Short communication

Magnetically recyclable Fe–Ni alloy catalyzed dehydrogenation of ammonia borane in aqueous solution under ambient atmosphere

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ABSTRACT

In this work, we report a very simple method to *in situ* prepare the $Fe_{1-x}Ni_x$ ($x = 0, 0.3, 0.4, 0.5, 0.7$ and 1) nano-alloys as the catalysts for H_2 generation from the aqueous NH_3BH_3 solution under ambient atmosphere at room temperature. The prepared nano-alloys possess Pt-like high catalytic activity, especially for the specimen of $Fe_{0.5}Ni_{0.5}$, with which the hydrolysis of NH_3BH_3 would totally complete in only 2.2 min. Moreover, these catalysts can be easily magnetically separated for recycle purpose, and can almost keep the same high activity even after 5 times of recycle under ambient atmosphere. Such alloy catalysts are expected to be useful for fuel cells, metal–air batteries and electrochemical sensors. Moreover, the concepts behind these preliminary results present a wide range of possibilities for the further development of synthesis of air and water-stable magnetic nano-alloys.

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1. Introduction

Bimetallic nano-alloys are currently attracting much attention as catalysts due to the distinct catalytic properties from those of the pure elemental nanomaterials [1–5]. As catalysts, their separation and recycling are essential steps and frequently affect the overall process economy. Recently, magnetic nanomaterials containing iron family elements (Fe, Co, and Ni), the typical ferromagnetic elements at room temperature (293 K) [6], with good stability are of great interest in catalysis applications because of the easy magnetic separation, especially in a liquid-phase reaction, which makes the recovery of such catalysts much easier than by filtration and centrifugation [7–12]. In this sense, magnetic nano-alloys as catalysts are therefore expected to occupy the superiorities of both nano-alloys and magnetic nanomaterials with different or better catalytic activities than their elemental counterparts and easy magnetically separable/reusable advantages. However, to our best knowledge, if application in an oxidization environment, such as in water or air, the other metallic part of magnetic nano-alloys is usually a noble metal, i.e. Pt or Au, etc. [13–16] One of the important reasons is because Fe family elements have extreme reactivity with respect to water and oxygen, especially in nanoscale, and the combining with the less-reactive metals, noble metals, will effectively enhance the oxygen-resistance ability and thus increase the air-stability as comparable to the pure Fe family metals [9]. Therefore, the application

of nano-alloy catalysts containing only Fe family metals, such as Fe–Ni alloy, under ambient atmosphere or water is now still a big challenge.

With increasing demand for clean 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 "Hydrogen energy society" [17–19]. Ammonia borane (NH_3BH_3) 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 [20–28]. The development of efficient, low-cost and stable catalysts to further improve the kinetic properties under moderate conditions is therefore important for the practical application of these systems [23–33].

In this work, we report a very simple method to *in situ* prepare the Fe–Ni nano-alloys, and apply the air/water-stable Fe–Ni alloys as the magnetically recyclable catalysts to the hydrogen generation from NH_3BH_3 aqueous solution under ambient atmosphere at room temperature.

2. Experiment

2.1. Chemicals

Ammonia borane (NH_3BH_3, Aldrich, 90%), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Wako Pure Chemical Industries, Ltd., >99%), nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Wako Pure Chemical Industries, Ltd., >98%), and sodium borohydride ($NaBH_4$, Aldrich, 99%) were used as received. Ultrapure water with the specific resis-

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tance of 18.3 MΩ•cm was obtained by reversed osmosis followed by ion exchange and filtration (Yamato-WQ 500, Millipore, Japan).

2.2. Catalytic study of the in situ synthesized $Fe_{1-x}Ni_x$ alloy particles

The process for the *in situ* synthesis of $Fe_{0.5}Ni_{0.5}$ alloy and its catalytic study is as follows: a mixture of $NaBH_4$ (11 mg) and NH_3BH_3 (55 mg) was kept in a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce aqueous solution of $FeSO_4$ and $NiCl_2$ mixture ($FeSO_4$: 0.096 mmol; $NiCl_2$: 0.096 mmol; H_2O: 10 mL). The reaction started when the aqueous solution was added to the mixture of $NaBH_4$ and NH_3BH_3 with violent shaking. The evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature (293 K) in argon and air, respectively.

The x value of $Fe_{1-x}Ni_x$ was changed from 0 to 1 (0, 0.3, 0.4, 0.5, 0.7 and 1) for the same catalytic reactions under ambient atmosphere.

2.3. Heat treatment of the in situ synthesized $Fe_{0.5}Ni_{0.5}$

After the *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ was separated from the solution and dried in argon atmosphere, it was transferred into a furnace where a continuous argon gas flow was introduced at the rate of 35 mL min^{-1}. Then the furnace temperature was elevated to 723 K and maintained for 2 h. The as-obtained sample after heat treatment was used for the XRD analysis.

2.4. Recycle/stability test of the in situ synthesized $Fe_{0.5}Ni_{0.5}$ nanoparticles under ambient atmosphere

After the hydrogen generation reaction was completed, the above *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ nanoparticles were magnetically attracted to the bottom of the reaction flask by a magnet, and the upper solution was removed. Then the new NH_3BH_3 aqueous solution (0.16 M, 10 mL) was added into the reaction flask. The evolution of gas was monitored using the gas burette. Such recycle experiments for the *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ catalyst were repeated for 5 times under ambient atmosphere.

2.5. Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a Rigaku RINT-2000 X-ray diffractometer with Cu Kα for the *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ nanoparticles after removed from the reaction solution and dried 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. XPS analysis was carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg Kalpha source (10 kV, 10 mA). Transmission electron microscope (TEM, JEOL, JEM-3000F) was applied for the detailed microstructure information. The TEM sample was prepared by depositing one or two droplets of the nanoparticle suspension onto the amorphous carbon coated copper grids, which were dried in argon atmosphere.

3. Results and discussion

The Fe–Ni bimetallic catalyst with the raw molar ratio of 0.5:0.5, which is denoted as $Fe_{0.5}Ni_{0.5}$, was *in situ* prepared by the reduction of $NaBH_4$ in NH_3BH_3 aqueous solution (0.16 M) under ambient atmosphere (NH_3BH_3:$FeSO_4$:$NiCl_2$:$NaBH_4$ = 1.0:0.06:0.06:0.17). The black $Fe_{0.5}Ni_{0.5}$ particles were rapidly generated at the first 10 s, which was accompanied by H_2 release. Thereafter, with the

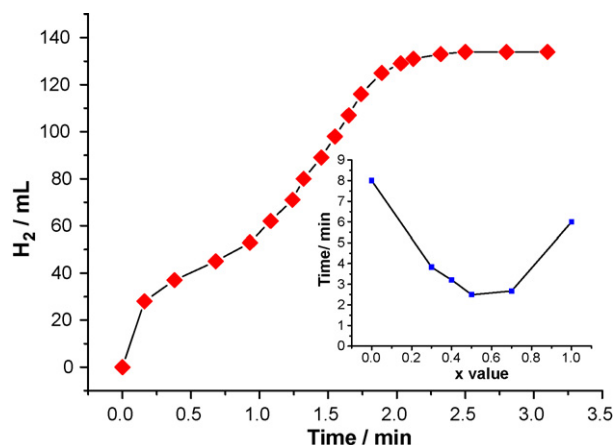**Fig. 1.** Hydrogen generation from the hydrolysis of NH_3BH_3 catalyzed by $Fe_{0.5}Ni_{0.5}$ ($Fe_{0.5}Ni_{0.5}$/NH_3BH_3 = 0.12) under ambient atmosphere and (inset) hydrolysis reaction time vs. different composition of $Fe_{1-x}Ni_x$ catalyst ($Fe_{1-x}Ni_x$/NH_3BH_3 = 0.12).

black bimetallic catalyst suspended in the solution, hydrolysis of NH_3BH_3 proceeds with intense H_2 generation from the solution. Fig. 1 demonstrates the time dependent H_2 generation from NH_3BH_3 catalyzed by the *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ particles under ambient atmosphere. The excellent catalytic activity of the as-prepared bimetallic particles can be directly evidenced by the very short reaction period (ca. 2.2 min). The molar ratio of hydrolytically generated H_2 to the initial NH_3BH_3 is close to 3.0, indicating the reaction is completed. The catalytic hydrolysis reaction can be briefly expressed as follows [28]:

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \tag{1}$$
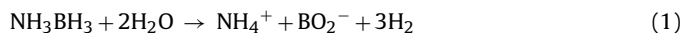
It is reported that Pt-based materials, such as Pt/C, PtO_2, Pt black, K_2PtCl_4 exhibit the highest activities to the hydrolysis of AB with the completion time ranging from 2 to 15 min [29]. Therefore, the *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ bimetallic catalyst here holds a Pt-like high catalytic activity in aqueous solution under ambient atmosphere.

Fig. 1 (inset) shows the hydrolysis reaction time vs. composition of $Fe_{1-x}Ni_x$ catalyst (NH_3BH_3:($FeSO_4 + NiCl_2$):$NaBH_4$ = 1.0:0.12:0.17). Obviously, by changing the Ni molar ratio (x = Ni:Ni + Fe), the $Fe_{1-x}Ni_x$ catalysts demonstrate different catalytic activities. The reaction catalyzed by Fe alone can be completed in approximately 8 min [23], while an increase in the Ni molar ratio from 0 to 0.5 effectively decreases the reaction time from 8 to 2.2 min; further increase in the Ni molar ratio to 1.0 results in the prolonging of the reaction time to about 6 min. Totally speaking, the catalytic properties of bimetallic $Fe_{1-x}Ni_x$ catalysts are superior to those containing Fe or Ni metal alone. With the increase in Ni molar ratio (x), the activity change of the $Fe_{1-x}Ni_x$ system is in the shape of "V", where the best x value is found to be 0.5.

In catalysis, the mutual influence of different neighboring atoms of alloy can lead to different catalytic behavior, which is often better than that of the monometallic catalyst [2]. Herein, the activity of the bimetallic catalyst can be obviously modified and fine tuned by the relative molar ratio of Fe to Ni. This may result from the alloying of the two elemental metals.

To verify the above hypothesis, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were applied to study the crystal structure and valent state of the typical sample, $Fe_{0.5}Ni_{0.5}$. Fig. 2a shows the XRD pattern of the *in situ* prepared $Fe_{0.5}Ni_{0.5}$ particles. A broad and faint peak is found at the position of around $2\theta = 43°$, implying that the *in situ* prepared $Fe_{0.5}Ni_{0.5}$ particles are in an amorphous phase or nano-sized (which can be evidenced later by the TEM result). After heat treatment at 723 K for 1 h in argon atmo-
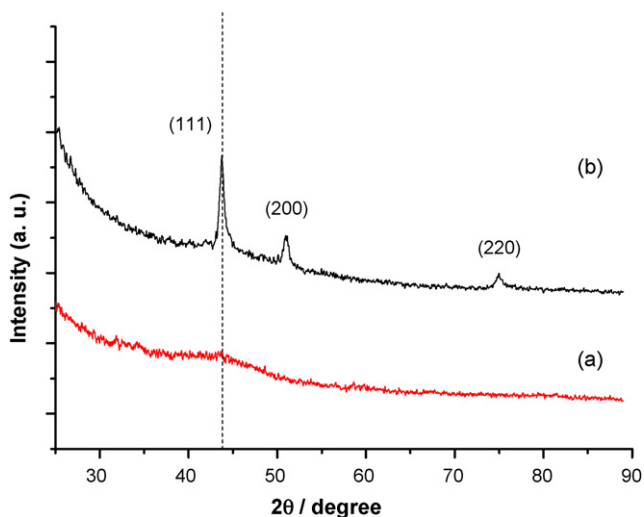
Fig. 2. X-ray diffraction patterns of (a) the *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ nanoparticles after dried at room temperature in argon atmosphere, and (b) the *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ nanoparticles after heat treatment at 723 K for 2 h in argon atmosphere.

**Fig. 3.** XPS results for (a) Ni 2p and (b) Fe 2p of the *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ nanoparticles.

sphere, this sample crystallized into the face-centered cubic (fcc) phase similar to pure Ni [34] with the strongest line at $2\theta = 43.81°$, as seen in Fig. 2b, clearly indicating the formation of a metallic alloy. The replacement of Fe does not change the Ni-type fcc structure in which the Fe and Ni atoms are distributed homogeneously and randomly at the Ni position. However, the cell parameter was calculated to be 0.3582 nm, which is larger than that of the pure fcc Ni (0.3535 nm) [34] due to the atomic radius of Fe is larger than that of Ni [35]. Fig. 3 shows the XPS results of the *in situ* prepared $Fe_{0.5}Ni_{0.5}$ particles. Elements of Fe and Ni are detected in this sample; moreover, both of the two elements are in their zero-valent states [36]. The above XRD and XPS results provide the certain evidence for the formation of the $Fe_{0.5}Ni_{0.5}$ alloy.

TEM image of $Fe_{0.5}Ni_{0.5}$ is presented in Fig. 4. Interestingly, without any dispersant, the prepared $Fe_{0.5}Ni_{0.5}$ nanoparticles are well-dispersed with the mean particle size of 3 nm. Normally, syntheses of well-dispersed magnetic nanoparticles often require the use of toxic and/or expensive precursors and dispersants [37]. In our present work, without any foreign dispersant, just using the cheap inorganic Ni (II) and Fe (II) salts as the metal precursors, the well-dispersed $Fe_{0.5}Ni_{0.5}$ magnetic nanoparticles can be successfully *in situ* synthesized. This simple method for preparing the $Fe_{1-x}Ni_x$ nano-alloy particles is expected to be used for the synthesis of other well-dispersed magnetic nano-alloys without dispansants.
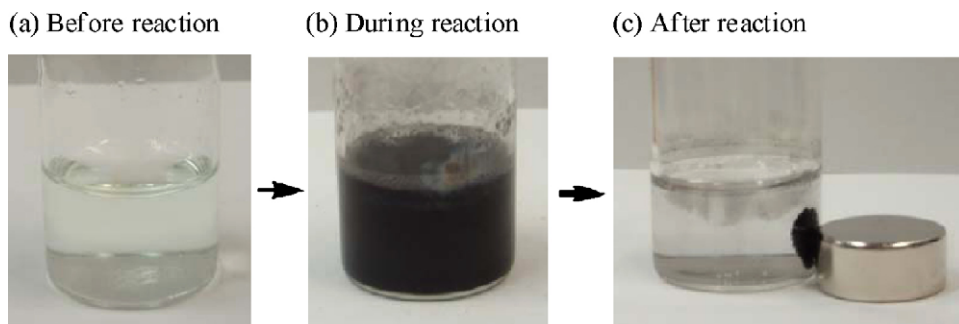
The stability or recycle ability is the key point for the practical application of every catalyst. Magnetic nanopaticles as the catalyst combine the advantages of both high reactivity and easy separation by a magnet. In our present case, during the reaction
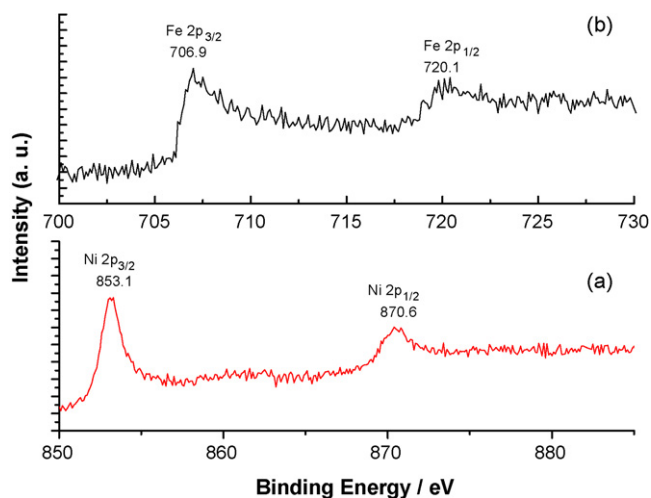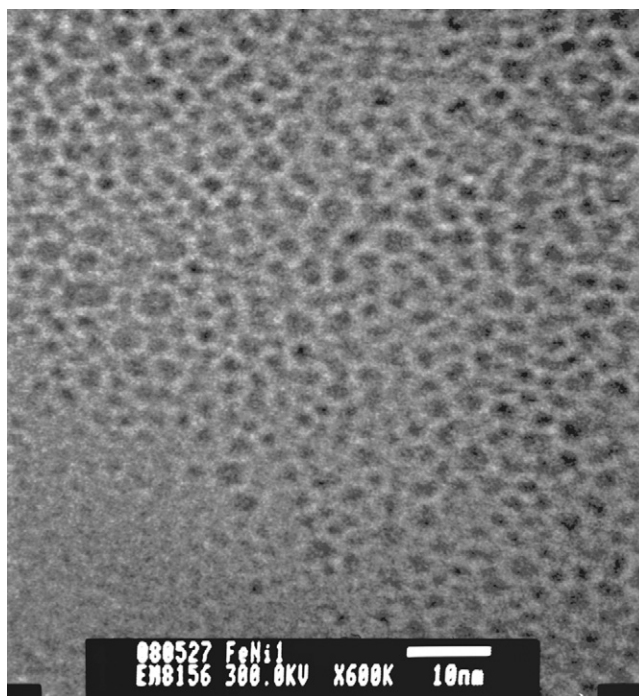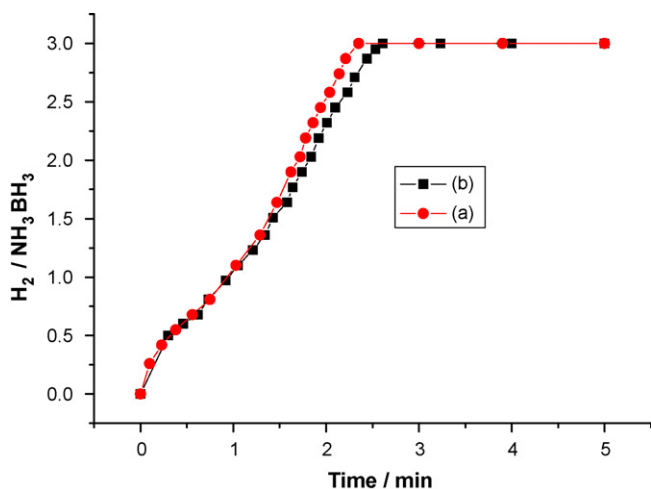

Fig. 4. TEM micrograph of *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ nanoparticles. The scale bar is 10 nm.

Fig. 5. Photographs of the hydrolysis reaction of NH_3BH_3 catalyzed by $Fe_{0.5}Ni_{0.5}$ nanoalloy.

Fig. 6. The H_2/NH_3BH_3 molar ratio of hydrogen generated from aqueous solution (0.16 M, 10 mL) vs. reaction time catalyzed by *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ at (a) recycle number 1 and (b) recycle number 5 ($Fe_{0.5}Ni_{0.5}/NH_3BH_3 = 0.12$) at room temperature under ambient atmosphere.

the black alloy particles can be suspended in the aqueous solution (Fig. 5b), while after reaction, the magnetic particles can be effectively congregated and separated by a magnet (Fig. 5c). The easy magnetic separation is greatly useful for the recycle application of the catalyst, especially in the solution system. Herein, the recycle stabilities of the $Fe_{0.5}Ni_{0.5}$ nanoparticles were tested by magnetic decantation. Fig. 6 shows the H_2/NH_3BH_3 molar ratio of hydrogen generated from aqueous solution (0.16 M, 10 mL) vs. reaction time catalyzed by *in situ* synthesized $Fe_{0.5}Ni_{0.5}$ at recycle numbers 1 and 5 ($Fe_{0.5}Ni_{0.5}/NH_3BH_3 = 0.12$) at room temperature under ambient atmosphere, respectively. Unexpectedly, even after 5 times of recycle, the activity of the as-prepared $Fe_{0.5}Ni_{0.5}$ nano-alloy catalyst has no obvious decrease.

4. Conclusions

In summary, we have successfully synthesized $Fe_{1-x}Ni_x$ magnetic nano-alloys by a simple, but very efficient method. The prepared nano-alloys possess Pt-like high catalytic activity for the H_2 generation from the aqueous ammonia borane solution under ambient atmosphere. Moreover, these catalysts can be easily magnetically separated for recycle purpose, and have good recycle stability. Such alloy catalysts are expected to be useful for fuel cells, metal–air batteries and electrochemical sensors. Moreover, the concepts behind these preliminary results present a wide range of possibilities for the further development of synthesis of air and water-stable magnetic nano-alloys.

References

[1] S. Alayoglu, A.U. Nilekar, M. Mavrikakis, B. Eichhorn, Nat. Mater. 7 (2008) 333–338.
[2] R. Ferrando, J. Jellinek, R.L. Johnston, Chem. Rev. 108 (2008) 845–910.
[3] S.P.Y.M.R.K.N.M.M.B. Marc Schrinner, Adv. Mater. 20 (2008) 1928–1933.
[4] T. Wei, J. Wang, D.W. Goodman, J. Phys. Chem. C 111 (2007) 8781–8788.
[5] F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A.M. Molenbroek, J.K. Norskov, I. Stensgaard, Science 279 (1998) 1913–1915.
[6] D.R. Lide, CRC Handbook of Chemistry and Physics, 82nd ed., CRC Press, Boca Raton, FL, 2001.
[7] C.P. Casey, H.R. Guan, J. Am. Chem. Soc. 129 (2007) 5816–5817.
[8] A.H. Lu, E.L. Salabas, F. Schuth, Angew. Chem. Int. Ed. 46 (2007) 1222–1244.
[9] D.L. Huber, Small 1 (2005) 482–501.
[10] M.A. Willard, L.K. Kurihara, E.E. Carpenter, S. Calvin, V.G. Harris, Int. Mater. Rev. 49 (2004) 125–170.
[11] Q.A. Pankhurst, J. Connolly, S.K. Jones, J. Dobson, J. Phys. D-appl. Phys. 36 (2003) R167–R181.
[12] R. Hirsch, E. Katz, I. Willner, J. Am. Chem. Soc. 122 (2000) 12053–12054.
[13] R. Nazir, M. Mazhar, M.J. Akhtar, M.R. Shah, N.A. Khan, M. Nadeem, M. Siddique, M. Mehmood, N.M. Butt, Nanotechnology 19 (2008) 185608.
[14] H. Yano, J.M. Song, H. Uchida, M. Watanabe, J. Phys. Chem. C 112 (2008) 8372–8380.
[15] V. Di Noto, E. Negro, R. Gliubizzi, S. Lavina, G. Pace, S. Gross, C. Maccato, Adv. Funct. Mater. 17 (2007) 3626–3638.
[16] R.M. Finch, N.A. Hodge, G.J. Hutchings, A. Meagher, Q.A. Pankhurst, M.R.H. Siddiqui, F.E. Wagner, R. Whyman, Phys. Chem. Chem. Phys. 1 (1999) 485–489.
[17] W. Grochala, P.P. Edwards, Chem. Rev. 104 (2004) 1283–1316.
[18] (a) P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, Nature 420 (2002) 302–304;
     (b) L. Schlapbach, A. Zuttel, Nature 414 (2001) 353–358.
[19] J.M. Ogden, Annu. Rev. Ene. Env. 24 (1999) 227–279.
[20] Y.S. Chen, J.L. Fulton, J.C. Linehan, T. Autrey, J. Am. Chem. Soc. 127 (2005) 3254–3255.
[21] A. Gutowska, L.Y. Li, Y.S. Shin, C.M.M. Wang, X.H.S. Li, J.C. Linehan, R.S. Smith, B.D. Kay, B. Schmid, W. Shaw, M. Gutowski, T. Autrey, Angew. Chem. Int. Ed. 44 (2005) 3578–3582.
[22] V. Sit, R.A. Geanangel, W.W. Wendlandt, Thermochimi. Acta 113 (1987) 379–382.
[23] J.M. Yan, X.B. Zhang, S. Han, H. Shioyama, Q. Xu, Angew. Chem. Int. Ed. 47 (2008) 2287–2289.
[24] C.M. Ankan Paul, Angew. Chem. Int. Ed. 46 (2007) 8153–8156.
[25] M. Chandra, Q. Xu, J. Power Sources 168 (2007) 135–142;
     (d) F.Y. Cheng, H. Ma, Y.M. Li, J. Chen, Inorg. Chem. 46 (2007) 788–794.
[26] T.J. Clark, G.R. Whittell, I. Manners, Inorg. Chem. 46 (2007) 7522–7527.
[27] M. Chandra, Q. Xu, J. Power Sources 156 (2006) 190–194;
     (g) Q. Xu, M. Chandra, J. Power Sources 163 (2006) 364–370.
[28] C.W. Yoon, L.G. Sneddon, J. Am. Chem. Soc. 128 (2006) 13992–13993.
[29] R.J. Keaton, J.M. Blacquiere, R.T. Baker, J. Am. Chem. Soc. 129 (2007) 1844–1845.
[30] F.H. Stephens, R.T. Baker, M.H. Matus, D.J. Grant, D.A. Dixon, Angew. Chem. Int. Ed. 46 (2007) 746–749.
[31] F.H. Stephens, V. Pons, R.T. Baker, Dalton Trans. (2007) 2613–2626.
[32] M.E. Bluhm, M.G. Bradley, R. Butterick Iii, U. Kusari, L.G. Sneddon, J. Am. Chem. Soc. 128 (2006) 7748–7749.
[33] M.C. Denney, V. Pons, T.J. Hebden, D.M. Heinekey, K.I. Goldberg, J. Am. Chem. Soc. 128 (2006) 12048–12049.
[34] T.G. Xu, D.J. Xu, Acta Crystallographica Section E-Structure Reports Online 60 (2004) M27.
[35] http://en.wikipedia.org/wiki/Atomic_radii_of_the_elements_(data_page)#Atomic_radii.
[36] K. Kishi, Y. Motoyoshi, S. Ikeda, Surf. Sci. 105 (1981) 313–324.
[37] S. Peng, C. Wang, J. Xie, S.H. Sun, J. Am. Chem. Soc. 128 (2006) 10676–10677.