Powder Technology 221 (2012) 359–364

Contents lists available at SciVerse ScienceDirect

Powder Technology

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

Synthesis of homogeneously dispersed cobalt nanoparticles in the pores of functionalized SBA-15 silica

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ARTICLE INFO

Article history:
Received 18 July 2011
Received in revised form 3 November 2011
Accepted 16 January 2012
Available online 24 January 2012

Keywords:
Functionalization
Cobalt
Cobalt oxide
Nanoparticles
SBA-15 silica
Sodium borohydride

ABSTRACT

Cobalt nanoparticles were prepared at room temperature by reducing cobalt sulfate heptahydrate with sodium borohydride using functionalized SBA-15 mesoporous silica as a hard template. It was found that both external and internal fuctionalization of silica walls play a crucial role on the infiltration and reaction of the reagents in the silica framework. Subsequent heat treatment of the impregnated silica at 500 °C in air or nitrogen atmospheres leads to growth of crystals of the deposited cobalt and formation of cobalt oxide and cobalt nanoparticles, respectively. Dissolution of the silica template by NaOH resulted in well dispersed Co and Co_3O_4 nanoparticles ranging in size between 2 and 4 nm. The functionalization of the silica was studied by FTIR, N_2-physisorption, and thermogravimetric techniques and the obtained nanoparticles were characterized by XRD, TEM and EDX analysis.

1. Introduction

In recent years the synthesis of metals and metal oxides in nanoparticle form with well-defined sizes, shapes, and crystallinity has received increasing attention because of their unique physicochemical properties, which make them desirable in many technological applications such as sensors [1], catalysis [2], and hydrogenation processes [3]. The unique characteristics of cobalt metal, especially the magnetic properties, make it attractive in a wide range of applications, e.g. data information storage [4], recording devices, and magnetic refrigeration including biomedical systems [5].

Cobalt nanoparticles can be synthesized using various techniques, such as thermal decomposition [6], pressure drop-induced decomposition [7], microemulsion methods [8], chemical reduction of cobalt salts by borohydride derivates and hydrazine hydrate as the reducing agent [9]. Depending on the synthesis method, cobalt particles with different morphologies and sizes can be obtained, e.g. dendritic structures [10], nanorods [11], and microspheres [12]. However, size and dispersion control of synthesized Co-nanoparticles remain subjects to explore.

Selective functionalization of the silica surface has been used as a method to synthesize Ag nanoparticles in the channels of SBA-15 by using formaldehyde as the reducing agent [13,14]. However, to reduce other metals such as cobalt from its salt solution, a strong reducing agent is needed. Recently, Bahadur and co-workers [15] have successfully synthesized iron-cobalt alloy nanoparticles by reduction from cobalt and iron chlorides using sodium borohydride, which is a widely used and powerful reducing agent in wet-chemical processes.

In this study, we present an effective approach to synthesize monodisperse cobalt nanoparticles with a narrow size distribution by modifying internal and external surfaces of SBA-15 mesoporous materials with two different functional groups (see Scheme 1).

2. Experimental details

2.1. Materials

Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Aldrich), tetraethyl orthosilicate (TEOS) (reagent grade, 98%, Aldrich), hydrochloric acid (purity ≥ 37%, puriss. p.a., Fluka, ACS Reagent, fuming), toluene (anhydrous 99,9%), Trimethylchlorosilane (TMCS ≥ 99%, Aldrich), 3-Aminopropyltrimethoxysilane (APTMS 97%, Aldrich), sodium hydroxide pellets (purity ≥ 97%, purum. p.a., Fluka), cobalt (II) sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$, 99%, Aldrich), sodium borohydride ($NaBH_4$, 99%, Aldrich), were used as received.

2.2. Synthesis

The steps involved in the synthesis are illustrated in Scheme 1. Monodispersed mesoporous silica SBA-15 with a hexagonal pore arrangement (Scheme 1a) was synthesized and used as molds for templating of cobalt and cobalt oxide nanoparticles. The detailed

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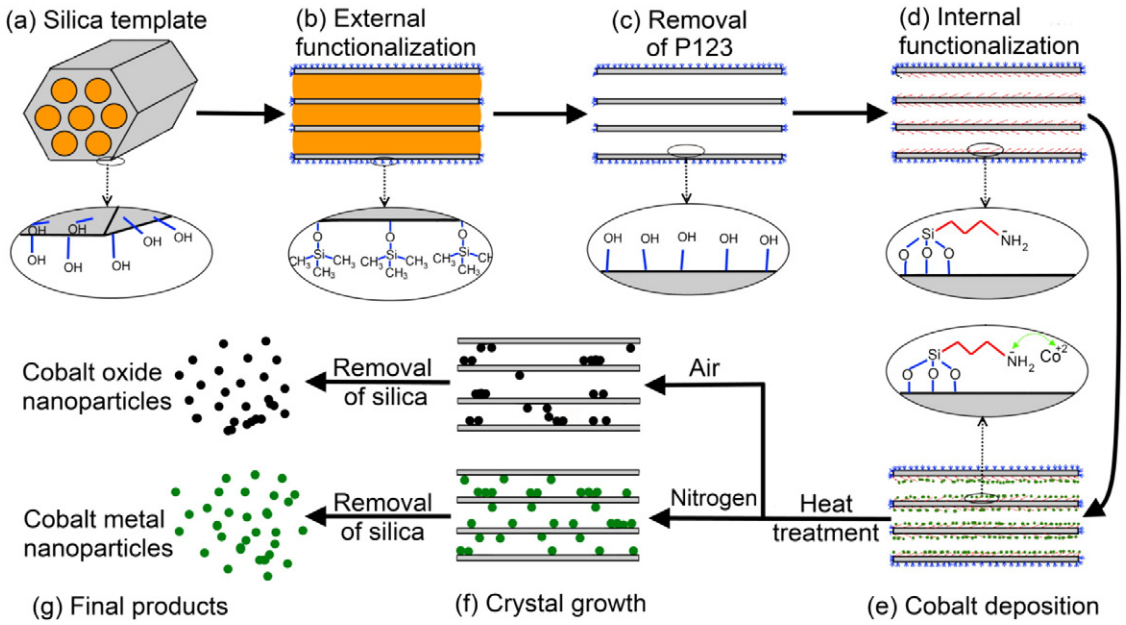
doi:10.1016/j.powtec.2012.01.025



Scheme 1. Steps involved in the synthesis of cobalt nanoparticles.

description of the synthesis route was reported by Sayari et al. [16], where the triblock copolymer Pluronic P123 was used as a structure directing agent, and tetraethyl orthosilicate TEOS as silica source in acidic condition. The obtained silica sample is labeled as (as-SBA-15).

The external surface of the as-SBA-15 sample was functionalized by trimethylchlorosilane (TMCS) according to the earlier procedure developed by Zhang et al. [14]. Typically, 1.0 g of as-synthesized silica (as-SBA-15) was stirred into 100 mL of toluene in a round bottom flask for 30 min at room temperature. Subsequently, 15 mL of trimethylchlorosilane was added and heated at 80 °C for 8 h under stirring. The filtrated solid was washed twice with toluene and dried at room temperature (Scheme 1b). The obtained sample was labeled (TMCS-SBA-15). Subsequently, to remove P123 from the pores, the functionalized silica was calcinated at 300 °C for 5 h (Scheme 1c). This sample is labeled (300-TMCS-SBA-15).

The modification of the internal walls of the silica was carried out using 3-aminopropyl-trimethoxisilane (APTMS), where $-Si(CH_2)_3NH_2$ groups are grafted into the channels of silica through the reaction between silanol groups and 3-aminopropyl-trimethoxysilane (Scheme 1d). The procedure applied is a modification to what has been previously reported [13,17]. Typically, 0.5 g of 300-TMCS-SBA-15 sample was suspended for 30 min in 80 mL of toluene, and then 5.0 mL of APTMS was added and stirred at room temperature for 24 h. After that the solid was refluxed for 5 h by soxlet extraction in 80 mL of toluene in order to remove the physical sorption of APTMS. The obtained sample was labeled (TMCS-APTMS-SBA-15).

The method to reduce cobalt salt sources inside channels of the silica (Scheme 1e) was performed as follows: 0.5 g of dried TMCS-APTMS-SBA-15 sample was transferred to a round bottom flask and mixed with 30 mL of cobalt (II) sulfate solution (0.02 M), and sonicated for 15 min at room temperature. In order to remove the excess of cobalt precursor the sample was filtered and dried, and subsequently 30 mL of $NaBH_4$ aqueous solution (0.1 M) was added drop wise during magnetic stirring for 20 min to reduce the cobalt ions; the mixture was then kept in a sonication bath for 15 min at room temperature. The obtained sample was labeled (TMCS-APTMS-Co-SBA-15).

Growth of the cobalt and cobalt oxide nanocrystals was achieved by heat treatment of the sample TMCS-APTMS-Co-SBA-15 under air or N_2 atmospheres to obtain cobalt oxide and cobalt metal, respectively (Scheme 1f). The temperature was increased with a heating rate of 10 °C /min to 500 °C and held for 5 h. Finally, to remove the silica template, a solution of NaOH (0.25 M) was mixed with the sample and sonicated at 55 °C for 5 h; the synthesized nanoparticles (Scheme 1g) were collected using centrifugation (4100 rpm/15 min).

2.3. Characterization

The crystalline structure was determined by powder X-ray diffractometry (XRD) using a Siemens D 5000 diffractometer and Cu Kα radiation. Transmission electron microscopy (TEM) was performed with an FEI Tecnai G2 microscope operated at 200 kV, and the chemical composition determined by energy dispersive X-ray spectroscopy (EDX) in the TEM. For preparing TEM samples, the product of interest was dispersed in acetone and then deposited onto carbon copper grids and allowed to dry before analysis.

Nitrogen adsorption–desorption measurements were performed at 77 K using a Micromeritics ASAP 2020 surface area and porosity analyzer. The samples were degassed at 373 K for 9 h before the measurement. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) model [18] over a relative pressure (P/P_0) range of 0.08–0.2; the pore size distribution was derived from the adsorption isotherm branch using Kruk–Jaroniec–Sayari (KJS) method [19]. Finally the total pore volume was calculated from the amount of adsorbed N_2 at $P/P_0 = 0.975$.

The study of functional groups on the surfaces of silica by Fourier transformed infrared spectroscopy (FTIR) was performed using a Shimadzu FTIR-8400S spectrophotometer, using pressed KBr pellets. To prepare the pellets, 0.8 mg of sample and 120 mg of KBr powder were finely ground to remove scattering effects, and the powder mixture pressed to a pellet size suitable for the instrument.

Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses were performed using a Netzsch STA 449C Jupiter instrument. The measurements were carried out in air and nitrogen. Approximately 20 mg of material was placed in a sintered alumina crucible and the temperature was increased from room temperature to 700 °C at a heating rate of 10 °C/min.