A Facile Approach of Preparing Nickel Nanoparticles on Porous Silicon Surface and its Catalytic Activities on Reducing of Nitroaromatics

Xiang Liu* and Heming Cheng
School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, China.
liuxiang@ahut.edu.cn*

(Received on 7th February 2013, accepted in revised from 8th August 2013)

Summary: A facile approach of preparing nickel nanoparticles (Ni NPs) on porous silicon (PSi) surface and the catalysis towards reduction of nitroaromatics are depicted in this work in detail. When the PSi chip was immersed in the mixture of 40 % ammonium fluoride and 0.02 M nickel sulfate solutions with volume ratio of 1:1 at 60°C for 15 min, a large number of Ni NPs were generated on PSi surface, which exhibited high catalytic activities on reducing nitro groups of aromatics in the presence of sodium borohydride at ambient temperature. A suggested mechanism of Ni NPs generation on PSi surface was put forward according to theoretical and experimental analyses. The resultant Ni NPs on PSi surface were demonstrated with scanning electron microscopy and the reducing reactions are monitored with ultraviolet-visible spectroscopy.

Keywords: porous silicon; nickel nanoparticle; Si-H_x bonds; nitroaromatic; reduction.

Introduction

Nanoparticles attract extensive interests due to their special properties and vast applications in different domains. [1-5] The techniques of preparing nickel nanoparticles (Ni NPs) on solid substrate are various. [4, 6-13] But most of them are complicated. [7-9, 11] Ni NPs could be prepared by in-situ reduction of NiO-loaded carbon with hydrogen while the NiO were obtained by calcining nickel nitrate in air at 300°C for 1 h. [14] Such Ni NPs/activated carbon could catalyze the conversion of silane into silanol. Nickel(II) acetylacetonate, as a nickel source, could be impregnated into carbon aerogel in supercritical carbon dioxide under 30 MPa and 60°C followed by thermal or chemical disposal with hydrogen to synthesize Ni-carbon aerogel nanocomposites. [15] The calcined SBA-15 also could be used as a template to absorb Ni(II) which were reduced into Ni NPs in hydrogen gas flow at 873 K for 1 h. Such Ni NPs/SBA-15 performed well in selective removal of sulfur compound in diesel. [9] Sahiner and his coauthors reported several methods to build a proper template for preparation of nanoparticles. [8, 16-20] Monomers of 2-acrylamidoglycolic acid monohydrate were polymerized as a hydrogel which absorbed Ni(II) via the coordination of carboxylate. Then the Ni NPs were obtained by in-situ reduction in the presence of sodium borohydride ($NaBH_4$). [18, 19] This method ensured the well dispersion of the generated Ni NPs and the solid template retarded their aggregation during the catalytic process. Photo polymerization of 2-acrylamido-2-methyl-1-propansulfonic acid produced a hydrogel which in favor of production of Ni NPs in its inside networks with $NaBH_4$. The obtained Ni NPs accelerated the decomposition of $NaBH_4$ to generate hydrogen [20] and catalyzed the reduction reaction of nitrophenols. [8] These polymers constructed networks which stabilized the resultant Ni NPs and maximized their catalytic capabilities. Similarly, Ni NPs could be prepared inside the composite of polyvinylamine/SBA-15. The amino groups of polyvinylamine served as anchor of Ni(II) which were reduced by $NaBH_4$. [11] The obtained Ni NPs exhibited catalysis on reduction of nitroaromatics. Ni NPs-loaded carbon nanotubes (CNTs) could be obtained by heating the mixture of Ni(II) and CNTs at 350°C under a mixed atmosphere of H_2/Ar. The Ni NPs-modified CNTs enhanced the electrochemical storage of hydrogen in alkali electrolyte. [21] Apart from the stated applications, Ni NPs-anchored mesoporous ZSM-5 could be used as a catalyst in reforming of methane with carbon dioxide to produce synthetic gas with H_2/CO mole ratio of 1:1 at atmospheric pressure. [22] Ni NPs-loaded carbon fiber paste electrode was applied in enzyme-free measurement of ethanol. [6]

So the in-situ reduction of Ni NPs on solid surface provides a wonderful way of preparing well dispersed nanoparticles. In some cases, Ni NPs are manufactured under rigorous conditions of high temperature followed with reduction of explosive hydrogen. Some polymers with properly functional groups are utilized as a platform to plant Ni NPs inside their networks thus the stability of Ni NPs enhances. But the preparations of these polymers are complicated. Herein, we will report a facile method of preparing Ni NPs on surface of porous silicon (PSi)

*To whom all correspondence should be addressed.

in solutions of Ni(II) and fluorides under rather mild conditions without adding any reductant. [23] And the pH value of such solutions need not modulate with buffer solutions. [4] PSi chips are obtained by chemical etching method, which provide wonderful templates [24] to deposit Ni NPs. Such Ni NPs/PSi chips perform well in catalytic reducing reaction of nitroaromatics in the presence of $NaBH_4$.

Results and discussion

Generation of Ni NPs on PSi surface

The SEM image of PSi, shown in Fig. 1(a), displays the porous surface with plentiful pores. Such PSi chip possesses huge surface areas with various crystal planes such as 111-, 110-, and 100-orientation planes on sidewalls of the internal channels. [25, 26] In NH_4F aqueous solutions, hydrofluoric acid (HF) produces by virtue of hydrolysis of NH_4F. Here, we choose 111-orientated silicon as an example to illuminate the generation of Ni NPs on surface of the PSi. The species of Si_{n-2}·Si-SiF_3 on silicon surface were produced when Si(111) chip was immersed in HF aqueous solution. [27] On account of the strong polarity of fluorine, the Si-Si bonds of Si_{n-2}Si-SiF_3 are polarized intensively which benefits for the attack of HF producing surface monohydride of Si-H. The reaction process is described in reaction (a).

$$Si_{n-2}\cdot Si-SiF_3 + HF \rightarrow Si_{n-2}\cdot Si-H + SiF_4 \quad (a)$$

Similarly, surface silicon of Si(100) and Si(110) are liable to produce surface Si-H_2 and Si-H_3. [28-30] These active Si-H_x (x = 1, 2 or 3) species involve in the reduction of Ni(II) while Si-H_x are oxidated into H_2. The redox reactions are depicted in the following electrochemical reactions of (b) and (c).

$$Si_{n-2}\cdot Si-H(\text{solid surface}) + F^-(\text{aqueous}) - e \rightarrow$$
$$Si_{n-2}(\text{solid}) + \frac{1}{2}H_2(\text{gas}) + SiF(\text{aqueous}) \quad (b)$$

$$\frac{1}{2}Ni^{2+}(\text{aqueous}) + e \rightarrow \frac{1}{2}Ni(\text{solid}) \quad (c)$$

Thus Ni(II)/Ni and H_2/SiH,F^- compose an electrochemical system. According to electrode reaction (b), surface Si-H_x are exhausted gradually and new silicon surfaces of Si_{n-2} are produced. The surface Si_{n-2} is changed into Si_{n-4}·Si-SiF_3 in HF solutions and successively involves reaction (a) again giving a new surface Si-H_x. Then surface Si-H_x take part in the reaction (b) subsequently. As a result, Ni(II) was reduced continuously in accordance with (c). Finally, the PSi was covered completely by black Ni NPs. The SEM image of Fig. 1(b) exhibits that a large number of Ni NPs stacked on the PSi surface. The liberated H_2 gases result in many channels inside the honeycomb-like Ni NPs. The cross-sectional image of Fig. 1(c) illuminates the numerous Ni NPs inside the PSi with nanosize of about 50 nm shown in Fig. 1(d).

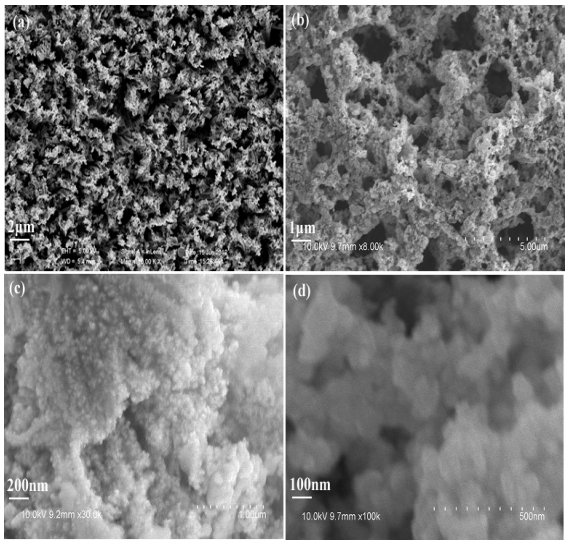

Fig. 1: Top views of PSi and Ni NPs/PSi of scanning electron microscopy images (SEM) correspond with (a) and (b). The cross-sectional view of Ni NPs/PSi and its magnification are showed in (c) and (d) respectively.

That is to say, the surface Si-H_x species possess a strong reducing ability which should be ascribed to the following reasons: the resulted SiF species of reaction (b) reacts with water immediately leading to its rapid disappearance meanwhile the produced H_2 escapes from the solutions instantly. This gives rise to the spontaneous proceeding of reaction (b) in thermodynamics. [3] The numbers of surface silicon atoms are enhanced extremely as the silicon wafer becomes porous which results in more surface Si-H_x when it is etched by HF according to reaction (a) and (b). Therefore the porous structure is indispensable for manufacturing such a large amount of Ni NPs in this case. The surface Si-H_x species donate electrons which accepted by Ni(II) bringing about manufacture of Ni NPs on surface of PSi. That

means surface Si-H_x bonds play a important role in the course of reducing Ni(II). This resembles the formation of Ag NPs on porous silicon reduced by surface Si-H_x. [31] But here the reduction of Ni(II) is more difficult than that of Ag(I) as the electrode couple of Ni(II)/Ni has a negative reducing electrode potential. The concentrated NH_4F solution and heating condition in this reaction benefit the reduction of Ni(II). In a word, the porous architectures of silicon surface which bring vast surface Si-H_x species play vital roles in producing Ni NPs on PSi surface.

Reduction of p-NA and m-NBS

The as-prepared Ni NPs/PSi chip can be a candidate of catalysts in reducing nitro compounds in the presence of $NaBH_4$. The progresses of reducing p-Nitroaniline (p-NA) at 301 K and at 311 K respectively are monitored with UV-Vis spectra which displayed in Fig. 2 corresponding with (a) and (b). Peak 381 nm decreases gradually within 60 min while it remains unchanged in a control experiment without catalyst of Ni NPs/PSi chip. Additionally, band 381 nm drops more rapidly at 311 K than that of 301 K. We assume the reaction rate is proportional with first order of concentration of $NaBH_4$ ([$NaBH_4$]) and p-NA ([p-NA]) respectively. As for the [$NaBH_4$] largely excess the [p-NA] and is considered to be approximately constant during the course of the reaction, the pseudo-first-order reaction rate constant (k') equals first-order reaction rate constant (k) multiply [$NaBH_4$]. The k' values are displayed in Fig. 3 which obtained by linear fitting between natural logarithm of absorbances (ln[A]) at 381 nm and reaction time (t). A good linear correlation between ln[A] and t is obtained, as is shown in the plots. Thus the first-order reaction rate constants (k) can be estimated to be 22.0 and 27.5 min^{-1} corresponding with 301 K and 311 K. Hence the activation energy is calculated to be 17.38 $kJ \cdot mol^{-1}$ according to Arrhenius equation. Notably, when the temperature raises 10 K the increment of k is too small. This may be ascribed to the enhanced rate of decomposition of $NaBH_4$ at a higher temperature. In this case, the decomposition of $NaBH_4$ becomes more rapid, which results in some of the liberated H_2 can not involve the reducing reactions. The smaller value of apparent activation energy means high catalytic activation of Ni NPs/PSi in such reducing reaction. The porous architectures of PSi keep the resultant Ni NPs well distributed which favors to the catalysis in such reducing reactions.

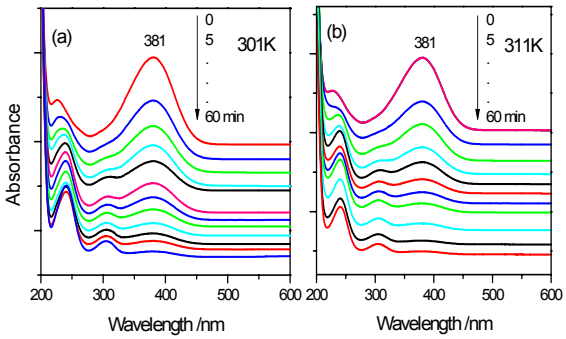

Fig. 2: Successive ultraviolet-visible (UV-Vis) spectra of reducing p-Nitroaniline (p-NA) in the presence of $NaBH_4$ catalyzed with an as-prepared Ni NPs/PSi chip.

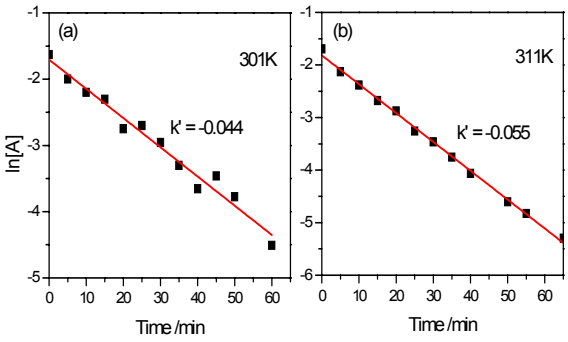

Fig. 3: Plots of ln[A] (A = absorbance of p-NA at 381 nm) vs. reaction time at 301 K and 311 K in (a) and (b) respectively. The k' is the slope of the fitting line.

The as-prepared Ni NPs/PSi chip displays a similar catalysis on reducing m-NBS in the presence of $NaBH_4$. The reaction is traced with UV-Vis spectra which displayed in Fig. 4. Band 261 nm, character of nitrobenzene, drops sharply in only 5 min together with the occurrence of 237 and 289 nm peaks which assigned to B and E band of aniline respectively. The reaction finishes in only 30 min which illuminates the high catalytic efficiency and activity of such a Ni NPs/PSi chip with size of 16 mm × 5 mm.

It is well known that Raney Ni catalyst is applied widely in hydrogenation reactions. [22] It is generally accepted that chemical adsorption of H_2 on surface of Ni catalyst is a crucial step which decides whether the reaction proceeds. Ni NPs quicken the decomposition of $NaBH_4$ in aqueous solution [20] which can be observed clearly while putting the Ni

NPs/PSi chip into the reaction system. Some of the generated H_2 molecules may be adsorbed chemically via its unoccupied antibonding molecular orbital overlapping with d orbital of atom Ni. H_2 receives the electrons of Ni and becomes active accordingly. On the other hand, nitroaromatics such as p-NA or m-NBS can be absorbed chemically through coordination between atom O of nitro group and Ni. Thus the activated H_2 reacts with nitroaromatics on surface of Ni NPs [32] rather than BH_4^- reacts with nitro group directly, [33, 34] which is proved by a control experiment at the absence of Ni NPs/PSi chip.

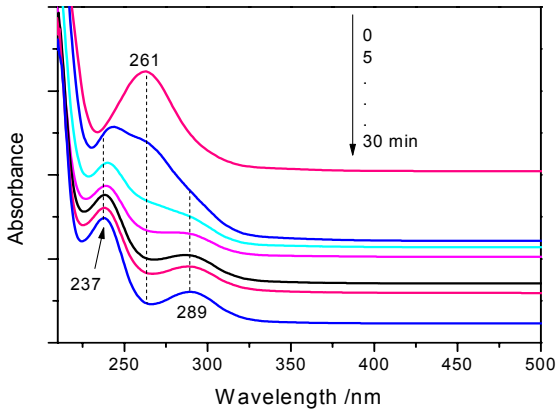

Fig. 4: UV-Vis spectra of measuring the reduction of m-nitrobenzenesulfonate (m-NBS) catalyzed by Ni NPs/PSi in the presence of $NaBH_4$.

Experimental

Materials

Double-side polished silicon wafer (p-type, boron-doped with thickness of 450 ± 50 μm and a resistivity of 3–10 Ω cm) were sliced into sizes of 30 mm × 5 mm. Before use they were put into piranha solutions with a heating of 150°C for 2 h to wipe out any foulings on their surfaces. [35] Then they were cleaned thoroughly in supersonic cleaner with copious amount of water for three times. Ammonium fluoride, nickelous sulfate hexahydate were purchased from Guoyao Chemical Company (Shanghai, China). p-Nitroaniline, sodium m-nitrobenzenesulfonate, sodium borohydride were commercially provided by Xiya Chemical Company (Chengdu, China). These chemicals were used as receive without any purifications. Double-distilled water was used throughout in preparing aqueous solutions.

Preparation of Ni NPs/PSi chip

PSi chips were prepared in accordance to the techniques which reported elsewhere. [36] A PSi chip was immersed in 5 mL 0.02 M $NiSO_4$ solutions for more than 5 min at room temperature to absorb Ni(II) onto the surfaces of the inside pore of PSi. Then the $NiSO_4$ solutions mixed with 5 mL 40 % NH_4F solutions and the mixtures were heated with a water bath of 60°C. After the PSi chip were put into the mixtures for a few seconds, its surface became dark, accompanied with a large amount of occurred gases. The PSi chip was picked up after 15 min and was washed with copious water to remove any inorganic impurities. It was obvious that the PSi was covered by black materials which could be attracted by a magnet. The Ni NPs on PSi was observed with field emission scanning electron microscopy (Nano SEM 430, FEI Company).

Application of Ni NPs/PSi in reducing reaction of nitroaromatics

Firstly, 5 mL 2×10^{-3} M p-NA aqueous solutions were mixed with 25 mL water. Then 76 mg (2 mmol) $NaBH_4$ were added in such a solution. A Ni NPs/PSi chip was tied with a Teflon thread and immersed in the reaction system with a magnetic agitation. The reactions performed respectively at 301 K and 311 K. The changes of UV-Vis spectra were recorded during the course of the reaction to calculate the reaction rate constant and apparent activation energy which used to estimate the catalytic activities. Additionally, 200 mg (0.89 mmol) m-NBS and 675 mg (17.76 mmol) $NaBH_4$ were dissolved in 30 mL water which also catalyzed with a Ni NPs/PSi chip so as to appraise the practical application of Ni NPs/PSi chip in organic syntheses.

Conclusion

Ni NPs/PSi composites are manufactured by such a easy way of putting the PSi chip in aqueous solutions of NH_4F and $NiSO_4$ at 60°C for 15 min. PSi is etched by fluorides producing surface Si-H_x bonds which reduce Ni(II) yielding Ni NPs on PSi surface. We assume that the oxidation of Si-H_x in the presence of F^- proceeds spontaneously in thermodynamics which contributes the reduction of Ni(II). The PSi not only provide large amount of surface Si-H_x bonds which is favorable for producing Ni NPs but also prevent the aggregation of resultant Ni NPs. Hence, the Ni NPs/PSi chip performs well in catalytic reduction of nitroaromatics. Such simple ways of

preparing Ni NPs/PSi will open a wider utilization of PSi.

Acknowledgements

This work was supported by Educational Commission of Anhui province of China (KJ2012A051).

References

1. X. Ling, X. Zhu, J. Zhang, T. Zhu, M. Liu, L. Tong and Z. Liu, *Journal of Chemical Physics B*, **109**, 2657 (2005).
2. J. He, T. Kunitake, *Langmuir*, **22**, 7881 (2006).
3. Z. Kang, C. H. A. Tsang, Z. Zhang, M. Zhang, N. Wong, J. A. Zapien, Y. Shan and S. Lee, *Journal of the American Chemical Society*, **129**, 5326 (2007).
4. X. Zhang and K. Tu, *Journal of the American Chemical Society*, **128**, 15036 (2006).
5. P. Granitzer and K. Rumpf, *Materials*, **4**, 908 (2011).
6. Y. Liu, L. Zhang, Q. Guo, H. Hou and T. You, *Analytica Chimica Acta*, **663**, 153 (2010).
7. S. K. Ghosh, M. Mandal, S. Kundu, S. Nath and T. Pal, *Applied Catalysis* A*: General*, **268**, 61 (2004).
8. N. Sahiner, H. Ozay, O. Ozay and N. Aktas, *Applied Catalysis A: General*, **385**, 201 (2010).
9. C. H. Ko, J. G. Park, J. C. Park, H. Song, S. Han and J. Kim, *Applied Surface Science*, **253**, 5864 (2007).
10. J. Li, Q. Guo, J. Shi, X. Gao, Z. Feng, Z. Fan and L. Liu, *Carbon*, **50**, 2045 (2012).
11. R. J. Kalbasi, A. A. Nourbakhsh and F. Babaknezhad, *Catalysis Communications*, **12**, 955 (2011).
12. T. Nakamura and S. Adachi, *AIP Advances*, **2**, 32167 (2012).
13. E. R. Leite, N. L. V. Carreño, E. Longo, A. Valentini and L. F. D. Probst, *Journal of Nanoscience and Nanotechnology*, **2**, 89 (2002).
14. K. Shimizu, K. Shimura, Naomichi, Imaiida and A. Satsuma, *Journal of Molecular Catalysis* A*: Chemical*, **353**, 171 (2012).
15. S. E. Bozbag, L. C. Zhang, M. Aindow and C. Erkey, *Journal of Supercritical Fluids*, **66**, 265 (2012).
16. N. Sahiner, H. Ozay, O. Ozay and N. Aktas, *Applied Catalysis* B*: Environmental*, **101**, 137 (2010).
17. N. Sahiner, A. Kaynak and S. Butun, *Journal of Non-Crystalline Solids*, **358**, 758 (2012).
18. N. Sahiner, S. Butun and T. Turhan, *Chemical Engineering Science*, **82**, 114 (2012).
19. S. Butun and N. Sahiner, *Polymer*, **52**, 4834 (2011).
20. O. Ozay, N. Aktas, E. Inger and N. Sahiner, *International Journal of Hydrogen Energy*, **36**, 1998 (2011).
21. C. Hsieh, Y. Chou and J. Lin, *International Journal of Hydrogen Energy*, **32**, 3457 (2007).
22. B. Sarkar, R. Tiwari, R. K. Singha, S. Suman, S. Ghosh, S. S. Acharyya, K. Mantri, L. N. S. Konathala, C. Pendem and R. Bal, *Catalysis Today*, **198**, 209 (2012).
23. F. Miao, B. Tao, L. Sun, T. Liu, J. You, L. Wang and P. K. Chu, *Sensors and Actuators* B, **141**, 338 (2009).
24. K. Peng, A. Lu, R. Zhang and S. Lee, *Advanced Functional Materials*, **18**, 3026 (2008).
25. S. Chattopadhyay and P. W. Bohn, *Analytical Chemistry*, **78**, 6058 (2006).
26. R. Boukherroub, S. Morin, D. D. M. Wayner, F. Bensebaa, G. I. Sproule, J. M. Baribeau and D. J. Lockwood, *Chemistry of Materials*, **13**, 2002 (2001).
27. H. Ubara, T. Imura and A. Hiraki, *Solid State Communications*, **50**, 673 (1984).
28. S. A. Alekseev, V. Lysenko, V. N. Zaitsev and D. Barbier, *Journal of Chemical Physics C*, **111**, 15217 (2007).
29. Y. Li and J. M. Buriak, *Inorganic Chemistry*, **45**, 1096 (2006).
30. D. Dattilo, L. Armelao, M. Maggini, G. Fois and G. Mistura, *Langmuir*, **22**, 8764 (2006).
31. J. Yin, X. Qi, L. Yang, G. Hao and J. Li, J. Zhong, *Electrochimica Acta*, **56**, 3884 (2011).
32. P. Veerakumar, M. Velayudham, K. Lu and S. Rajagopal, *Applied Catalysis* A*: General*, **439**, 197 (2012).
33. D. K. Bhui and A. Misra, *Carbohydrate Polymers*, **89**, 830 (2012).
34. S. Kundu, M. Mandal, S. K. Ghosh and T. Pal, *Journal of Colloid and Interface Science*, **272**, 134 (2004).
35. X. Liu, H. Zheng, Q. Yan, C. Wang, Y. Ma, Y. Tang and S. Xiao, *Surface Science*, **605**, 1106 (2011).
36. K. Peng, Y. Yan, S. Gao and J. Zhu, *Advanced Materials*, **14**, 1164 (2002).