Metallic Ni nanoparticles confined in hexagonally ordered mesoporous silica material†

Katsutoshi Yamamoto, Yoji Sunagawa, Hideyuki Takahashi and Atsushi Muramatsu*

Received (in Cambridge, UK) 21st July 2004, Accepted 14th October 2004
First published as an Advance Article on the web 25th November 2004
DOI: 10.1039/b411074a

Single nanometer-sized metallic Ni particles have been successfully deposited inside a hexagonally ordered mesoporous silica material by using a liquid-phase reductive deposition method.

The synthesis of orderly arrayed nanoparticles of semiconductors or metals is attracting a lot of interest because they are expected to show unique physical or chemical properties.[1–3] Recently, various metallic nanoparticles or nanowires confined in hexagonally ordered mesoporous silica materials have been synthesized and verified by TEM and/or N_2 adsorption.[4–10] However, the components of such materials are limited to easily reducible noble metals such as Pt,[4–8,10] Rh[7,8] or Au.[9,10] Because base metals are widely used as catalysts or electric and magnetic devices, the extension of component elements to base metals widens the application area of such nanocomposites. Zhang *et al.* recently reported the preparation of Ni nanowires secondarily deposited in mesopores by electroless plating using preliminarily introduced Pd nanoparticles as a catalyst.[11] Although there are a few reports claiming the direct introduction of metallic Ni nanoparticles into mesoporous silica materials, further characterization seems to be necessary for these materials. As a synthesis method for single nanometer-sized ($\leqslant 9$ nm) metallic particles, we have proposed a liquid-phase reductive deposition method,[12,13] which can be applied not only to noble metals but also to base metals. It has already been revealed that metallic Ni nanoparticles can be stably deposited on titania supports and that the addition of zinc decreases the size of deposited Ni nanoparticles.[13] Here we report a simple and efficient route to synthesize metallic Ni nanoparticles confined in the hexagonally ordered mesoporous silica material SBA-15, which is realized by adopting a modified liquid-phase reductive deposition method in the presence of zinc. The introduction of Ni nanoparticles into mesopores is demonstrated directly by TEM observations and indirectly by N_2 adsorption measurements and catalytic performances.

SBA-15 was synthesized according to the literature.[14] In the modified liquid-phase reductive deposition method, a nickel precursor together with a zinc precursor was introduced into the mesopore of SBA-15 and successively reduced in the liquid phase. Nickel acetylacetonate and zinc acetylacetonate were dissolved in 2-propanol (Zn : Ni = 0.2 in molar ratio) and impregnated on calcined SBA-15 to make the Ni-loading 10 wt%. This Ni-impregnated SBA-15 material was dispersed in 2-propanol, and the nickel precursor was reduced by adding a $NaBH_4$–2-propanol solution under refluxing conditions to obtain Ni–Zn($NaBH_4$)/SBA-15. Ni–Zn(H_2)/SBA-15 was prepared by treating the Ni-impregnated SBA-15 material in a H_2 atmosphere at 200 °C for 2 h. The XPS measurements indicated that the nickel species in these nanocomposites were of a metallic state, although zinc species are deposited as an oxide.[15] The XRD measurements suggest that the hexagonally ordered structure of SBA-15 was retained after each reduction treatment and that metallic Ni species have an amorphous structure.[13] Ni–Zn($NaBH_4$)/SBA-15 and Ni–Zn($NaBH_4$), prepared without employing an SBA-15 support, were used as catalysts for the hydrogenation of 1-octene, which was conducted at 80 °C in 2-propanol as the solvent.

The TEM images of the Ni/SBA-15 materials are exhibited in Fig. 1. In Ni–Zn($NaBH_4$)/SBA-15 (Fig. 1a), nanometer-sized Ni particles confined inside the mesopores of SBA-15 are observed, although Ni nanoparticles unsupported or supported outside of SBA-15 are also observed. On the other hand, in the sample reduced by H_2 (Fig. 1b), Ni particles larger than the mesopore diameter are observed outside the mesopores. Heat treatment in a

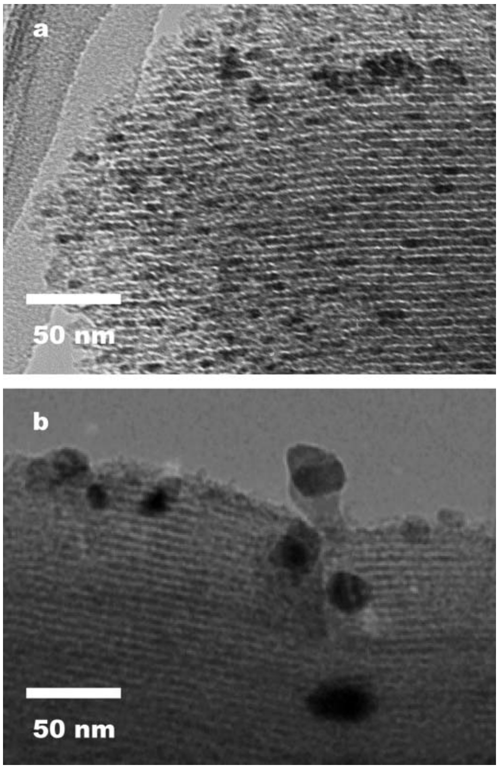

Fig. 1 TEM images of (a) Ni–Zn($NaBH_4$)/SBA-15 and (b) Ni–Zn(H_2)/SBA-15.

---

† Electronic supplementary information (ESI) available: XRD patterns, XPS spectra, and TEM image of Ni-deposited SBA-15 materials. See http://www.rsc.org/suppdata/cc/b4/b411074a/
*mura@tagen.tohoku.ac.jp

H_2 atmosphere would induce Ni species in the mesopores to move out and aggregate.

When nickel precursors were reduced in the absence of zinc by the liquid-phase reduction method, Ni particles were observed outside the pores only. In the case of Ni nanoparticle deposition on non-porous titania, concomitant zinc species adsorbed around the nickel species act as a physical obstacle preventing Ni nanoparticles from aggregating.[16] Also in this case, adsorbed zinc species would forbid the neighbouring Ni particles from moving out of the pores and aggregating. The choice of nickel source and solvent is also one of the most important factors; for example, when nickel nitrate as a nickel source was reduced by $NaBH_4$ in water as a solvent, the nickel particles obtained were larger than 10 nm and were deposited only on the outer surface of SBA-15.

Table 1 compares the catalytic activities of supported/unsupported Ni nanoparticles in the hydrogenation of 1-octene. The catalytic activity of Ni–Zn($NaBH_4$)/SBA-15 is higher than that of unsupported nanoparticles presumably because Ni–Zn nanoparticles are stably deposited on the silica support, which prevents the catalytically active nanoparticles from aggregating.[13] However, despite the larger BET surface area of the support, Ni–Zn($NaBH_4$)/SBA-15 shows much lower catalytic activity than Ni–Zn nanoparticles deposited on non-porous silica (Ni–Zn($NaBH_4$)/SiO_2 in Table 1). In this catalyst, all the Ni particles are located outside of the support thereby rendering them easily accessible for reactant molecules. In the case of Ni–Zn($NaBH_4$)/SBA-15, Ni nanoparticles deposited deep inside the mesopores could not be effectively used due to pore blockages by other nanoparticles. Therefore, the lower catalytic activity observed for Ni–Zn($NaBH_4$)/SBA-15 strongly indicates that Ni nanoparticles are mainly deposited inside the mesopores of SBA-15.

The N_2 adsorption/desorption isotherms of SBA-15 materials with/without Ni deposition are shown in Fig. 2. It is to be noted that the hysteresis loop of Ni–Zn($NaBH_4$)/SBA-15 has a different shape, which is characteristic of a material with ink-bottle type mesopores.[17] By the liquid-phase reductive deposition method, Ni nanoparticles would be deposited inside the mesopores of SBA-15 to form ink-bottle type constricted pores. In addition, the pore volume of Ni–Zn($NaBH_4$)/SBA-15 is estimated at 0.40 cm^3 g^{-1} based on the N_2 adsorption isotherm. Supposing that all the Ni particles were deposited outside the mesopores, the pore volume of the parent SBA-15 material (1.04 cm^3 g^{-1}) would be reduced to 0.93 cm^3 g^{-1}, which is much larger than the actual value. This discrepancy also suggests that Ni nanoparticles are located inside the mesopores and block them to decrease the apparent pore volume value. In contrast, the pore volume of Ni(H_2)/SBA-15 (0.84 cm^3 g^{-1}) would indicate little introduction of Ni particles into mesopores, which is in good agreement with the TEM observation.

Table 1 Catalytic activities in 1-octene hydrogenation[a]

Catalyst	BET surface area of support (m^2 g^{-1})	*n*-Octane yield (%)
Ni–Zn($NaBH_4$)	—	2.1
Ni–Zn($NaBH_4$)/SBA-15[b]	980	11
Ni–Zn($NaBH_4$)/SiO_2[b]	180	41

[a] Catalyst 0.01 g as Ni (Zn/Ni = 0.2), 1-octene 5 ml, 2-propanol 50 ml as solvent, 80 °C, 2 h. [b] Ni-loading 10 wt%.

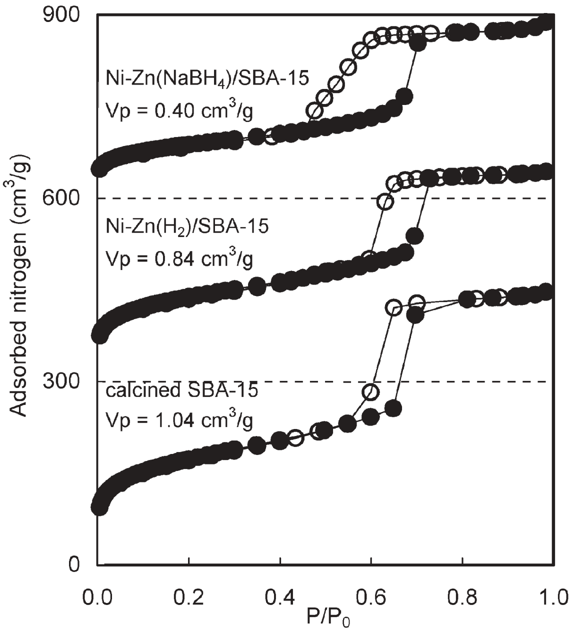

Fig. 2 Nitrogen adsorption/desorption isotherms of Ni-loaded SBA-15 materials. *x* Axes for Ni(H_2)/SBA-15 and Ni($NaBH_4$)/SBA-15 are shifted by 300 and 600 cm^3 g^{-1}, respectively.

In conclusion, by employing the modified liquid-phase reductive deposition method, a new class of Ni/SBA-15 nanocomposite has been successfully synthesized, which cannot be obtained by the usual H_2 reduction. Further efficient nanoparticle deposition procedures and the synthesis of Ni-based alloy nanoparticles are under investigation. This novel nanocomposite is expected to act as a catalyst for various functional materials such as orderly arrayed carbon nanotubes.

Authors are grateful to Mr M. Ito at IMRAM, Tohoku University for the XPS measurements, Mr E. Aoyagi and Mr Y. Hayasaka at HVEM, Tohoku University for the technical support for TEM, and Dr K. Nakai at Bel Japan Co. for the useful suggestions about N_2 adsorption measurements.

Katsutoshi Yamamoto, Yoji Sunagawa, Hideyuki Takahashi and Atsushi Muramatsu*
Institute for Multidisciplinary Research of Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-0855, Japan.
E-mail: mura@tagen.tohoku.ac.jp; Fax: +81 22 217 5165;
Tel: +81 22 217 5163

Notes and references

1 P. V. Braun, P. Osenar and S. I. Stupp, *Nature*, 1996, **380**, 325.
2 S. L. Burkett and S. Mann, *Chem. Commun.*, 1996, 321.
3 P. C. Ohara, J. R. Heath and M. Gelbart, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1078.
4 U. Junges, W. Jacobs, I. Voigt-Martin, B. Krutzsch and F. Schüth, *J. Chem. Soc., Chem. Commun.*, 1995, 2283.
5 C. H. Ko and R. Ryoo, *Chem. Commun.*, 1996, 2467.
6 Z. Liu, Y. Sakamoto, T. Ohsuna, K. Hiraga, O. Terasaki, C. H. Ko, H. J. Shin and R. Ryoo, *Angew. Chem., Int. Ed.*, 2000, **39**, 3107.
7 A. Fukuoka, Y. Sakamoto, S. Guan, S. Inagaki, N. Sugimoto, Y. Fukushima, K. Hirahara, S. Iijima and M. Ichikawa, *J. Am. Chem. Soc.*, 2001, **123**, 3373.

8 A. Fukuoka, N. Higashimoto, Y. Sakamoto, S. Inagaki, Y. Fukushima and M. Ichikawa, *Microporous Mesoporous Mater.*, 2001, **48**, 171.
9 H. Araki, A. Fukuoka, Y. Sakamoto, S. Inagaki, N. Sugimoto, Y. Fukushima and M. Ichikawa, *J. Mol. Catal. A: Chem.*, 2003, **199**, 95.
10 C. Yang, P. Liu, Y. Ho, C. Chiu and K. Chao, *Chem. Mater.*, 2003, **15**, 275.
11 Z. Zhang, S. Dai, D. A. Blom and J. Shen, *Chem. Mater.*, 2002, **14**, 965.
12 A. Muramatsu, S. Shitara, H. Sasaki and S. Usui, *Shigen to Sozai*, 1990, **106**, 805.
13 H. Takahashi, Y. Sunagawa, S. Myagmarjav, K. Yamamoto, N. Sato and A. Muramatsu, *Mater. Trans., JIM*, 2003, **44**, 2414.
14 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
15 S. Myagmarjav, H. Takahashi, Y. Sunagawa, K. Yamamoto, N. Sato, E. Matsubara and A. Muramatsu, *Mater. Trans., JIM*, 2004, **45**, 2035.
16 H. Takahashi, S. Myagmarjav, Y. Sunagawa, N. Sato, K. Yamamoto and A. Muramatsu, in TiO_2 support effect on the formation of Ni–Zn nanoparticles by liquid-phase reduction method, *Proceedings of 93rd CATSJ Meeting, Toyonaka*, Catalysis Society of Japan, Tokyo, 2004, 86.
17 J. W. McBain, *J. Am. Chem. Soc.*, 1935, **57**, 699.