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# In situ synthesized spherical nickel–silica composite particles for hydrolytic dehydrogenation of ammonia borane

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ABSTRACT

Spherical nickel–silica composite particles were synthesized by sol–gel based method in various solvents followed by in situ activation in aqueous sodium borohydride ($NaBH_4$)/ammonia borane ($NH_3BH_3$) solutions. The resulting products prepared in methyl alcohol, ethyl alcohol, and 2-propyl alcohol include spherical particles with the diameters of 600–800, 200–400 nm, and 200–400 nm, respectively. The evolution of 56, 58, and 62 mL hydrogen was finished in about 50, 90, and 65 min in the presence of the spherical nickel–silica composite particles from aqueous $NaBH_4/NH_3BH_3$, respectively. Introducing additional aqueous ammonia borane solution to the solution including the in situ synthesized particles, the evolution of 58, 50, and 63 mL hydrogen was finished in about 45, 90, and 45 min, respectively, indicating that all the in situ synthesized particles have the recyclability as the catalysts for hydrolysis of $NH_3BH_3$. The in situ synthesized particles prepared in methyl alcohol and 2-propyl alcohol show higher rate and amount of hydrogen evolution than in situ synthesized particles prepared in ethyl alcohol.

## 1. Introduction

Ammonia borane ($NH_3BH_3$) is expected as a hydrogen storage material for polymer membrane fuel cells for mobile use because hydrogen with high purity is able to be generated from $NH_3BH_3$ at room temperature. It is reported that nickel-based catalyst is one of the highly active catalysts for this reaction [1–7]. The results indicate that dispersion of active metals and/or amorphousness of active phase play important roles in the catalytic performances for hydrogen generation from aqueous $NH_3BH_3$ solution [1–7]. The morphological effect of nickel–silica composite catalyst was reported by comparing the activity between composite catalyst and supported catalyst [4]. In recent years, the fabrication 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 [8–13]. There have been developed several strategies, such as heterophase polymerization/combined with a sol–gel process [14,15], emulsion/interfacial polymerization approach [16], spray-drying method [17], self assembly technique [18], surface living polymerization process [19], and the template-based route [20–23] to prepare hollow spheres comprising polymeric or ceramic materials.

In this study, we investigated the influence of solvents in morphology of spherical nickel–silica composite particles followed by in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions and catalytic activity. In addition, we also investigated the reusability of the in situ synthesized particles for hydrolysis of $NH_3BH_3$.

## 2. Experimental

As-prepared spherical nickel–silica composite particles were prepared by the following sol–gel based techniques. 9.0 mL of an mixed aqueous solution of nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, Soekawa Chem. Co., >99.0%) and L(+)-arginine (Acros, >98%), as a promoter for the reaction to form silica spheres [24], was added to 180 mL of methyl alcohol (Kanto Chem. Co., >99.5%), ethyl alcohol (Kanto Chem. Co., >99.5%), or 2-propyl alcohol (Kanto Chem. Co., >99.5%), and then the solution was stirred at 323 K for 17 h after adding 215.2 μL of tetraethoxysilane (TEOS, Kanto Chem. Co., >99.5%) into the methyl alcohol, ethyl alcohol, or 2-propyl alcohol solution. The resulting solution was filtered, washed in ethyl alcohol, and dried in a desiccator.

The obtained powder was mixed with 5 mg of $NaBH_4$ (Kanto Chemical Co., >98.5%), 27.5 mg of $NH_3BH_3$ (Aldrich, 90%) 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 the distilled water (5 mL). The reaction started when the distilled water was added to the mixture of the catalyst, $NaBH_4$, and $NH_3BH_3$, and the evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature in air.

In order to confirm recyclability of in situ synthesized spherical nickel–silica composite particles, a further aliquot of the aqueous $NH_3BH_3$ solution (0.16 M, 5 mL) was subsequently added to the reaction flask and the evolution of gas was monitored using the gas burette after the hydrogen generation reaction was completed.

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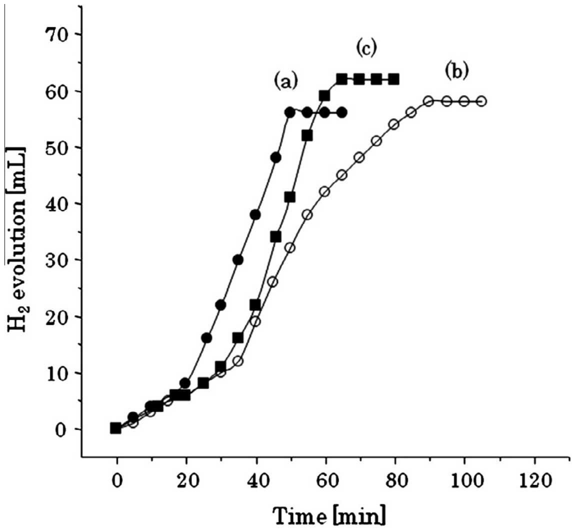

**Fig. 1.** Hydrogen generation from hydrolysis of $NH_3BH_3$ (0.16 M, 5 mL) with sodium borohydride in the presence of spherical nickel–silica composite particles prepared in (a) methyl alcohol, (b) ethyl alcohol, and (c) 2-propyl alcohol at room temperature in air ($Ni/NH_3BH_3 = 0.06$).

The morphologies of the catalysts were observed using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. 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 200–800 nm.

## 3. Results and discussion

Fig. 1 shows time course of the hydrogen evolution from aqueous $NaBH_4/NH_3BH_3$ solutions in the presence of spherical nickel–silica composite particles prepared in various solvents. The reaction rate and the amount of hydrogen evolution depend on the catalysts. The evolution of 56, 58, and 62 mL hydrogen was finished in 50, 90, and 65 min the presence of the spherical particles prepared in methyl alcohol, in ethyl alcohol, and 2-propyl alcohol, respectively. The effect of $NaBH_4$ has been reported about nickel based catalyst for hydrolysis of $NH_3BH_3$ [2–4]. 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);

$$4Ni^{2+} + BH_4^- + 2H_2O \rightarrow 4Ni + BO_2^- + 8H^+ \quad (1)$$

$$NaBH_4 + 2H_2O \rightarrow Na^+ + BO^{2-} + 4H_2 \quad (2)$$

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \quad (3)$$

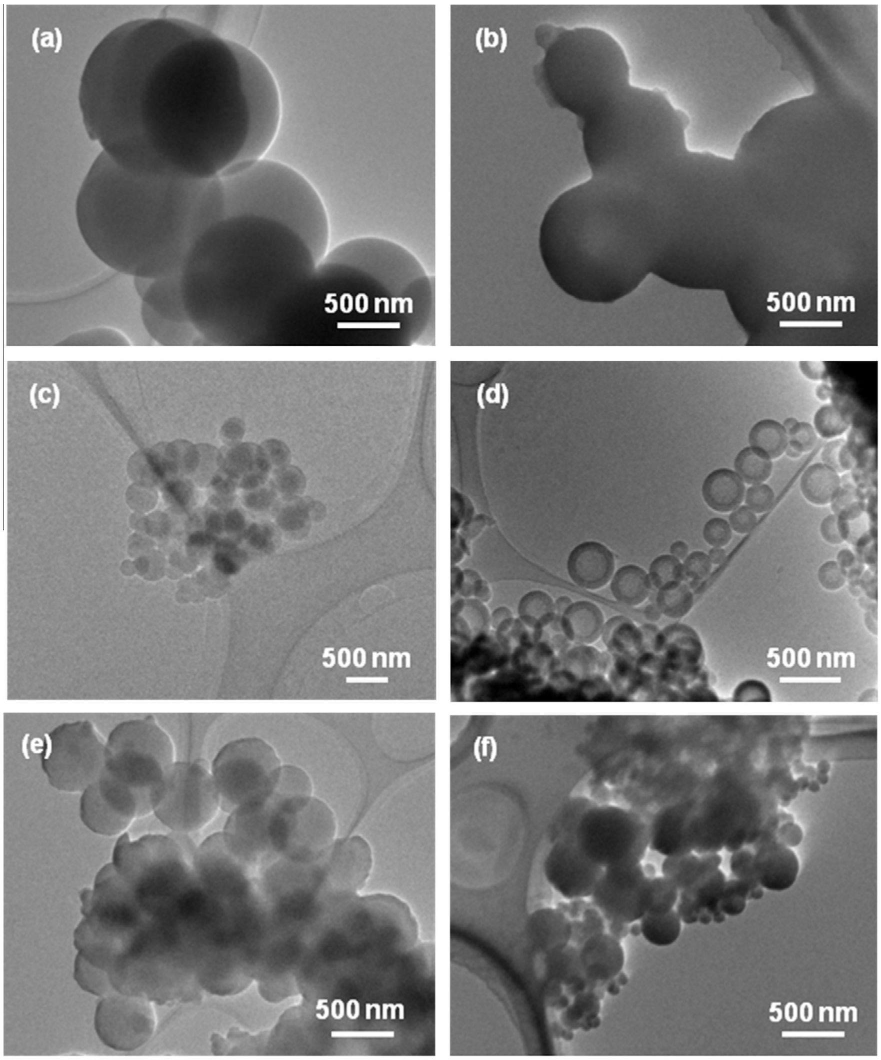

**Fig. 2.** TEM images of spherical nickel–silica composite spheres prepared in (a and b) methyl alcohol, (c and d) ethyl alcohol, and (e and f) 2-propyl alcohol before and after in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions.

Under the present reaction condition, about 12 mL of hydrogen ($4.8 \times 10^{-4}$ mol) is generated via reaction (2) from residual amount of $NaBH_4$ consumed via the reaction (1) ($1.3 \times 10^{-4}$ (total amount of $NaBH_4$)$-0.1 \times 10^{-4}$ (amount of $NaBH_4$ consumed via the reaction (1)) = $1.2 \times 10^{-4}$ mol), and about 59 mL of hydrogen ($24.0 \times 10^{-4}$ mol) is generated via reaction (3), experimentally. The molar ratio of hydrolytically generated hydrogen to the initial $NH_3BH_3$ in the presence of the spherical particles prepared in methyl alcohol, ethyl alcohol, and 2-propyl alcohol, are 2.4, 2.6, and 2.6, respectively. The results indicate that the spherical particles prepared in methyl alcohol and 2-propyl alcohol followed by in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions show higher reaction rate of hydrogen evolution than the spherical particles prepared in ethyl alcohol followed by in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions.

Fig. 2 illustrates TEM images of the spherical nickel–silica composite particles before and after in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions. The as-prepared samples prepared in methyl alcohol, ethyl alcohol, and 2-propyl alcohol include spherical particles with the diameter of ca. 600–800, 200–400, and 200–400 nm as shown in Fig. 2a, c, and e, respectively. After in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions, the hollow nickel–silica composite spheres were obtained. All the catalysts maintain the particle size same as the as-prepared spherical particles, however, each catalyst has intrinsic hollow structure. The sample prepared in methyl alcohol followed by in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions has few spherical particles with hollow structure as shown in Fig. 2b. From the figure, the diameter of the spherical particles was the same as that of the particles of the as-prepared sample. On the other hand, from Fig. 2d, the sample prepared in ethyl alcohol followed by in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions has hollow spheres with the wall thickness of ca. 60 nm and the diameter of the hollow spheres same as that of the particles in the as-prepared sample, indicating that the hollow nickel–silica composite spheres was formed during the dehydrogenation in aqueous $NaBH_4/NH_3BH_3$ solution. The sample prepared in 2-propyl alcohol followed by in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions has few spherical particles with hollow structure as shown in Fig. 2f. From the figure, the diameter of the spherical particles was the same as that of the particles of the as-prepared sample.

Fig. 3 shows the diffuse reflectance of UV–Vis (DRUV–Vis) absorption spectra of spherical nickel–silica composite particles before and after in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions. In all the spectra before the reaction, the observed absorption bands can be attributed to the electronic transitions assigned as ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ and ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ located at 350–400 nm and at 550–650 nm for $Ni^{2+}$, respectively [25], indicating that all the samples before the reaction include octahedral coordination of Ni(II). Compared with the spectra of all the samples before the reaction, the intensity of those peaks in the spectra of all the samples after the reaction decreased. These results and the results in Fig. 1 indicate that nickel species in all the as-prepared spherical particles can be sufficiently reduced to show high activity for hydrolytic dehydrogenation of $NH_3BH_3$ in aqueous $NaBH_4/NH_3BH_3$ solution.

Fig. 4 shows hydrogen evolution from aqueous $NH_3BH_3$ solution in the presence of the in situ synthesized spherical nickel–silica composite particles. All the in situ synthesized spherical particles show the catalytic activity for the dehydrogenation of $NH_3BH_3$ introducing additional aqueous $NH_3BH_3$ solution in the suspension of the in situ synthesized spherical particles. The reaction rate and the amount of hydrogen evolution depend on the catalysts. The evolution of 58, 50, and 63 mL hydrogen was finished in 45, 90, and 45 min in the presence of the in situ synthesized spherical particles prepared in methyl alcohol, ethyl alcohol, and 2-propyl alcohol introducing additional aqueous $NH_3BH_3$ solution in the solution, respectively. The result indicates that all the in situ synthesized spherical particles have the ability for recycle use for hydrolysis of $NH_3BH_3$, and the hydrogen evolution rate and amount depend on the catalyst. The in situ synthesized spherical particles obtained from as-prepared samples prepared in methyl

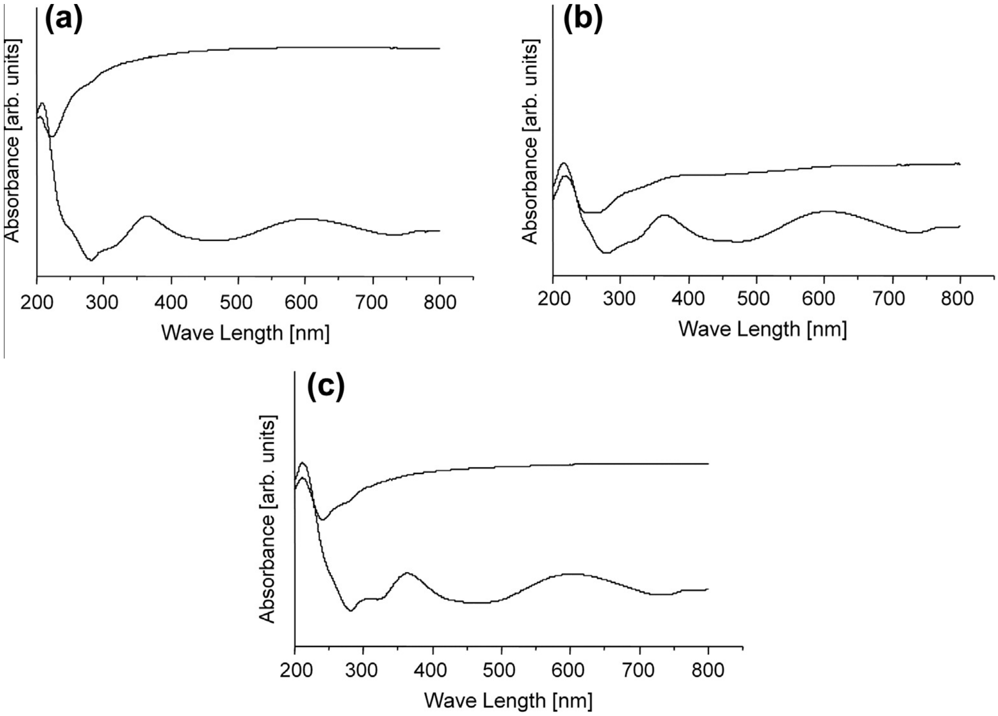

**Fig. 3.** DRUV–Vis spectra of spherical nickel–silica composite particles prepared in (a) methyl alcohol, (b) ethyl alcohol, and (c) 2-propyl alcohol before and after in situ activation in aqueous $NaBH_4/NH_3BH_3$ solutions.

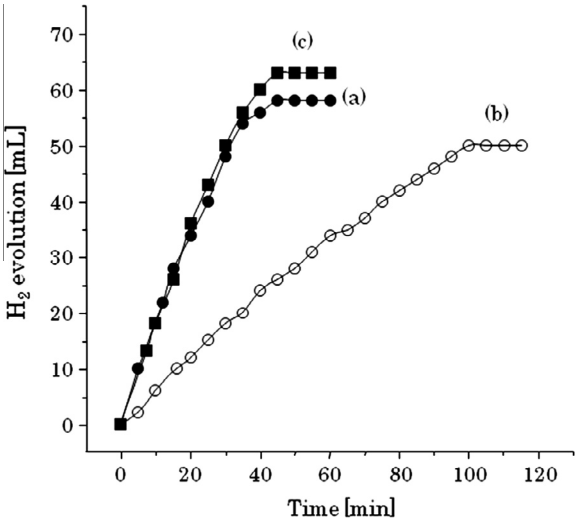

**Fig. 4.** Hydrogen generation from the hydrolysis of $NH_3BH_3$ in the presence of in situ synthesized spherical nickel–silica composite particles prepared in (a) methyl alcohol, (b) ethyl alcohol, and (c) 2-propyl alcohol. Ni/$NH_3BH_3$ = 0.06 (at each cycle) at room temperature in air.

alcohol and 2-propyl alcohol show higher rate and amount of hydrogen evolution than in situ synthesized spherical particles obtained from as-prepared samples prepared in ethyl alcohol. It has been reported that the catalytic activity of the hollow nickel–silica composite spheres depends on the reducibility of active nickel species included in the hollow spheres and that the reducibility of the nickel species depends on the preparation conditions of the hollow spheres [26]. While the difference of the hydrogen evolution rates and amounts among the catalysts in this study was not so large, it might be related with the reducibility of the active nickel species included in the spherical particles.

## 4. Conclusion

Spherical nickel–silica composite particles were synthesized by sol–gel based method in various solvent using L(+)-arginine as a promoter for the reaction followed by in situ activation in aqueous $NaBH_4$/$NH_3BH_3$ solutions. The resulting powder products prepared in methyl alcohol, ethyl alcohol, and 2-propyl alcohol include spherical particles with the diameters of nm, 600–800, 200–400 nm, and 200–400 nm, respectively. The evolution of 56, 58, and 62 mL hydrogen was finished in about 50, 90, and 65 min in the presence of the spherical nickel–silica composite particles prepared in methyl alcohol, ethyl alcohol, and 2-propyl alcohol from aqueous $NaBH_4$/$NH_3BH_3$ solution, respectively, indicating that the hydrogen evolution rate in the presence of spherical particles prepared in each solvent are the same as each other. The evolution of 58, 50, and 63 mL hydrogen was finished in about 45, 90, and 45 min introducing additional aqueous $NH_3BH_3$ solution to the solution in the presence of the in situ synthesized spherical nickel–silica composite particles prepared in methyl alcohol, ethyl alcohol, and 2-propyl alcohol, respectively, indicating all the in situ synthesized spherical particles have the ability for recycle use for hydrolysis of $NH_3BH_3$. The in situ synthesized spherical particles prepared in methyl alcohol and 2-propyl alcohol show higher rate and amount of hydrogen evolution than in situ synthesized spherical particles prepared in ethyl alcohol.

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## References

[1] Q. Xu, M. Chandra, J. Power Sources 163 (2006) 364–370.
[2] J.-M. Yan, X.-B. Zhang, S. Han, H. Shioyama, Q. Xu, Inorg. Chem. 48 (15) (2009) 7389–7393.
[3] T. Umegaki, J.-M. Yan, Z.-B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, Int. J. Hydrogen Energy 34 (9) (2009) 3816–3822.
[4] T. Umegaki, J.-M. Yan, X.-B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, J. Power Sources 191 (2009) 209–216.
[5] Ö. Metin, S. Özkar, S. Sun, Nano Res. 3 (9) (2010) 676–684.
[6] Ö. Metin, S. Özkar, Int. J. Hydrogen Energy 36 (2011) 1424–1432.
[7] P.Z. Li, K. Aranishi, Q. Xu, Chem. Commun. 48 (26) (2012) 3173–3175.
[8] M. Yang, J. Ma, C.L. Zhang, Z.Z. Yang, Y.F. Lu, Angew. Chem. Int. Ed. 44 (2005) 6727–6730.
[9] D.G. Shchukin, E.A. Ustinovich, G.B.H. Sukhorukov Mohwald, D.V. Sviridov, Adv. Mater. 17 (2005) 468–472.
[10] M.M. Ren, R. Ravikrishna, K.T. Valsaraj, Environ. Sci. Technol. 40 (2006) 7029–7033.
[11] P. Jiang, J.F. Bertone, V.L. Colvin, Science 291 (2001) 453–457.
[12] Y. Li, J. Shi, Z. Hua, H. Chen, M. Ruan, D. Yan, Nano Lett. 3 (2003) 609–612.
[13] U. Jeong, Y.L. Wang, M. Ibisate, Y.N. Xia, Adv. Funct. Mater. 15 (2005) 1907–1921.
[14] I. Tissot, J.P. Reymond, F. Lefebvre, E. Bourgeat-lami, Chem. Mater. 14 (3) (2002) 1325–1331.
[15] A. Imhof, Langmuir 17 (12) (2001) 3579–3585.
[16] P.J. Bruinsma, A.Y. Kim, J. Liu, S. Baskaran, Chem. Mater. 9 (11) (1997) 2507–2512.
[17] Y. Lu, H. Fan, A. Stump, T.L. Ward, T. Rieker, C.J. Brinker, Nature 398 (1999) 223–226.
[18] B.M. Discher, Y.Y. Won, D.S. Ege, J.C.M. Lee, F.S. Battes, D.E. Discher, Science 284 (1999) 1143–1146.
[19] T. von Werne, T.E. Patten, J. Am. Chem. Soc. 123 (31) (2001) 7497–7505.
[20] H. Wang, Y. Song, C.J. Medforth, J.A. Shelnutt, J. Am. Chem. Soc. 128 (29) (2006) 9284–9285.
[21] T. Chen, P.J. Colver, A.F. Bon, Adv. Mater. 19 (17) (2007) 2286–2289.
[22] P.M. Arnal, C. Weidenthaler, F. Schüth, Chem. Mater. 18 (11) (2006) 2733–2739.
[23] M. Titirici, M. Antonietti, A. Thomas, Chem. Mater. 18 (16) (2006) 3808–3812.
[24] T. Yokoi, Y. Sakamoto, O. Terasaki, Y. Kubota, T. Okubo, T. Tatsumi, J. Am. Chem. Soc 128 (42) (2006) 13664–13665.
[25] D. Brühwiler, H. Frei, J. Phys. Chem. B 107 (33) (2003) 8547–8556.
[26] T. Umegaki, C. Takei, Y. Watanuki, Q. Xu, Y. Kojima, J. Mol. Catal. A: Chem. 371 (2013) 1–7.