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Sol-gel synthesis of $CoFe_2O_4$:SiO_2 nanocomposites – insights into the thermal decomposition process of precursors

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ABSTRACT

Succinate precursors dispersed in the silica matrix were obtained by sol-gel synthesis using Co and Fe nitrates, 1,4-butanediol and tetraethyl orthosilicate. The thermal decomposition of Co and Fe succinates into cobalt ferrite ($CoFe_2O_4$) at different $CoFe_2O_4$:SiO_2 molar percentages was studied by thermal analysis, Fourier transformed infrared spectrometry (FT-IR) and X-ray diffraction. The morphology of nanoparticles was identified by transmission and scanning electron microscopy. The formation of succinates in the pores of the silica matrix and their decomposition to $CoFe_2O_4$ spinel was confirmed by the FT-IR spectra. The nanocrystallites size (7–33 nm) increases with the decrease of SiO_2 content, suggesting that the growth process of nanoparticles is reduced in the presence of silica matrix.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) nanocomposites (NCs) are widely used in a variety of applications, such as: catalysts, insulators, sensors, information and energy storage media, coatings, etc. Most of these applications require specific electrical, optical and/or magnetic properties, mainly determined by their structure and morphology [1–3].

Coprecipitation, hydrothermal, combustion, sol-gel, evaporation condensation, electrochemical or sonochemical are the most used methods to obtain NCs [4–6]. Coprecipitation is frequently used to prepare nanoparticles dispersed in different matrices, due to its high yield and simplicity, although the particle size and shape are difficult to control [7–9]. Hydrothermal synthesis requires simple processing and low temperatures, whereas solid-state method requires temperatures above 800 °C [10,11]. The combustion method is a simple and fast synthesis route, as by addition of low-cost, widely available organic compounds such as glucose sustains the self-propagating combustion and also acts as dispersant and reducing agent [8,12]. One of the most versatile synthesis routes is sol-gel method that allows the control of complex oxides stoichiometry and the production of high purity, homogeneous and crystalline nanoparticles in mild reaction conditions [13,14]. Among the disadvantages of the sol-gel method are: the sol is viscous, the transfer of sol precursor into nanopores is governed by weak capillary forces only and high irregularity of nanoparticles due to large amount of gas spurts during the decomposing of the organic solvents [15]. As nanoparticles have the tendency to agglomerate, their dispersion in the silica matrix is an excellent method to reduce particle agglomeration and allows the particles stabilization. The biocompatible, nontoxic, highly hydrophilic silica coatings are suitable for multifunctional surface modification, while the amorphous silica matrix is an excellent host for supporting guest nanoparticles [16–19].

In our previous studies, $CoFe_2O_4$ dispersed in silica was synthesized using 1,2-ethanediol, 1,2-propanediol and 1,3-propanediol [20–22]. In the present study, 1,4-butanediol (1,4-BD) was used as organic component of the precursor in the synthesis of $CoFe_2O_4$:SiO_2 NCs with variable molar percentage (10:90, 30:70, 50:50, 70:30 and 90:10). The synthesized NCs were characterized by thermal analysis (TG) coupled with mass spectrometer (TG-MS), differential thermal analysis (DTA), X-ray diffraction analysis (XRD), Fourier transformed infrared spectrometry (FT-IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) coupled with energy-dispersive X-ray spectroscopy (EDX).

2. Materials and methods

All used reagents were of analytical grade. NCs with $CoFe_2O_4$:SiO_2

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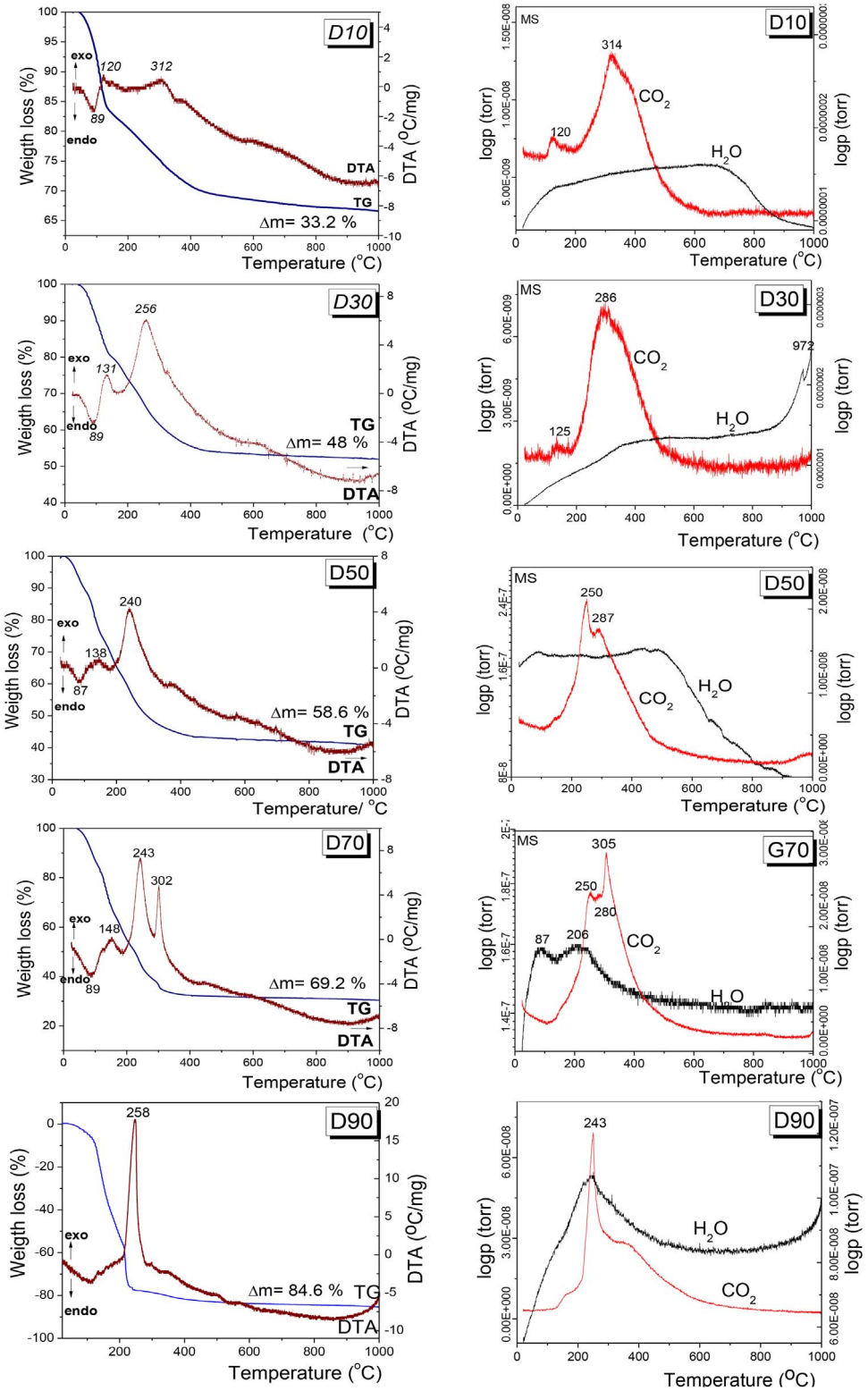

Fig. 1. TG-DTA and TG-MS diagrams for D10-D90 gels at 40 °C.

molar percentage of 10:90 (D10), 30:70 (D30), 50:50 (D50), 70:30 (D70) and 90:10 (D90) were synthesized by sol-gel method starting from iron nitrate ($Fe(NO_3)_3\ 9H_2O$), cobalt nitrate ($Co(NO_3)_2\ 6H_2O$), 1,4-BD and tetraethyl orthosilicate (TEOS) in ethanolic medium, under constant stirring and acid catalysis (HNO_3). The molar ratio of Co $(NO_3)_2{\cdot}6H_2O$:$Fe(NO_3)_3{\cdot}9H_2O$:1,4-BD was 1:2:8, while of NO_3^-:TEOS were 0.11 (D10), 0.43 (D30), 1 (D50), 2.35 (D70) and 8.89 (D90), respectively. The gelation times were 10 (D10 and D30), 12 (D50), 23 (D70) and 30 days (D90), respectively. The gels were grinded and dried at 40 °C for 5 h. The succinate precursors were obtained by redox