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PREPARATION AND CHARACTERIZATION OF Ni NANOPARTICLES IN AN MCM MESOPOROUS MATERIAL

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ABSTRACT

An aluminosilicate with the MCM-41 structure (A1MCM-41) was used as a host for the synthesis of nickel metal nanoparticles. Initially, ion exchange in aqueous solutions allows the introduction of nickel cations into A1MCM-41, and then reduction with sodium borohydride produces nanometer-sized nickel metal particles. Products (Ni-AlMCM-41) were characterized by elemental analysis, transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and magnetic susceptibility. Ni-AlMCM-41 was found to have a Ni:Al:Si ratio of ca. 1:4:28. The nickel metal particles were 1–2 nm in diameter and showed superparamagnetic behavior with a blocking temperature (T_b) of 5 K. *© 1999 Elsevier Science Ltd*

KEYWORDS: A. composites, A. nanostructures, B. chemical synthesis, C. X-ray diffraction, D. magnetic properties

INTRODUCTION

The design and synthesis of materials with nanometer dimensions in the so-called mesoscopic size range are currently the subject of intense research because their properties differ considerably from those of the corresponding bulk materials. In particular, samples with

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particle sizes in the range 1–10 nm can exhibit novel electronic, optical, magnetic, and chemical properties due to their extremely small proportions. These particles have many technological applications, e.g., in magnetic recording media, ferrofluids, and catalysts [1]. A critical obstacle in assembling and maintaining a nanoscale material is often high reactivity from the large surface ratio and the spontaneous production of macroscopic-sized agglomerates that lack the unique properties of nanoscale particles. In contrast to the conventional preparation methods, the use of an inorganic matrix as a host for nanocrystalline particles can provide an effective way of tailoring a uniform size and controlling the homogeneous dispersion of ultrafine clusters. Cross-linked ion-exchange polymer resins, inorganic molecular sieves, and sol-gel derived materials have been employed as porous hosts for synthesizing nanoclusters [2]. These methods offer excellent control of size distribution and morphology through the manipulation of the wet chemical processing parameters, and for the inorganic host structures, higher thermal stability.

Microporous molecular sieves have been widely used for hosting nanoclusters, but they are limited to pore openings of less than 1 nm [3]. The recent discovery of mesoporous MCM-41 offers a possibility for synthesizing 3D heterostructures in a previously inaccessible size range, by inclusion chemistry [4,5]. MCM-41 is a porous amorphous silica material with a hexagonal honeycomb structure that can be synthesized with controllable pore diameter in the range 2–10 nm. The pores are separated by amorphous silica walls with a thickness of approximately 0.8 nm, corresponding closely to the width of a silica double layer. Corma and co-workers [6,7] have reported that calcined AlMCM-41, with aluminum incorporated into the framework of the MCM-41, exhibited an acidity of medium strength comparable to that of USY zeolite. Kim et al. [8] investigated the exchange behavior of this material, and Bein and Wu [9] have reported exchange of copper for the synthesis of polyaniline within the MCM-41 channel. Specific studies involving the placement of nickel species into MCM-41 and AlMCM-41 have examined nickel oxide and Ni(I) species for use in catalysis [10]. In the present study, we employed mesoporous AlMCM-41 as a host material in the preparation of nickel metal nanoparticles. In this paper, the synthesis and characterization of these novel SiO_2-coated magnetic nanocomposites are presented.

EXPERIMENTAL

Materials. All reagents were used as received. The silica source, sodium silicate solution (27% SiO_2, 14% NaOH), hexadecyltrimethylammonium chloride (HTACl, 25% solution in water), ammonium hydroxide (28.0–30.0% NH_3 in water), nickel (II) bromide (98%), and $NaBH_4$ (98%) were obtained from Aldrich. Aluminum, in the form of sodium aluminate, was purchased from Sigma. Doubly distilled and deionized water were used in all preparations.

Synthesis. AlMCM-41 was prepared by a hydrothermal reaction method similar to that reported in the literature [8]. HTACl was dissolved in distilled water with vigorous stirring. The sodium silicate solution and ammonia were combined with the HTACl to give a surfactant-silicate gel with a molar composition for SiO_2, HTACl, Na_2O, NH_4OH, and water of 4:1:1:0.15:211. The solution was mixed thoroughly for 30 min before sealing the gel in a Teflon-lined Parr bomb. The vessel was heated at 100°C for 1 day. After cooling to room temperature, the pH of the surfactant-silicate gel mixture was decreased to 10.2 by dropwise addition of a 1 M H_2SO_4 solution. The sample was then heated an additional day at 100°C. Aluminum was introduced as a 5 wt% sodium aluminate solution with stirring. The resulting gel mixture was again heated hydrothermally to 100°C for 1 day. The pH adjustment of the mixture and subsequent hydrothermal reaction were repeated once more. After cooling the bomb to room temperature, the precipitated white powder was filtered, washed, and dried at 90°C. The surfactant was removed from the aluminosilicate framework by calcination in air; the sample was heated up to 540°C over a10 h period and held at this temperature for 10 h. The final product was found to have an aluminum:silicon ratio of 1:7.

Nickel nanoparticles were prepared in AlMCM-41 by a method similar to that described [11] for microporous mordenite. AlMCM-41 (0.2 g) was slowly stirred in 30 mL of 0.05 M $NiBr_2$ aqueous solution. The sample was then filtered and washed with distilled water. To maximize the extent of exchange, the ion exchange step was repeated five times. To remove the extra-pore Ni^{2+} ions from AlMCM-41 host material, the resulting Ni^{2+}-AlMCM-41 green powder was suspended in distilled water for 1 h [12]. To reduce the nickel cation in the AlMCM-41, a $NaBH_4$ solution was added dropwise with stirring into 20 ml distilled water containing the Ni^{2+}-AlMCM-41 powder (ca. 0.2 g). The resulting black solid, Ni-AlMCM-41, was then filtered, washed repeatedly, and dried.

Annealing studies were carried out on Ni-AlMCM-41 to gauge its effect on the both the host and the nickel metal particles. Samples were heated at 250, 500, and 750°C in sealed evacuated ($<10^{-3}$ Torr) Pyrex or fused silica tubes for 24 h.

Elemental Analysis, Electron Microscopy, and X-ray Diffraction. Quantitative analysis with inductively coupled plasma spectroscopy (ICP) was performed on a Perkin-Elmer Plasma 40 emission spectrometer. Nickel was extracted from the host material by an acid treatment, while the composition of the host itself was determined on samples dissolved in concentrated NaOH. TEM images were obtained on a Zeiss 100 microscope. Powder X-ray diffraction (XRD) data were collected on a Philips X'Pert MPD system equipped with copper radiation ($\lambda = 1.5418$ Å) and a graphite monochrometer.

Magnetic Measurements. The magnetic properties of the Ni-AlMCM-41 were characterized using a Quantum Design MPMS-5S SQUID susceptometer. Calibration and measurement procedures have been described in detail elsewhere [13]. Typically two types of experiments were conducted: dc magnetic susceptibility, both field-cooled (FC) and zero-field-cooled (ZFC), as a function of temperature down to 1.7 K and magnetization as a function of field (hysteresis) between 2 and 30 K.

RESULTS AND DISCUSSION

One of the most significant recent developments in mesoporous chemistry is the discovery that surfactants can template the synthesis of highly ordered mesoporous silicates and aluminosilicates, a family of materials known collectively as M41S [5]. Calcination of silicate and aluminosilicate gels in the presence of surfactants is used to build network materials with a high degree of long-range order. In terms of application, these porous framework systems are of considerable importance as ion exchangers, as molecular sieves for separation and purification of gases, and as catalysts [14–17]. Due to the large channel diameters, the MCM-41 hosts are excellent candidates for nanosized magnetic material synthesis.

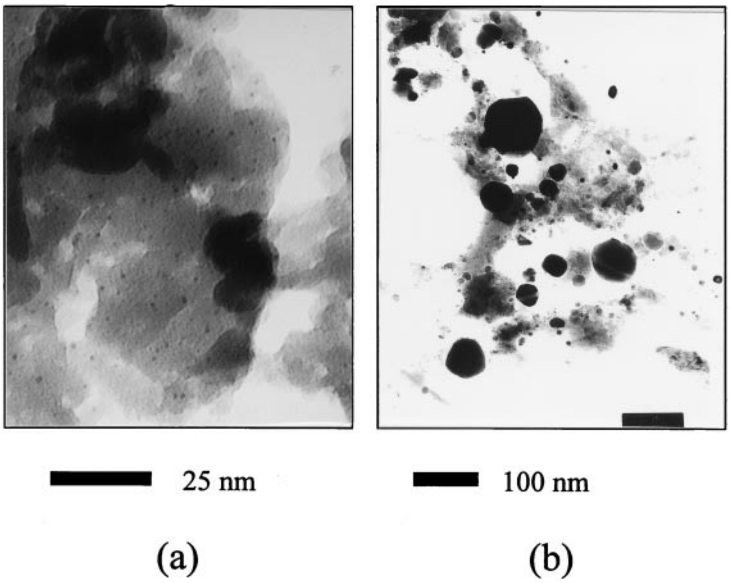

FIG. 1
Transmission electron micrographs of Ni-AlMCM41 before (a) and after (b) calcination at 750°C.

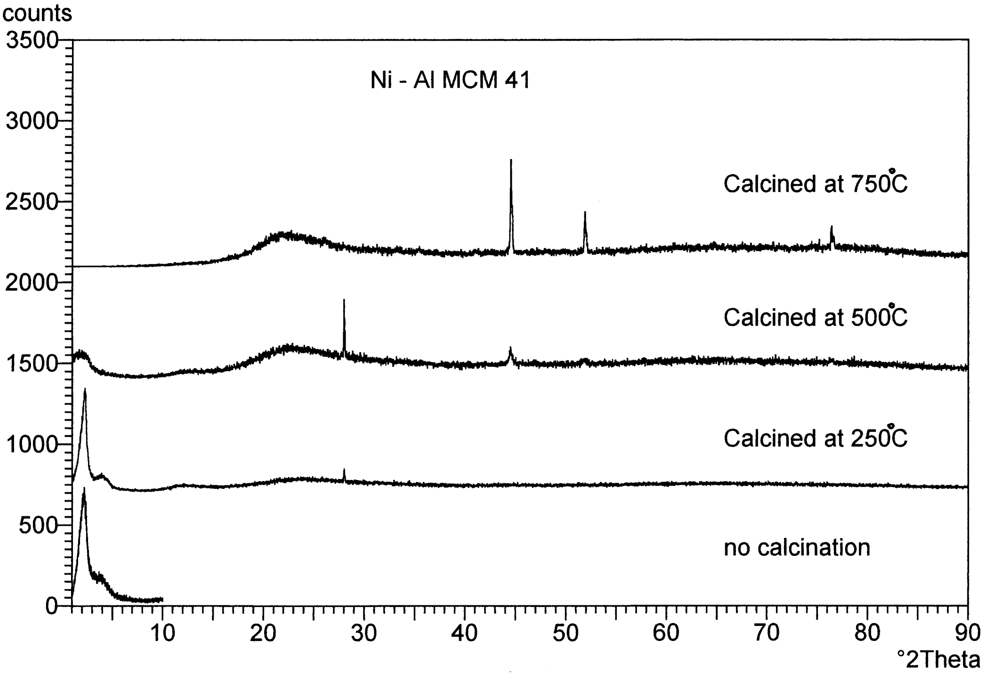

FIG. 2
XRD patterns of Ni-AlMCM41 samples as synthesized (a) and as calcined at 250°C (b), 500°C (c), and 750°C (d).

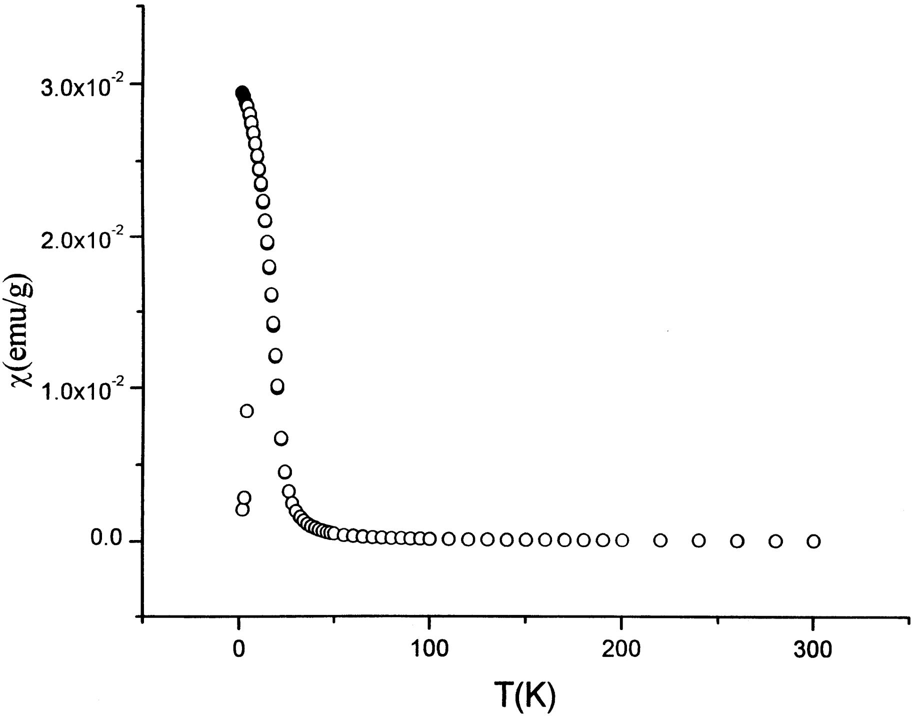

FIG. 3
Temperature-dependent field-cooled and zero-field-cooled dc magnetic susceptibility for the Ni-AlMCM41. The experiment was conducted with an applied field of 1000 G.

The goal of this work was to obtain reduced Ni metal nanoparticles trapped inside MCM channels, distributed homogeneously throughout the MCM without larger particles at the external surface. In this work, we used AlMCM-41 as a host for Ni ion exchange. Elemental analysis of the Ni-AlMCM-41 product showed that this material contained 1.48 wt% Ni. This loading is far from a complete filling of the MCM channels, due to the low negative charge on the framework (Si/Al = 7) and incomplete ion exchange (Ni/Al = 0.26). When the reduction of nickel metal ions by $NaBH_4$ takes place in the AlMCM-41 host material, the Ni metal atoms tend to agglomerate into small nanoparticles in the channels. The TEM micrograph in Figure 1a shows spherical clusters of 1–2 nm diameter within the AlMCM-41 host.

Powder X-ray diffraction was used in this work to check on AlMCM-41 stability and nickel particle growth as a function of temperature. In Figure 2, we present a series of powder X-ray diffraction patterns of annealed Ni-AlMCM-41 products. It is evident that the AlMCM-41 host material retains some degree of its regular pore structure up to 500°C. Concurrently, the nickel particles show significant grain growth. In the XRD pattern for the Ni metal appear three broad peaks at 2θ values of 44.5, 52.9, and 76.4, which correspond to three of the distinct peaks of Ni metal. The average crystallite sizes, as could be calculated from line broadening in the 500 and 750°C samples, were 12 nm and 76 nm, respectively. The TEM image in Figure 1b shows, however, that the annealed samples had a wide

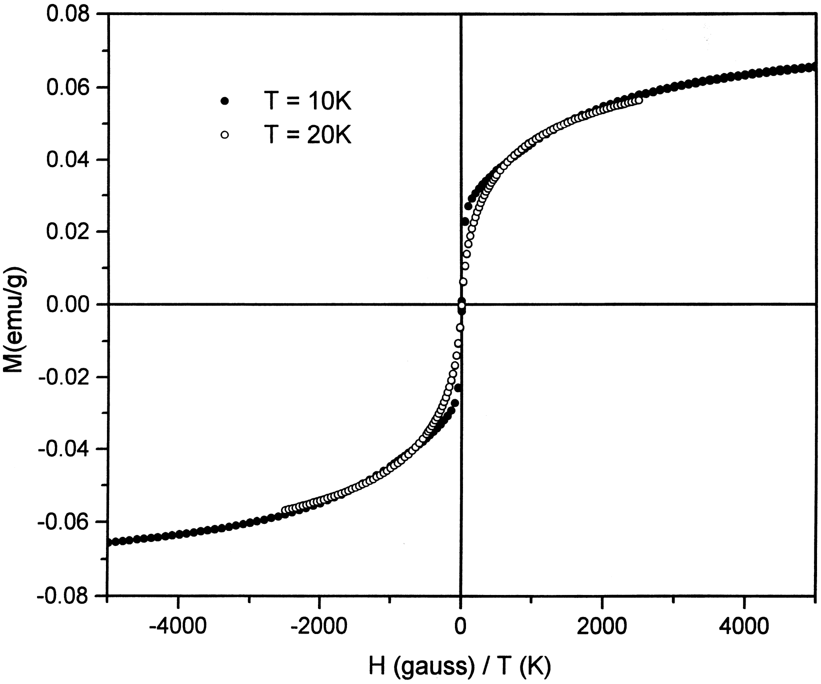

FIG. 4
Magnetic hysteresis loop for Ni-AlMCM41 at 10 and 20 K.

distribution of particle sizes, some approaching 100 nm. The broad peak centered at about 25° 2θ is attributed to the amorphous aluminosilicate wall, while the sharp peak at about 28° 2θ, which is seen only at intermediate temperatures, is attributed to the host and represents some level of ordering just prior to collapse.

FC and ZFC temperature-dependent dc magnetic susceptibility data for the unannealed Ni-AlMCM-41 sample are shown in Figure 3. Both data sets show that the magnetization exhibits identical behavior at temperatures above 5 K, but changes dramatically at lower temperatures. The plotted data for magnetization as a function of applied field (M vs. H curves), obtained at 10 and 20 K, show no hysteresis, and the two curves are superimposable (Fig. 4). Also, the magnetization curves show a significant hysteresis below 5 K (Fig. 5). This magnetic behavior confirms the superparamagnetism of the nanocomposite system with a blocking temperature (T_b) of 5 K [18]. The superimposition without deviation between the FC and ZFC curves also indicates that there is a uniform distribution in particle size and no interaction between them [19]. Further evidence for this narrow particle size distribution is given by the sharp maximum of ZFC at T_b of 5 K and the dramatic splitting between ZFC and FC curves just below T_b. At 5 K, the hysteresis loop of the nanocomposite corresponded to a remanence of 0.03 emu/g and a coercivity of 4500 G. The smaller remanence and larger coercivity of the nanocomposite relative to bulk Ni are due to the single domain size of the clusters, with the coercivity coming from the coherent rotation of the magnetization of the particle away from its easy axis.

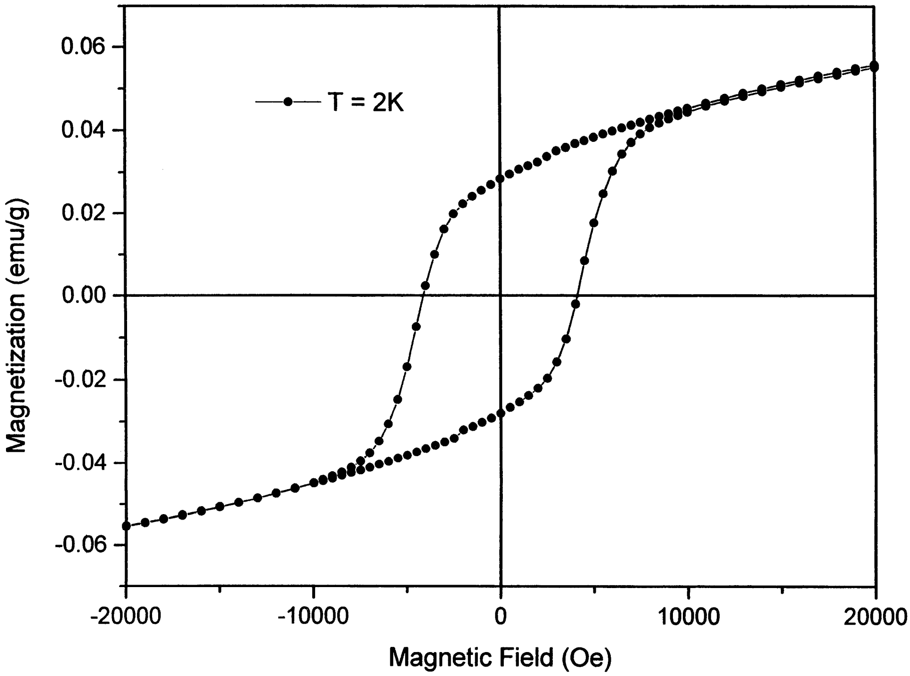

FIG. 5
Magnetic hysteresis loop at 2 K for Ni-AlMCM41.

CONCLUSIONS

Mesoporous materials based on the MCM-41 series are viable hosts for the controlled synthesis of metal nanoparticles. Through the use of the ALMCM-41 phase, ion exchange can be used to introduce magnetically interesting cations. Subsequent treatment of the exchange product with a reducing agent results in a narrow size distribution of finely divided nickel metal particles that demonstrate superparamagnetism. We are currently working to expand this approach, with the goal of utilizing the host pore to regulate the growth of larger magnetic nanoparticles.

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REFERENCES

1. J.L. Dormann and D. Fiorani, *Magnetic Properties of Fine Particles*, North-Holland, Amsterdam (1992).
2. R.F. Ziolo, E.P. Giannelis, B.A. Weinstein, M.P. O'Horo, B.N. Ganguly, V. Mehrotra, M.W. Russell, and D.R. Huffman, *Science* **257**, 219 (1992).

3. J.L. Garcia, F.J. Lazaro, C. Martinez, and A. Corma, *J. Magn. Magn. Mater.* **363**, 140 (1995).
4. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.J. Kresge, K.D. Schnitl, C.T.-W. Chu, K.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenken, *J. Am. Chem. Soc.* **114**, 10834 (1992).
5. A. Corma, *Chem. Rev.* **97**, 2373 (1997).
6. A. Corma, V. Fornes, M.T. Navarro, and J. Perz-Pariente, *J. Catal.* **148**, 569 (1994).
7. W. Kolodziegjski, A. Corma, M.T. Navarro, and J. Perz-Pariente, *Solid State Nucl. Magn. Reson.* **2**, 253 (1993).
8. J.M. Kim, J.H. Kwak, S. Jun, and R. Ryoo, *J. Phys. Chem.* **99**, 16742 (1995).
9. T. Bein, and C. Wu, *Chem. Mater.* **6**, 1109 (1994).
10. J. Cui, Y.-H. Yue, W.-Y. Dong, and Z. Gao, *Stud. Surf. Sci. Catal.* **105A**, 687 (1997); M. Hartmann, A. Pöppl, and L. Kevan, *J. Phys. Chem.* **99**, 17494 (1995); M. Hartmann, A. Pöppl, and L. Kevan, *J. Phys. Chem.* **100**, 9906 (1996).
11. L Zhang and A. Manthiram *J. Mater. Chem.* **6**, 999 (1996).
12. T. Abe, Y. Tachibana, T. Uematsu, and M. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1617 (1995).
13. C.J. O’Connor, *Prog. Inorg. Chem.* **29**, 203 (1982).
14. J.M. Thomas, *Nature* **368**, 289 (1994).
15. P.T. Tanev, M. Chibwe, and T.J. Pinnavaia, *Nature* **368**, 322 (1994).
16. R. Schmidt, M. Stocker, E. Hansen, D. Akporiaye, and O.H. Ellestad, *Microporous Mater.* **3**, 443 (1995).
17. C.G. Wu and T. Bein, *Science* **264**, 1757 (1994).
18. C.P. Bean and J.D. Livingston, *J. Appl. Phys.* **30**, 1205 (1959).
19. A.S. Waniewska, M. Gutowski, and H.K. Lachowicz, *Phys. Review B.* **46**, 14594 (1992).