c) 3.19 (aging time = 40 h), (d) 5.32 (aging time = 50 h), and (e) 10.64×10^{-3} mol (aging time = 100 h).

Figure 2 Particle size distribution of hollow silica-nickel composite spheres prepared with Si+Ni content = (a) 1.06 (aging time = 17 h), (b) 3.19 (aging time = 40 h), (c) 5.32 (aging time = 50 h), and (d) 10.64×10^{-3} mol (aging time = 100 h).

Figure 3 Hydrogen generation from the mixture of sodium borohydride and ammonia borane in the presence of hollow silica-nickel composite spheres prepared with Si+Ni content = (a) 1.06 (aging time = 17 h), (b) 3.19 (aging time = 40 h), (c) 5.32 (aging time = 50 h), and (d) 10.64×10^{-3} mol (aging time = 100 h).

Figure 4 DTG curve registered upon H_2 -TPR of hollow silica-nickel composite spheres prepared with Si+Ni content = (a) 1.06 (aging time = 17 h), (b) 3.19 (aging time = 40 h), (c) 5.32 (aging time = 50 h), and (d) 10.64×10^{-3} mol (aging time = 100 h).

Figure 5 FT-IR spectra of as-prepared hollow silica-nickel composite spheres prepared

at (a) 323 K (aging time = 17 h) and (b) 343 K (aging time = 7 h), and (c) hollow silica-nickel composite spheres prepared at 323 K following the treatment in toluene.

Figure 6 SEM images of as-prepared hollow silica-nickel composite spheres prepared at (a) 343 K (aging time = 7 h) and (b) hollow silica-nickel composite spheres prepared at 323 K following the treatment in toluene.

Figure 7 Hydrogen generation from the mixture of sodium borohydride and ammonia borane in the presence of hollow silica-nickel composite spheres prepared at (a) 323 K (aging time = 17 h) and (b) 343 K (aging time = 7 h), and (c) hollow silica-nickel composite spheres prepared at 323 K following the treatment in toluene.

Figure 8 FTIR spectra of as-prepared hollow silica-nickel composite spheres prepared with Si+Ni content = (a) 1.06 (aging time = 17 h), (b) 3.19 (aging time = 40 h), (c) 5.32 (aging time = 50 h), and (d) 10.64×10^{-3} mol (aging time = 100 h) following treatment of the samples in toluene.

Figure 9 SEM images of as-prepared hollow silica-nickel composite spheres prepared with Si+Ni content = (a) 1.06 (aging time = 17 h), (b) 3.19 (aging time = 40 h), (c) 5.32 (aging time = 50 h), and (d) 10.64×10^{-3} mol (aging time = 100 h) following treatment of the samples in toluene.

Figure 10 Hydrogen generation from the mixture of sodium borohydride and ammonia borane in the presence of hollow silica-nickel composite spheres prepared with Si+Ni content = (a) 1.06 (aging time = 17 h), (b) 3.19 (aging time = 40 h), (c) 5.32 (aging time = 50 h), and (d) 10.64×10^{-3} mol (aging time = 100 h) following treatment of the samples in toluene.

Figure 11 Arrhenius plots for the hydrolysis of NH_3BH_3 catalyzed by the hollow spheres with Si+Ni contents = (a) 1.06 (aging time = 17 h), (b) 3.19 (aging time = 40 h), (c) 5.32 (aging time = 50 h), and (d) 10.64×10^{-3} mol (aging time = 100 h) following treatment of the samples in toluene catalyzed hydrolysis of NH_3BH_3 .

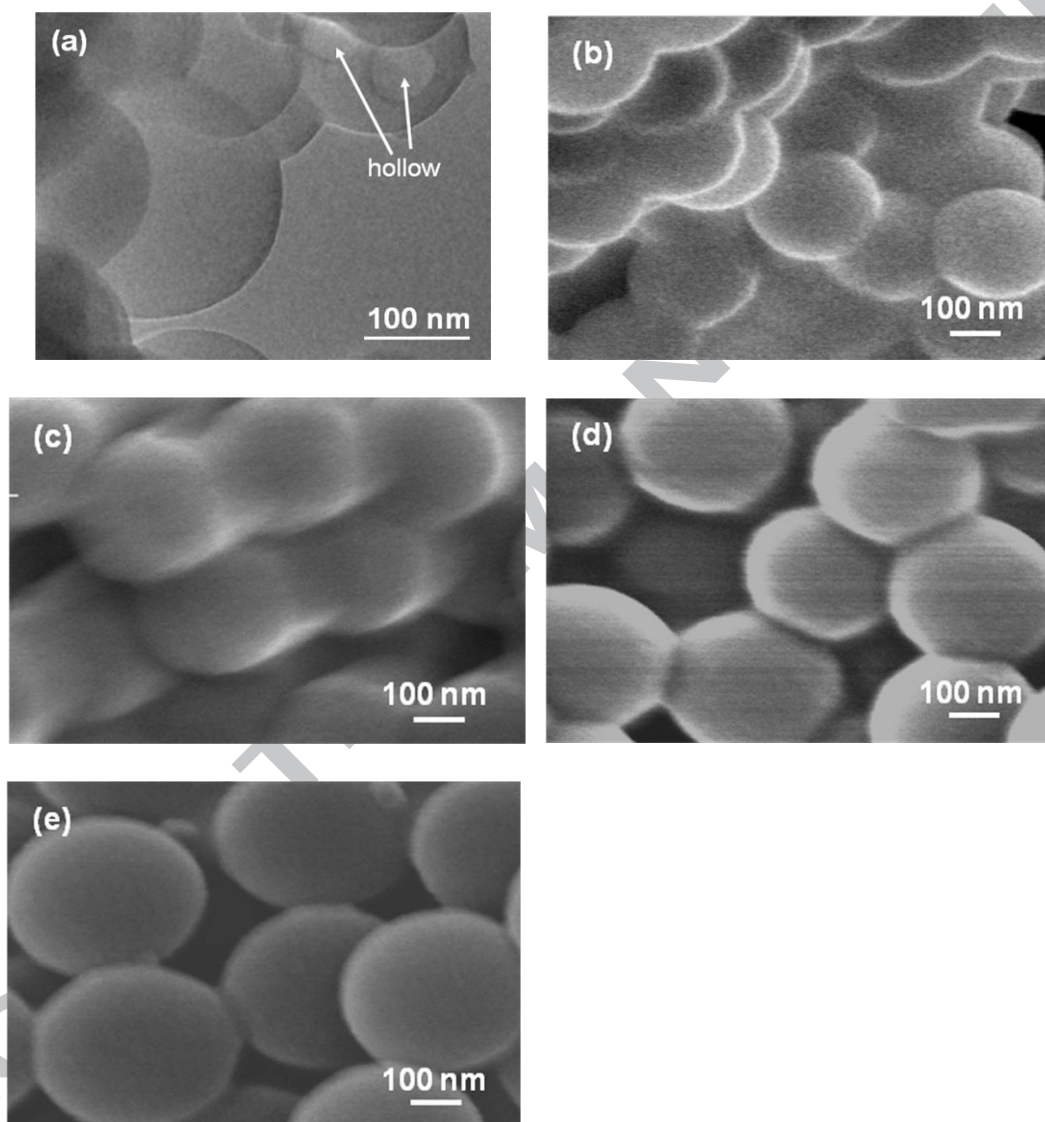


Fig. 1

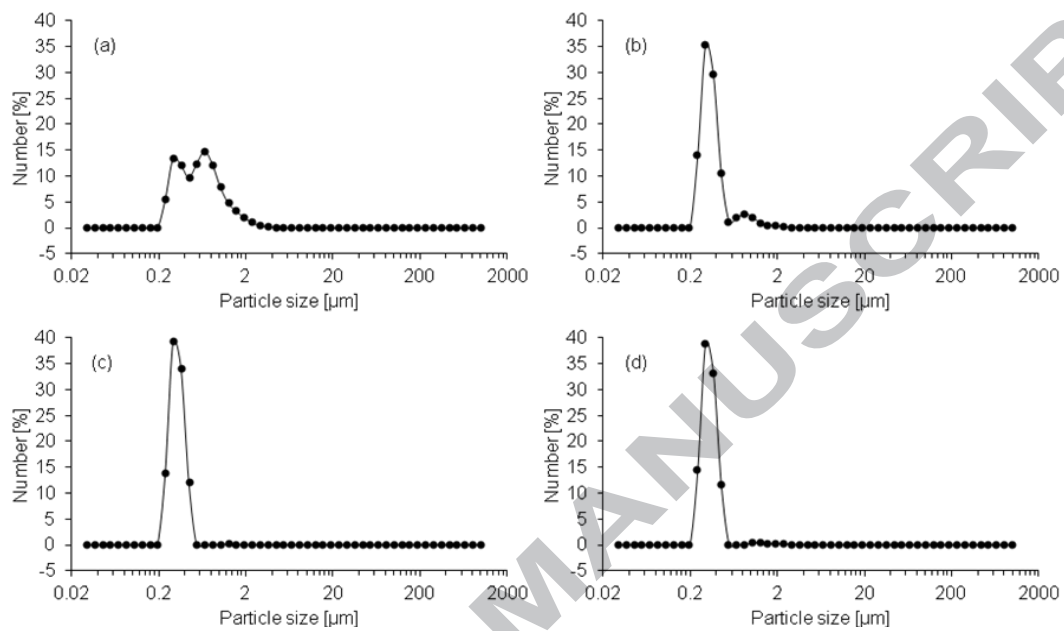


Fig. 2

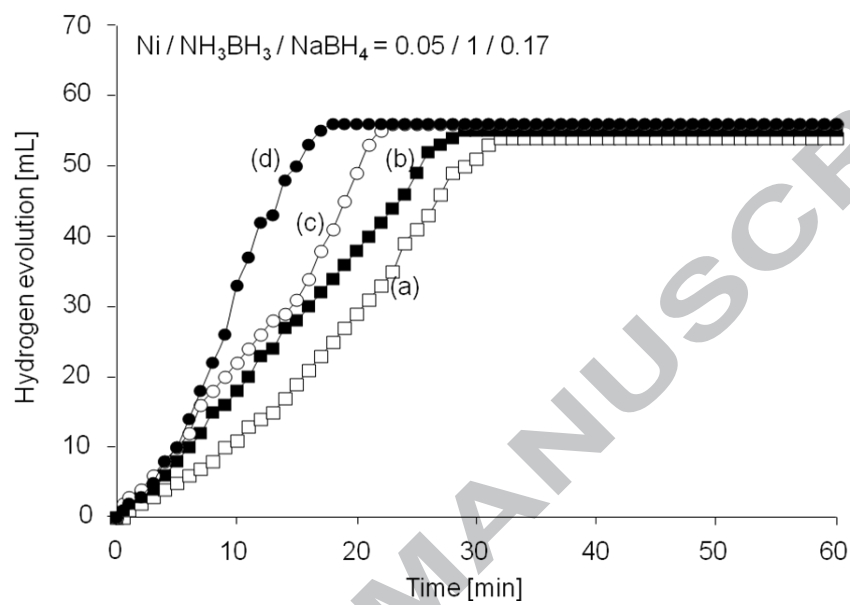


Fig. 3

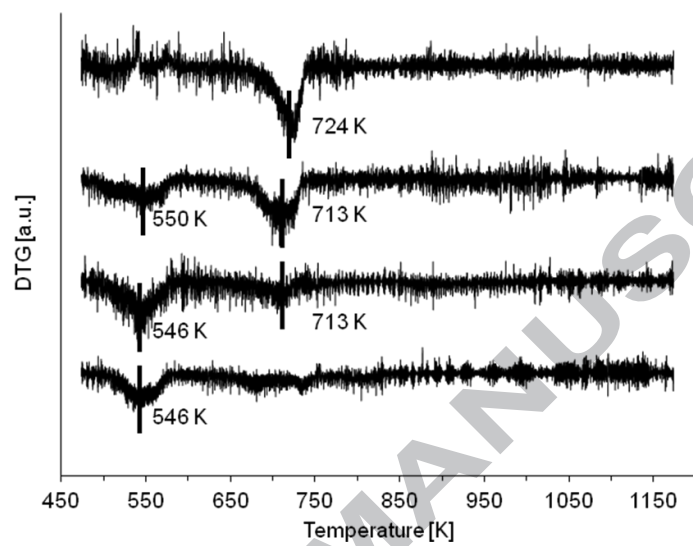


Fig. 4

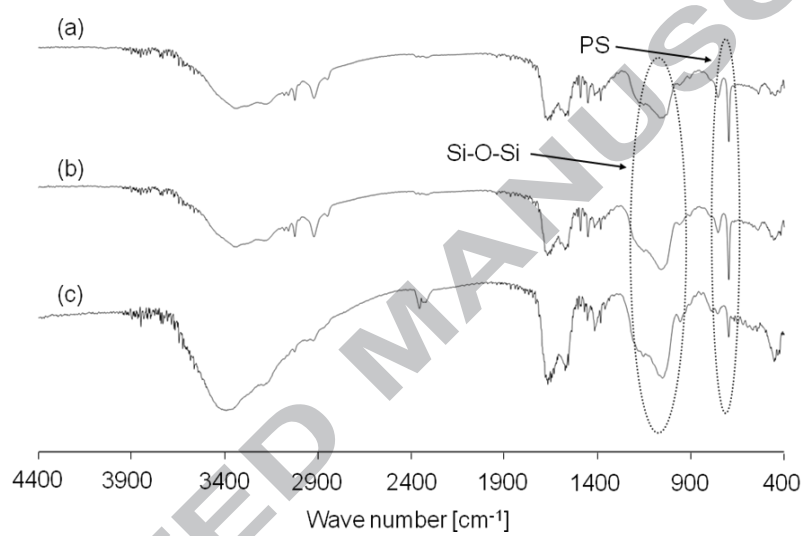


Fig. 5

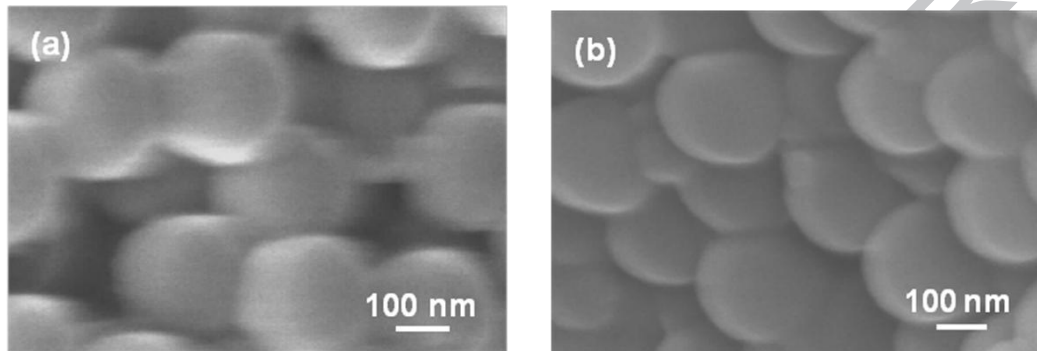
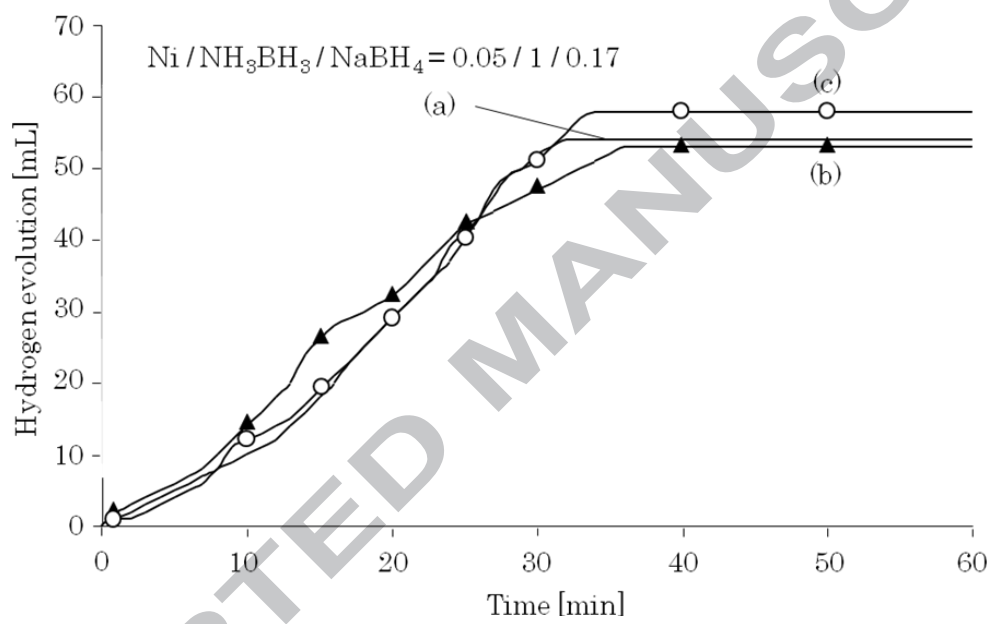


Fig.6



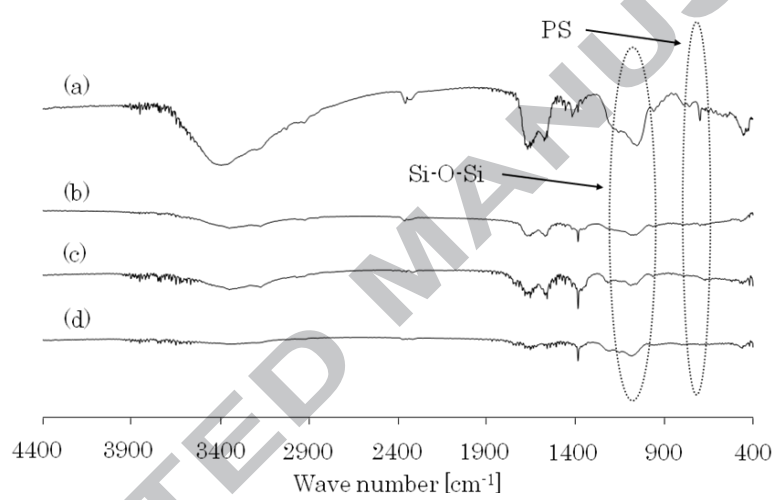


Fig. 8

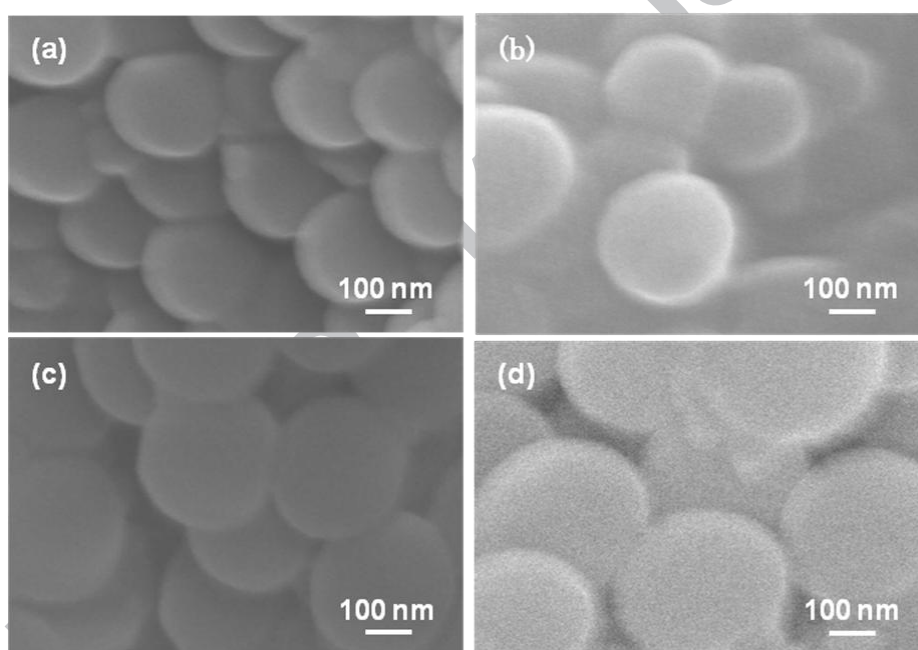


Fig. 9

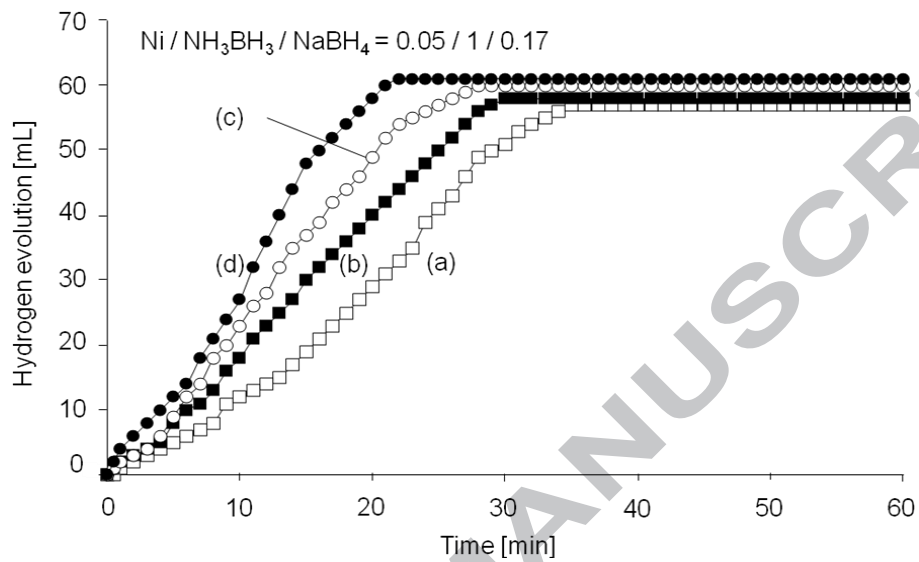


Fig. 10

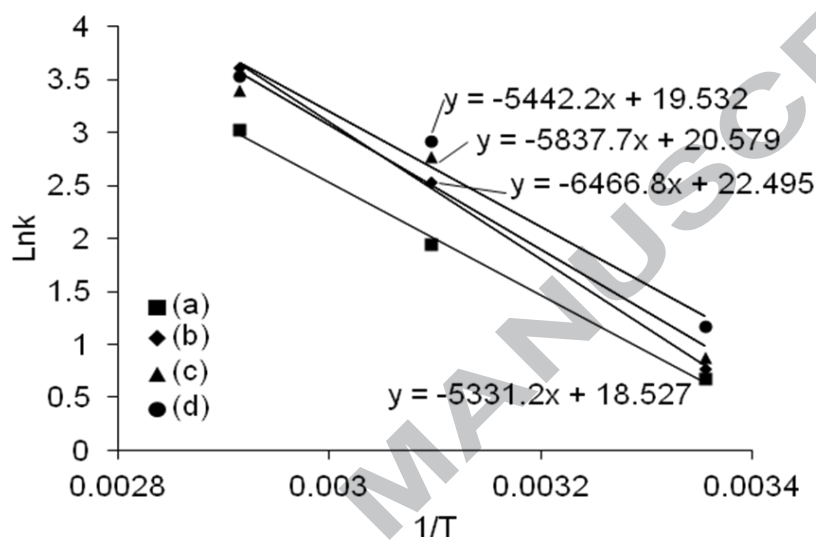


Fig. 11

Influence of preparation conditions of hollow silica-nickel composite spheres in their catalytic activity for hydrolytic dehydrogenation of ammonia borane

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Highlights

We study influence of preparation conditions on activity of hollow silica-nickel composite spheres.

The activity for hydrolytic dehydrogenation of NH_3BH_3 increases with increase of Si+Ni content.

The particle size distribution affects the activity and reducibility of active nickel species.

The amount of PS residue in the hollow spheres decreases by treatment of as-prepared sample in toluene.