



An X-ray absorption spectroscopy study of FeCo alloy nanoparticles embedded in ordered cubic mesoporous silica (SBA-16)

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ABSTRACT

Nanocomposites containing FeCo alloy nanoparticles dispersed in a highly ordered cubic mesoporous silica (SBA-16) matrix were prepared using two different synthetic methods, co-precipitation and impregnation. Extended X-ray Absorption Spectroscopy (EXAFS) technique at both Fe and Co K-edges was used to investigate the structure of FeCo nanoparticles and the presence of additional disordered oxide phases. EXAFS technique gives evidence of differences in the oxidation degree of the FeCo nanoparticles depending on the synthetic method used.

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1. Introduction

In recent years FeCo alloy nanoparticles have been a subject of research for their unique physical, chemical and magnetic properties [1], which are due in particular to their small size and high surface to volume ratio. In order to avoid the aggregation of the nanoparticles and increase their stability, they can be homogeneously dispersed in an amorphous matrix. The dispersion of nanoparticles in a matrix is particularly effective for the applications of nanoparticles in catalysis; in particular, an ideal matrix for catalyst particles should be highly porous and have high surface area since these properties influence the accessibility of the active catalytic particles and therefore affect the selectivity and the activity of the catalyst. Recently, active nanoparticles dispersed in a mesoporous silica matrix are receiving increasing attention. In particular, catalysts formed by FeCo nanoparticles dispersed in an ordered mesoporous support are very interesting for the oriented growth of carbon nanotubes (CNTs), which are very attractive materials for their peculiar chemical, electronic and mechanical properties [2]. The pore sizes in mesoporous silica (20–500 Å) are in the range of the usual diameters of CNTs and the uniform distribution of pore dimensions where nanoparticles are allocated facilitates the production of CNTs with a narrow distribution of diameters.

Until now, the research has been mainly focussed on the preparation of catalysts supported on the hexagonal mesoporous silica (SBA-15), characterized by a two-dimensional array of ordered mesopores. However, the corresponding cubic mesoporous silica, SBA-16, appears to be more promising as a catalysts support since it is

characterized by a three-dimensional ordered network of interconnected pores providing better accessibility for reactants [3–5]. Unlike the hexagonal form, cubic mesoporous silica has not been studied extensively, probably because it can only be produced in a narrow range of conditions [6]. In particular, very little work has been done on the synthesis of metal nanoparticles dispersed in a SBA-16 matrix. Only few works dealing with films of nanocomposites of Fe nanoparticles dispersed in SBA-16 used as catalyst for the growth of vertically aligned CNTs [7,8] and Fe-filled CNTs have appeared in the literature [9]. However, FeCo alloy nanoparticles have been shown to be more effective than isolated Fe nanoparticles for the growth of CNTs [10].

In this work we present the results of the preparation and characterization of catalysts for production of CNTs formed by a cubic ordered mesoporous silica SBA-16 support with embedded FeCo alloy nanoparticles.

The knowledge of the structure of active nanoparticles within the support is particularly important because it plays a key role into the selectivity and activity of the catalyst towards the production of CNTs. However, X-ray diffraction (XRD) provides limited information mostly because of the low concentration of the nanocrystalline phase with respect to the silica matrix, the very small size of the particles which causes peaks broadening and the difficulty of distinguishing cobalt and iron which have very similar atomic scattering factors. X-ray Absorption Spectroscopy (XAS) is an ideal technique to gain selective and detailed information on the nanophases formed, since it is element specific and sensitive to the local structure. In particular, our previous XAS experiments on FeCo–SiO₂ aerogels [11] have shown that the possibility of studying separately the Fe and Co environment is essential in proving the formation of FeCo alloy nanoparticles and the possible presence of additional phases, such as oxides. Therefore, in this work, we have

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used EXAFS at the Fe and Co K-edges in order to gather selective information on the Fe and Co environment in the catalysts.

2. Experimental

2.1. Synthesis

The preparation of the catalysts formed by an SBA-16 support with embedded FeCo alloy nanoparticles was carried out using two different procedures.

The first approach is a two-step procedure in which SBA-16 matrix was prepared first and then submitted to wet impregnation with an aqueous solution of Fe and Co nitrates. The SBA-16 matrix was prepared following the recipe of reference [6]. Pluronic F127 (P127, Aldrich) block copolymer, formed by a sequence of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO₁₀₆–PO₇₀–EO₁₀₆) units with high molecular weight ($M_{av} = 12600$) and high EO/PO ratio, was used as a structure directing agent. 4.0 g of P127 were added to a mixture of 30 g of water and 120 g of HCl 2 M under stirring at room temperature. 8.5 g of TEOS (Aldrich 98%) were then added to the solution which was left under stirring at room temperature for 20 h. The solution was aged for 2 days at 80 °C. The precipitate was separated from the mother solution by centrifugation, washed with distilled water and dried at room temperature. Calcination was performed by heating in air at 500 °C for 6 h with a heating step of 1 °C/min. In the second step, the nanocomposites were prepared by wet impregnation of 0.3 g of SBA-16 with 10 mL of an aqueous solution of Fe(NO₃)₃·9H₂O (Aldrich, 98%) and Co(NO₃)₂·6H₂O (Aldrich, 98%), having an overall metal molar concentration of 0.4 M and Fe:Co molar ratio equal to 1:1, and vigorously stirred for 24 h. The impregnated SBA-16 was separated from the solution by centrifugation.

In the second approach a one-step co-precipitation procedure was followed. 4.0 g of P127 (Aldrich) were added to the mixture of 30 g of water and 120 g of HCl 2 M at room temperature under stirring, followed by the addition of 8.5 g of TEOS. 0.959 g of Fe(NO₃)₃·9H₂O (Aldrich, 98%) and 0.690 g of Co(NO₃)₂·6H₂O (Aldrich, 98%) were then added under stirring (molar ratio of Fe:Co equal to 1:1). The solution was left under stirring at room temperature for 20 h. Aging of the solution was performed leaving the solution for 2 days at 80 °C. The obtained product was separated from the mother solution by centrifugation, washed with distilled water and dried at room temperature.

Nanocomposites prepared by both impregnation and co-precipitation were calcined by heating the product in air at 500 °C for 6 h with a heating step of 1 °C/min. After calcination, samples were further treated at 800 °C in H₂ flow with a heating step of 10 °C/min and held at 800 °C for 2 h, in order to form the FeCo alloy nanoparticles. Samples prepared by co-precipitation and impregnation will be hereafter indicated as CP_FeCo_r800 and IMP_FeCo_r800, respectively.

2.2. Characterization

Transmission Electron Microscopy (TEM) micrographs were recorded on a JEOL 200CX microscope operating at 200 kV. The samples were deposited on a holey carbon-coated copper grid.

Wide-angle XRD patterns were recorded on a X3000 Seifert diffractometer equipped with a graphite monochromator on the diffracted beam using Cu-K α radiation within the range 15–85° (2 θ).

EXAFS experiments were carried out at beamline 11.1 (XAFS) at the ELETTRA synchrotron (Trieste, Italy). Data at the Fe (7112 eV) and Co (7709 eV) K-edges were collected at room temperature using a Si (111) monochromator. Samples with a suitable and highly uniform optical thickness were prepared as pellets by diluting the powder in polyvinylpyrrolidone. The EXAFS spectra were processed using the

program Viper [12] to sum the data, identify the beginning of the absorption edge, E_0 , fit pre and post edge backgrounds, and hence to obtain the normalized absorbance χ as a function of the modulus of the photoelectron wavevector k . Fourier transforms (FTs) of EXAFS oscillations, corrected for the phase shifts, were calculated in the range 2.5–12 Å⁻¹ using the modular package DL_EXCURV [13], based on the EXCURV98 code.

3. Results

Fig. 1 shows TEM and XRD results of the samples prepared by co-precipitation and by impregnation. In the TEM images of CP_FeCo_r800 and IMP_FeCo_r800, reported in Fig. 1A and B, respectively, the highly ordered arrangement of mesopores of the silica matrix can be clearly observed. The three-dimensional cage-like cubic porous structure was confirmed by a variety of techniques, reported in Ref. 14 and 15. TEM images of both nanocomposites also show the presence of spherical nanoparticles of about 4–7 nm dispersed in the matrix.

The XRD patterns of CP_FeCo_r800 and IMP_FeCo_r800 shown in Fig. 1C are very similar. They show a halo at 2 θ ~20–30° due to

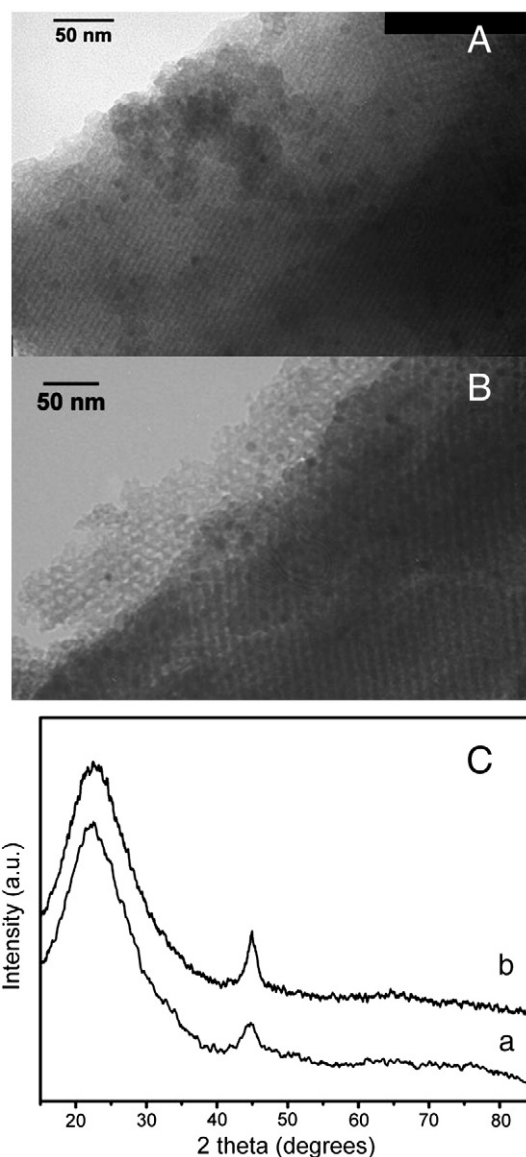


Fig. 1. (A): TEM image of CP_FeCo_r800; (B): TEM image of IMP_FeCo_r800; (C): XRD patterns of: (a) CP_FeCo_r800, (b) IMP_FeCo_r800.

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