Materials Letters 111 (2013) 154–157

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

In situ observation of sintering of nickel nanoparticles during nanocasting into mesoporous silica

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ARTICLE INFO

Article history:
Received 21 May 2013
Accepted 18 August 2013
Available online 26 August 2013

Keywords:
Electron microscopy
Sintering
Nanocasting
Nickel
Mesoporous silica
Monolith

ABSTRACT

Hierarchically porous metals are of interest in several application fields, including heterogeneous catalysis. Here, we report the nanocasting of nickel metal into hierarchically porous SBA-15 type monoliths containing ordered arrays of mesopores. Upon removal of the silica template, nickel replicas showed no evidence of an ordered mesopore structure. TEM images and XRD measurements of the nickel–silica composite show that nickel nanoparticles larger than the silica mesopores have formed. *In situ* heated stage TEM measurements indicate that sintering of nickel nanoparticles occurs, which leads to rapid disruption of the silica template in vacuum. This disruption appears to occur more rapidly in vacuum than under hydrogen atmosphere.

1. Introduction

Porous metals have a variety of potential application fields, including catalysis, electrochemical chromatography, and separation [1]. Current syntheses of porous metals include metal foams [2], aerogels [3], and sintering of metal nanoparticles [4], but many of these processes lead to poor control over the final structure and wide pore size distributions are usually obtained. The process of nanocasting has recently been applied to several metals, such as gold [5] and platinum [6], in mesoporous silica particles, as well as some in monolithic form, such as nickel [7]. These nickel metal monoliths have been found to be similar to Rainey nickel in catalytic efficiency [8], but higher surface area and better control over pore size are still desired.

To reach these goals, the underlying process of the nanocasting of metal must be better understood. Herein, we report the use of *in-situ* transmission electron microscopy to follow the evolution of nickel in ordered mesoporous silica monoliths as a function of temperature. At elevated temperatures, sintering of the nickel metal crystallites disrupts the mesoporous silica template, leading to loss of order in the nickel replica.

2. Experimental

Materials: Tetramethyl orthosilicate (TMOS) was purchased from Alfa Aesar. Pluronic 123 (P123) surfactant was provided by BASF Corporation. Acetic acid, nickel nitrate, and potassium hydroxide were purchased from VWR. All materials were used as received.

Preparation of silica template: The SBA-15type monolithic silica template was prepared as previously reported [9]. For a typical synthesis, 6.25 g of P123 was dissolved in 20 mL 0.02 M acetic acid. After fully dissolved, the solution was cooled to 0 °C and 8 g TMOS was added and stirring continued for 30 min. The solution was then transferred into molds, gelled at 40 °C for 24 h, and then 60 °C for 24 h. The monoliths then underwent a steam treatment in an autoclave for 12 h at 100 °C, followed by a water treatment at 100 °C. The surfactant was removed by calcination up to 600 °C at a ramp rate of 1 °C/min.

Preparation of nickel/silica composites: A solution of 4.2 M nickel nitrate was used. Silica monoliths were vacuum infiltrated with solution, followed by heating under 5% H_2/N_2 at 150 °C for 10 h, then heating up to 300 °C at a ramp rate of 1 °C/min, and held for 4 h before being cooled down to room temperature [7,10]. For the replica, this process was repeated 4 additional times, followed by removal of the silica in 3 M KOH. For heated stage experiments, only one cycle of infiltration/heating was performed.

Characterization: SEM images were taken on a JEOL 7000 FE-SEM. TEM images were taken on an FEI Tecnai F-20 transmission electron microscope (TEM). Heated stage experiments utilized a Gatan double-tilt holder with heated stage and Gatan Smart Set Model 901 hot stage controller. Sample preparation consisted of grinding the monoliths, sonicating the resulting powder in ethanol, and then dispersing the slurry onto the TEM grid. The heating experiments were performed under vacuum. Nitrogen sorption measurements were taken on a Quantachrome Nova

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0167-577X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.08.080

2200 in helium mode. X-ray diffraction was performed on a Bruker D8 discover with GADDS detector.

3. Results and discussion

The parent silica monolith used for nanocasting has a surface area of 760 m^2/g. The isotherm (Fig. S1) shows a steep uptake between relative pressures of 0.6 and 0.8, which indicates a uniform pore size. BJH pore distribution reveals a sharp peak at about 8 nm, which is consistent with previous reports of SBA-15 type silica pores. SEM and TEM images of the parent silica can be seen in Fig. S2.

The isotherm for the nickel–silica composite (Fig. 1), shows nitrogen uptake between 0.15 and 0.6 in relative pressure. This is shifted to a lower pressure range than for the parent silica, indicating that there is some pore blockage by the deposited nickel (evidenced by the wide hysteresis), and/or that the silica template has not remained intact. The surface area of the composite is 124 m^2/g. The pore size distribution shows a much broader peak than seen in the parent silica template. After etching, the surface area of the nickel monolith is 77 m^2/g, which is

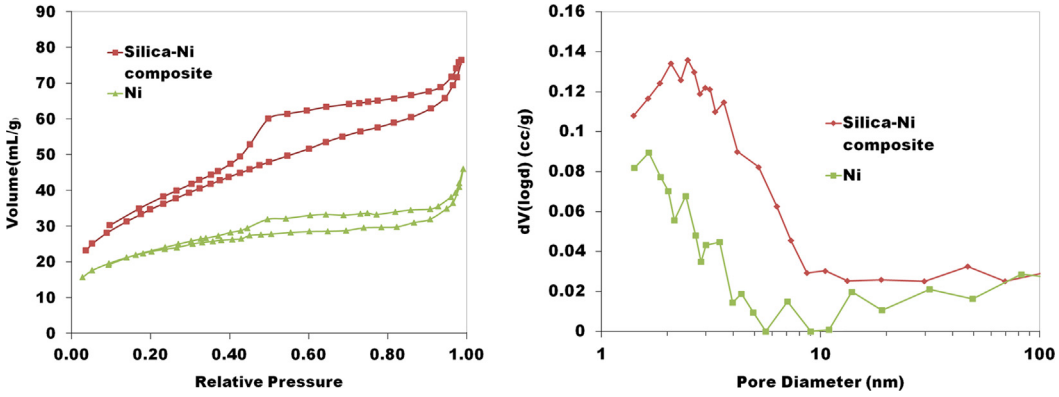

Fig. 1. Left, nitrogen sorption isotherms, and right, BJH pore size distribution for silica-nickel composite and nickel replica.

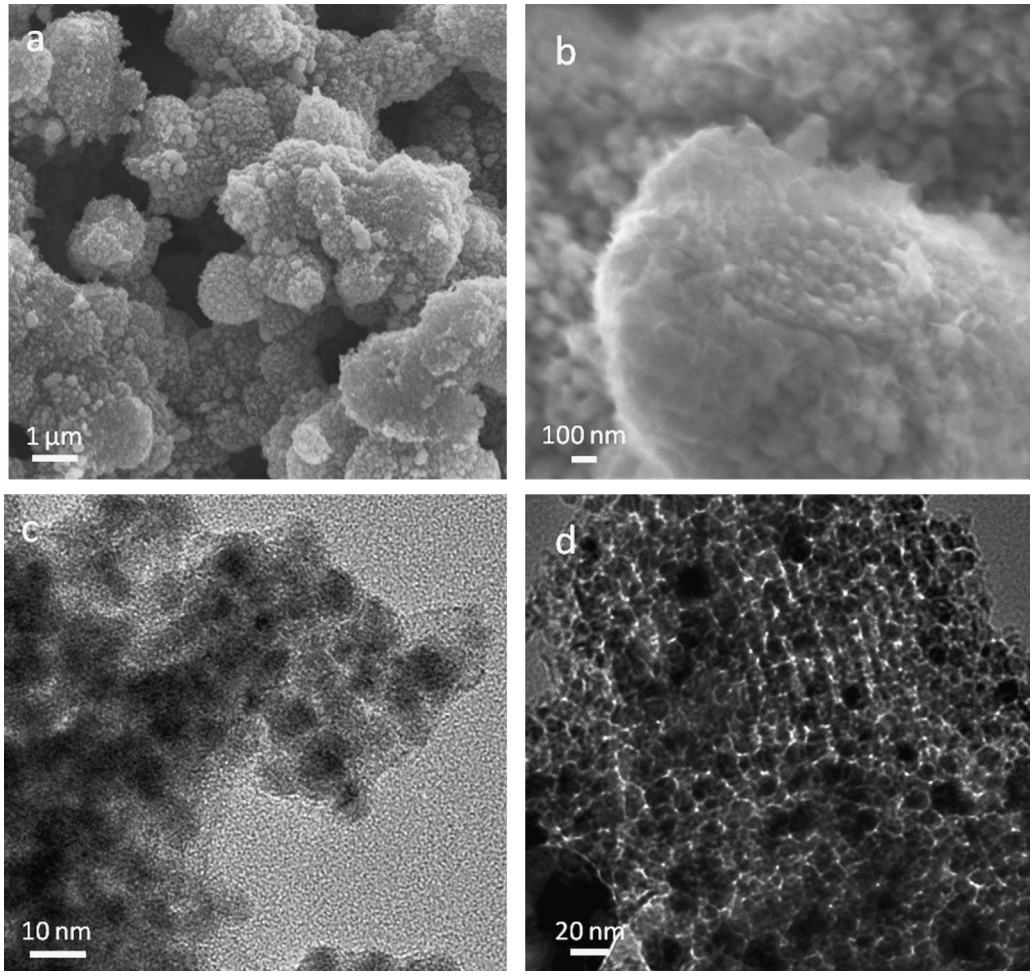

Fig. 2. (a and b) SEM image of etched nickel replica, (c) Representative TEM image of etched sample, and (d) TEM of silica–nickel composite.