

Synthesis of Longtime Water/Air-Stable Ni Nanoparticles and Their High Catalytic Activity for Hydrolysis of Ammonia–Borane for Hydrogen Generation

Jun-Min Yan, Xin-Bo Zhang, Song Han, Hiroshi Shioyama, and Qiang Xu*

National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan

Received May 12, 2009

In this paper, two kinds of Ni nanoparticles have been successfully synthesized without and with starch as the “green” protective material and investigated as catalysts for generating hydrogen from ammonia borane (NH_3BH_3 , AB). Experimental investigations have demonstrated that both of the Ni nanoparticles possess high catalytic activities for H_2 generation from aqueous solution of AB. However, the catalytic activities of Ni nanoparticles without starch decrease seriously in the course of the lifetime tests. In contrast, the catalytic activities of the Ni nanoparticles with starch almost keep unchanged even after 240 h. Moreover, the XPS results show that the surface of the Ni nanoparticles in starch solution is still metallic Ni even after 240 h, while that in pure water is nickel oxide. This means that starch can successfully keep the Ni nanoparticles in aqueous solution from the oxidation in air. The present efficient, low-cost, and longtime water/air stable Ni catalyst represents a promising step toward the development of AB as a viable on-board hydrogen storage and supply material.

Introduction

With the energy crisis and greenhouse gas emissions affecting political and environmental climates, there have been intensive studies to develop efficient and safe methods for hydrogen storage to overcome this major hurdle along the

way to a “hydrogen energy” society.¹ Ammonia-borane (NH_3BH_3 , AB) has a hydrogen content of 19.6 wt %, which exceeds that of gasoline and therefore makes it an attractive candidate for chemical hydrogen-storage applications.^{2–4} 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.^{3,4} 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 AB with high efficiency.⁵ However, the success in their application highly depends on the stability of the nanoparticles because of their high tendency to form agglomerates and their extreme reactivity toward water and oxygen.⁶

*To whom correspondence should be addressed. E-mail: q.xu@aist.go.jp.

- (1) (a) Grochala, W.; Edwards, P. P. *Chem. Rev.* **2004**, *104*, 1283–1316. (b) Chen, P.; Xiong, Z.; Luo, J.; Lin, J.; Tan, K. L. *Nature* **2002**, *420*, 302–304. (c) Schlappbach, L.; Züttel, A. *Nature* **2001**, *414*, 353–358. (d) Ogden, J. M. *Annu. Rev. Energ. Env.* **1999**, *24*, 227–279. (2) (a) Gutowska, A.; Li, L. Y.; Shin, Y. S.; Wang, C. M. M.; Li, X. H. S.; Linehan, J. C.; Smith, R. S.; Kay, B. D.; Schmid, B.; Shaw, W.; Gutowski, M.; Autrey, T. *Angew. Chem.* **2005**, *117*, 3644–3648. *Angew. Chem., Int. Ed.* **2005**, *44*, 3578–3582. (b) Chen, Y. S.; Fulton, J. L.; Linehan, J. C.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254–3255. (c) Sit, V.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1987**, *113*, 379–382. (3) (a) Yan, J.-M.; Zhang, X.-B.; Han, S.; Shioyama, H.; Xu, Q. *Angew. Chem.* **2008**, *120*, 2319–2321. *Angew. Chem., Int. Ed.* **2008**, *47*, 2287–2289. (b) Clark, T. J.; Whittell, G. R.; Manners, I. *Inorg. Chem.* **2007**, *46*, 7522–7527. (c) Cheng, F. Y.; Ma, H.; Li, Y. M.; Chen, J. *Inorg. Chem.* **2007**, *46*, 788–794. (d) Chandra, M.; Xu, Q. *J. Power Sources* **2007**, *168*, 135–142. (e) Paul, A.; Musgrave, C. B. *Angew. Chem.* **2007**, *119*, 8301–8304. *Angew. Chem., Int. Ed.* **2007**, *46*, 8153–8156. (f) Yoon, C. W.; Sneddon, L. G. *J. Am. Chem. Soc.* **2006**, *128*, 13992–13993. (g) Xu, Q.; Chandra, M. *J. Power Sources* **2006**, *163*, 364–370. (h) Chandra, M.; Xu, Q. *J. Power Sources* **2006**, *159*, 855–860. (i) Chandra, M.; Xu, Q. *J. Power Sources* **2006**, *156*, 190–194. (j) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *Chem. Commun.* **2001**, *11*, 962–963. (4) (a) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613–2626. (b) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem.* **2007**, *119*, 760–763. *Angew. Chem., Int. Ed.* **2007**, *46*, 746–749. (c) Keaton, R. J.; Blacque, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844–1845. (d) Denney, M. C.; Pons, V.; Hebdon, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048–12049. (e) Bluhm, M. E.; Bradley, M. G.; Butterick III, R.; Kusari, U.; Sneddon, L. G. *J. Am. Chem. Soc.* **2006**, *128*, 7748–7749.

- (5) (a) Kawamura, M.; Sato, K. *Chem. Commun.* **2006**, 4718–4719. (b) Jun, C. H.; Park, Y. J.; Yeon, Y. R.; Choi, J.; Lee, W.; Ko, S.; Cheon, J. *Chem. Commun.* **2006**, 1619–1621. (c) Hu, A.; Yee, G. T.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 12486–12487. (d) Ambashta, R. D.; Mohammad Yusuf, S.; Mukadam, M. D.; Singh, S.; Kishan Wattal, P.; Bahadur, D. *J. Magn. Magn. Mater.* **2005**, *293*, 8–14. (e) Lu, A. H.; Schmidt, W.; Matoussevitch, N.; Bönnemann, H.; Spliethoff, B.; Tesche, B.; Bill, E.; Kiefer, W.; Schüth, F. *Angew. Chem.* **2004**, *116*, 4403–4406. *Angew. Chem., Int. Ed.* **2004**, *43*, 4303–4306. (f) Gao, X.; Yu, K. M. K.; Tam, K. Y.; Tsang, S. C. *Chem. Commun.* **2003**, 2998–2999. (g) Hirsch, R.; Katz, E.; Willner, I. *J. Am. Chem. Soc.* **2000**, *122*, 12053–12054. (h) Kalidindi, S. B.; Indirani, M.; Jagirdar, B. R. *Inorg. Chem.* **2008**, *47*, 7424–7429. (i) Kalidindi, S. B.; Sanyal, U.; Jagirdar, B. R. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5870–5874. (6) (a) Lu, A. H.; Salabas, E. L.; Schüth, F. *Angew. Chem.* **2007**, *119*, 1242–1266. *Angew. Chem., Int. Ed.* **2007**, *46*, 1222–1244. (b) Grass, R. N.; Athanassiou, E. K.; Stark, W. J. *Angew. Chem.* **2007**, *46*, 4909–4912. *Angew. Chem., Int. Ed.* **2007**, *46*, 4909–4912. (c) Dobson, J. *Gene Ther.* **2006**, *13*, 283–287. (d) Huber, D. L. *Small* **2005**, *1*, 482–501.

A general solution to stabilize or protect the metallic nanoparticles is to coat them with some outer materials including the precious metals, silica, transition-metal oxides, carbon, and also polymers.⁷ Among these coating materials, only polymers have the relatively weak binding interaction with the nanoparticles which is vital for the catalytic application where surface catalytically active sites are urgently needed.⁸ However, those metallic nanoparticles dispersed in the solution of polymeric materials are commonly not air stable.^{6a} Moreover, most of the preparation procedures reported to date rely heavily on organic solvents (not an aqueous phase, mainly because of the hydrophobicity of the capping agent used), expensive and/or toxic organometallic compounds (metal precursors), and synthetic macromolecules (capping and/or dispersing agents), as well as high temperature and high dilution conditions,^{7a,c,e} and thus inevitably resulting in high production cost and serious environmental issues while addressing industrial production. Therefore, finding suitable and effective protection agents to maintain and exert the potent catalytic ability of magnetic nanoparticles in aqueous solution or even in air is still a challenge to be faced.

Soluble starch (amylose), a renewable polymer, is the main component of starch which is the main energy reserve of all higher plants, and can form a dispersion in water.⁹ Recently, it has been successfully applied as the dispersing agent for synthesis of some relatively inoxidizable metal nanoparticles, such as noble metal nanoparticles.¹⁰ Although starch binds gently to inner nanoparticles and thus is very favorable to be used as protecting agent for nanoparticles for catalytic application, there is no experimental result to dispel the major misgiving that those polymer-coated metallic magnetic nanoparticles are commonly not air stable.

Herein, we first apply soluble starch not only as the dispersing agent but also as the air resistance coatings for the facile synthesis of Ni nanoparticles in aqueous solution in air (water/air) at room temperature, which completely avoid the use of volatile organic solvents, expensive organometallic precursors, and synthetic macromolecules. This is of pivotal importance from a "green" synthetic strategy and industrial scale manufacture perspective. The Ni nanoparticles as synthesized possess high catalytic activity to hydrolyze NH_3BH_3 for chemical hydrogen storage at room temperature. Most importantly, the present work is the first case that Ni nanoparticles could possess water/air stability and keep their catalytic activity over a longtime period (240 h).

(7) (a) Thunemann, A. F.; Schutt, D.; Kaufner, L.; Pison, U.; Mohwald, H. *Langmuir* **2006**, *22*, 2351–2357. (b) Sen, T.; Sebastianelli, A.; Bruce, I. J. *J. Am. Chem. Soc.* **2006**, *128*, 7130–7131. (c) Peng, S.; Wang, C.; Xie, J.; Sun, S. H. *J. Am. Chem. Soc.* **2006**, *128*, 10676–10677. (d) Lee, I. S.; Lee, N.; Park, J.; Kim, B. H.; Yi, Y. W.; Kim, T.; Kim, T. K.; Lee, I. H.; Paik, S. R.; Hyeon, T. *J. Am. Chem. Soc.* **2006**, *128*, 10658–10659. (e) Puentes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115–2117. (f) Park, J. I.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5743–5746. (g) Hayashi, T.; Hirono, S.; Tomita, M.; Umemura, S. *Nature* **1996**, *381*, 772–774.

(8) (a) Heiz, U.; Landman, U.; *Nanocatalysis*; Springer: Berlin, 2006. (b) Helveg, S.; Lopez-Cartes, C.; Sehested, J.; Hansen, P. L.; Clausen, B. S.; Rostrup-Nielsen, J. R.; Abild-Pedersen, F.; Norskov, J. K. *Nature* **2004**, *427*, 426–429. (c) Somorjai, G. A.; Blakely, D. W. *Nature* **1975**, *258*, 580–583.

(9) van Soest, J. J. G.; Tournois, H.; de Wit, D.; Vliegthart, J. F. G. *Carbohydr. Res.* **1995**, *279*, 201–214.

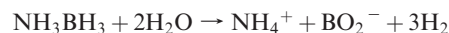
(10) (a) Batabyal, S. K.; Basu, C.; Das, A. R.; Sanyal, G. S. *J. Biobased Mater. Bioenergy* **2007**, *1*, 143–147. (b) Raveendran, P.; Fu, J.; Wallen, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13940–13941.

Experimental Section

Chemicals. Ammonia–borane (NH_3BH_3 , AB, Aldrich, 90%), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Wako Pure Chemical Industries, Ltd., > 98%), and sodium borohydride (NaBH_4 , Aldrich, 99%), starch from potatoes ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$, Aldrich, solubility: 20 mg/mL H_2O), sodium hydroxide (NaOH , Aldrich, 97%) were used as received. Ultrapure water with the specific resistance of $18.2 \text{ M}\Omega \cdot \text{cm}$ was obtained by reversed osmosis followed by ion-exchange and filtration (RFU 555DA, Toyo Roshi Kaisha, Ltd., Japan).

Preparation of Starch Solution. Starch powder was added into the ultrapure water (1 wt %), heated at 368 K for 15 min, and then the clear solution was cooled down to room temperature and was ready for use.

In Situ Synthesis of Ni Particles in Starch Solution and Their Catalytic Activity to AB Hydrolysis under Ambient Atmosphere. A mixture of AB (90.0 mg) and NaBH_4 (14.0 mg) was kept in a two-necked round-bottom flask. One neck was connected to a gas buret, and the other was connected to a pressure-equalization funnel where 62.2 mg of NiCl_2 was added into 10 mL of a 1.0 wt % aqueous solution of soluble starch. The reaction was started when the aqueous NiCl_2 and starch solution was added to the mixture of NaBH_4 and AB with vigorous shaking. The hydrolysis of AB can be briefly expressed as follows:^{3a,b–d,3g–i,5h,i}



The evolution of gas was monitored using the gas buret. The reactions were carried out at room temperature under ambient atmosphere. Mass spectrum (Balzers Prisma QMS 200 mass spectrometer) was used to analyze the gas composition generated from the hydrolysis of AB.

In Situ Synthesis of Ni Particles in Pure Water and Their Catalytic Activity to AB Hydrolysis under Ambient and Argon Atmospheres. A mixture of AB (90.0 mg) and NaBH_4 (14.0 mg) was kept in a two-necked round-bottom flask. One neck was connected to a gas buret, and the other was connected to a pressure-equalization funnel to introduce the aqueous solution of NiCl_2 (0.26 M, 10 mL). The reaction was started when the aqueous NiCl_2 solution was added to the mixture of NaBH_4 and AB with vigorous shaking. The reactions were carried out at room temperature under ambient and argon atmospheres. The evolution of gas was monitored using the gas buret. The mass spectrum was used to analyze the gas composition generated from the hydrolysis of AB.

Heat Treatment of the in Situ Synthesized Ni Catalyst. The *in situ* synthesized Ni particles were washed with water and dried in argon, and then were transferred into a furnace where a continuous argon gas flow was introduced at the rate of 30 mL/min. The furnace temperature was elevated to 773 K and maintained for 2.5 h. After heat treatment, the Ni specimen was used for the X-ray diffraction (XRD) analysis.

Uninterrupted Lifetime Experiments of the Ni Nanoparticles with/without Starch under Ambient Atmosphere. After the hydrogen generation reaction was completed, another equivalent of AB (90 mg) was immediately added to the reactor containing the mixture of reaction solution and the Ni catalyst. The released gas was then monitored by the gas buret. Such lifetime experiments were repeated for 10 times for Ni particles with and without starch under ambient atmosphere, respectively.

Long-term Lifetime Experiments of the Ni Nanoparticles with/without Starch under Ambient Atmosphere. Keeping the Ni nanoparticles with and without starch protection in their reaction solution in air and, after every 24 h, another equivalent of AB (90 mg) was added to the two reaction systems, and the released gas was monitored by the gas buret.

Catalyst Characterization. XRD was performed on a Rigaku RINT-2000 X-ray diffractometer with $\text{Cu K}\alpha$ for the *in situ*

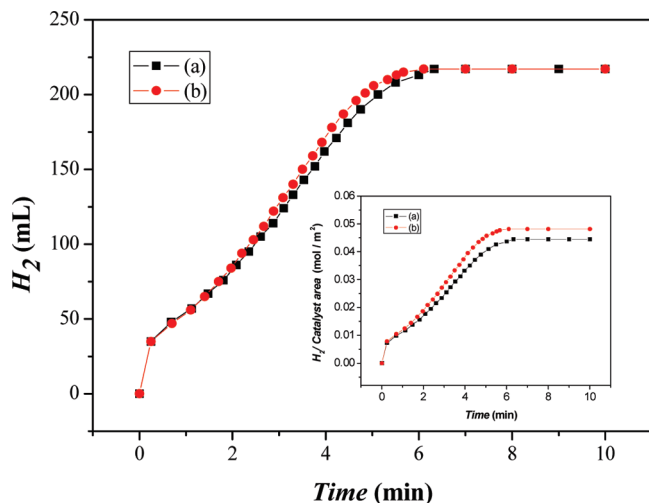


Figure 1. Hydrogen generation from the hydrolysis of AB catalyzed by Ni nanoparticles ($\text{Ni}/\text{AB} = 0.10$) (a) in starch solution (1 wt %, 10 mL) and (b) in pure water (10 mL) under ambient atmosphere at room temperature. Inset is the catalytic activity denoted as the ratio of the generated H_2 (mol) to the specific surface area (m^2) of Ni nanoparticles (a) in starch solution (1 wt %, 10 mL) and (b) in pure water (10 mL) under ambient atmosphere at room temperature.

synthesized Ni nanoparticles with/without starch after removing from the reaction solution, washing with water, and drying in argon atmosphere. A glass substrate holding the powder sample was covered by an adhesive tape on the surface to prevent the sample from exposure to air during the measurements. Transmission electron microscopy (TEM, Hitachi H-9000NA) were applied for the detailed microstructure information of the *in situ* synthesized Ni particles (with/without starch) before and after the lifetime experiments. The TEM samples were prepared by depositing one or two droplets of the nanoparticle suspensions onto the amorphous carbon coated copper grids, which were dried in argon atmosphere. X-ray photoelectron spectrometry (XPS) analysis was applied after the catalysts were washed with water and dried in argon on a Shimadzu ESCA-3400 using an Mg K α source (10 kV, 10 mA). Nitrogen sorption measurements were carried out on an automatic volumetric adsorption equipment (BEL mini, Japan) using the Brunauer–Emmett–Teller (BET) method to test the surface areas of the *in situ* synthesized catalysts with/without starch after washing with water and vacuum drying at 90 °C.

Results and Discussion

Figure 1a demonstrates the hydrogen generation from AB catalyzed by the *in situ* synthesized Ni particles dispersed in starch solution (Ni/AB is 0.10) under ambient atmosphere. The black particles were rapidly generated in the first 15 s. Then these particles exert good catalytic activity, with which the hydrolysis reaction of AB is completed within only 6 min. The molar ratio of hydrolytically generated H_2 to the initial AB is close to 3.0, indicating dehydrogenation is completed. The excellent catalytic activity may be attributed to its amorphous state (as shown in Figure 2a), which is considered to hold many more catalytic active sites than its crystalline counterpart.^{3g,11} More interestingly, the above-mentioned *in situ* prepared Ni particles with starch possess excellent lifetime capability than those *in situ* synthesized in pure water under ambient atmosphere (vide infra).

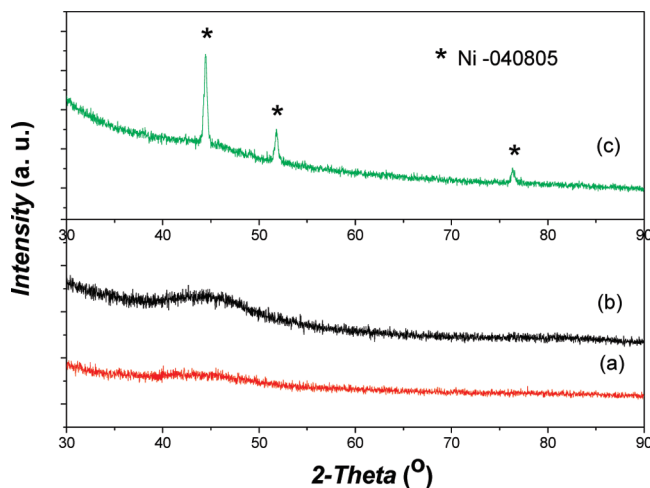


Figure 2. X-ray diffraction patterns of *in situ* synthesized Ni specimens of (a) with starch and (b) without starch after washing and drying at room temperature in argon atmosphere, and (c) XRD pattern of sample (a) after heat treatment at 773 K for 2.5 h in argon.

Figure 1b presents the hydrogen generation of AB in pure water catalyzed by *in situ* synthesized Ni particles ($\text{AB}/\text{NiCl}_2/\text{NaBH}_4 = 1.0:0.10:0.14$) under ambient atmosphere. For comparison, we also carried out the same reaction in pure water in argon.¹² The results prove that, whether under ambient atmosphere or in argon, the hydrolysis reaction catalyzed by the “naked” Ni particles (without protection of starch) can be completed within the same period as that catalyzed by the starched Ni particles. Moreover, the Ni particles without starch are also in an amorphous state, as shown in Figure 2b.

The obtained BET surface areas for the two Ni specimens synthesized with and without starch under ambient atmosphere are 13 and 12 m^2/g , respectively. On the basis of the BET surface areas and the H_2 generation data of Figure 1, we calculated the ratio of the generated H_2 (mol) to the specific surface area (m^2) of the two Ni specimens as the function of the reaction time, as seen in Figure 1 (inset). The two samples with and without starch show values of 4.4×10^{-2} and 4.8×10^{-2} mol/m^2 , respectively, which are close to each other.

Evidenced by Figure 1, the starch does not obviously suppress the catalytic reaction between the catalyst and the reactant, namely, the surface active sites of Ni are mostly maintained with the presence of foreign protection shell, soluble starch. This also implies that the binding interaction between starch and the Ni nanoparticles is very weak; thus, the protection should be easily reversible, enabling the easy separation of these particles.

To investigate the composition of the solid catalysts, XPS analysis was applied for the *in situ* synthesized Ni nanoparticles with starch after washing with water and drying in argon. The results were presented in Figure 3. The Ni 2p $_{3/2}$ and Ni 2p $_{1/2}$ are centered at approximately 852.4 and 869.7 eV respectively, which coincides with those of metallic Ni.¹³ Moreover, no element of B is found in the sample as seen from Figure 2b, which means that no metal borides are formed in present case. This can also be proved by the XRD result of the same Ni sample after annealing at 773 K for 2.5 h (Figure 2c). After annealing, the amorphous Ni

(11) (a) Deng, J. F.; Li, H.; Wang, W. *Catal. Today* **1999**, *51*, 113–125.
(b) Cao, H.; Suib, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5334–5342.

(12) See Supporting Information.

(13) Furstenau, R. P.; McDougall, G.; Langell, M. A. *Surf. Sci.* **1985**, *150*, 55.

sample crystallizes into metallic Ni phase, and no boride phase is found in the diffraction pattern. Therefore, on the basis of the XPS and XRD results, it can be concluded that the present *in situ* synthesized Ni catalyst has the component of pure metallic Ni phase.

TEM of the two Ni samples synthesized in starch solution and pure water are displayed in Figure 4, panels a and b, respectively. Without starch, the Ni particles are made of aggregates with diameters of about 40 nm; each aggregate is an assembly of many smaller Ni nanoparticles. Moreover, those aggregates are further condensed to form some macroscopical particles in the solution. On the contrary, with starch, the Ni particles have smaller sizes (less than 10 nm) than that in the solution without starch, although they are also some aggregates of small particles.¹² Notably, the Ni nanoparticles with starch are dispersed well, and these well dispersed particles can form a good suspension even after 10 days. Therefore, it has been shown that soluble starch can be used to synthesize robust and well-dispersed Ni nanoparticles.

In our present work, very cheap inorganic Ni salt and starch from potatoes were successfully used as the metal precursor and dispersing/protecting material, respectively. The use of environmentally benign and renewable materials as the dispersing/protecting agent offers numerous benefits ranging from environmental safety to ready integration of these nanoparticles to biologically relevant systems.

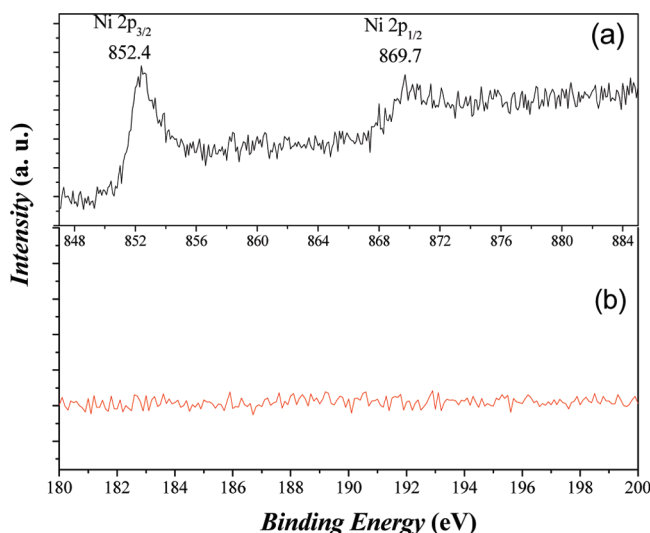


Figure 3. XPS results for elements of (a) Ni and (b) B of the *in situ* synthesized Ni nanoparticles in starch after washing with water and drying in argon.

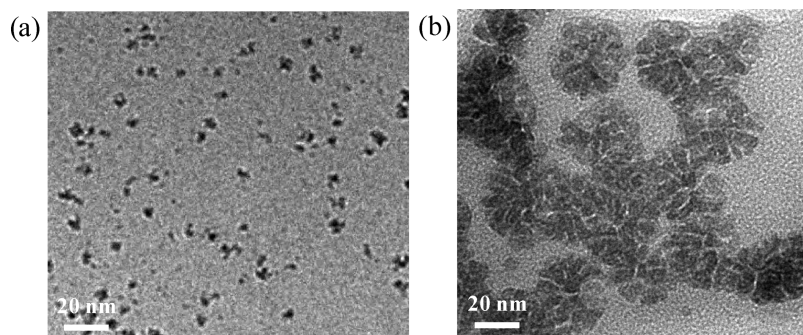


Figure 4. TEM micrographs of Ni nanoparticles *in situ* synthesized (a) in starch solution and (b) in pure water.

Additionally, using a gentle binding agent, starch-protected nanoparticles could be easily functionalized.^{10b}

The stability or lifetime ability is very important for the practical application of every catalyst. In this sense, the lifetime experiments of the Ni nanoparticles dispersed in starch solution and water were both tested under ambient atmosphere for comparison. The uninterrupted lifetime stability (another equivalent of AB was added immediately after the previous cycle) of the prepared Ni catalyst with and without starch is shown in Figure 5 (inset). Interestingly, without starch, the reaction time was almost linearly increased from 6 to approximately 100 min after 10 cycles, while the starched Ni nanoparticles showed no obvious activity decrease after the same cycles. Further, the longtime stability of the above two samples were investigated by lifetime tests after every 24 h under ambient atmosphere. Unexpectedly, the reaction time for a system of starched Ni catalyst was about 17 min even after 240 h under ambient atmosphere (Figure 5a), whereas the reaction time for a system of “naked” Ni catalyst was significantly increased during the same period under ambient atmosphere to 413 min (Figure 5b). This excellent longtime water/air stability would be ascribed to starch which is believed to protect well the surface of Ni nanoparticles against oxidation based on the results of XPS.¹² It is interesting that the metal atoms on the nanoparticle surface are accessible to the ammonia-borane substrate, but not for dioxygen molecule. This might

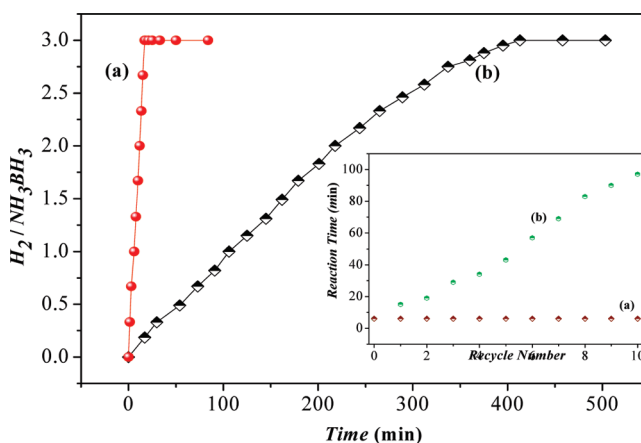


Figure 5. Hydrogen generation from the hydrolysis of AB catalyzed by Ni nanoparticles (Ni/AB = 0.10) (a) with starch and (b) without starch at the 10th 24 h lifetime experiment under ambient atmosphere at room temperature. Inset: The reaction time for the uninterrupted lifetime testing of Ni nanoparticles (a) with starch and (b) without starch vs the cycle number.

be understood in that the hydroxyl ($-OH$) groups make starch hydrophilic and thus the starch protected Ni nanoparticles can be readily accessible for the hydrophilic ammonia-borane molecules, but not for the hydrophobic dioxygen molecules. After 240 h under ambient atmosphere, the Ni nanoparticles still show a good homogeneous suspension in the starch aqueous solution, and the particle size is almost the same,¹² while the surface-oxidized Ni nanoparticles without protection of starch are heavily aggregated and settled down to the bottom of the reactor.

In summary, we have explored a facile and low-cost, but very efficient, method to prepare long-term water/air stable Ni nanoparticles by using the green dispersing/protecting agent, soluble starch. The Ni nanoparticles used as synthesized possess high catalytic activity and excellent cyclic stability for the H_2 generation from ammonia borane under ambient atmosphere. The efficient and low-cost catalyst and the mild reaction condition represent a promising step toward the development of AB as a viable on-board hydrogen storage medium. Such a catalyst is expected to be

useful for fuel cells, metal-air batteries, and electrochemical sensors. Moreover, the use of environmentally benign and renewable materials as the dispersing/protecting agent for preparing water/air stable magnetic nanoparticles offers numerous benefits ranging from environmental safety to ready integration of these nanoparticles to biologically relevant systems. Additionally, using a gentle binding agent, starch-protected nanoparticles could be easily functionalized. The concepts behind these preliminary results present a wide range of possibilities for the further development of green synthesis of air and water-stable magnetic nanoparticles.

Acknowledgment. We gratefully thank AIST and NEDO for financial support.

Supporting Information Available: MS analysis of generated gases, XRD, XPS, and TEM results of the catalysts. This material is available free of charge via the Internet at <http://pubs.acs.org>.