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Characteristics of Co_3O_4 and cobalt nanostructured microspheres: Morphology, structure, reduction process, and magnetic properties

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ABSTRACT

Nanostructured magnetic cobalt microspheres were synthesized using a two-stage method. First, nanostructured cobalt oxide Co_3O_4 microspheres were produced by ultrasonic spray pyrolysis at different temperatures from 800 to 1100C. Second, the nanostructured powders obtained were reduced to metal cobalt in an hydrogen atmosphere at different temperatures from 220 to 350C. In this study the evolution of the morphology from Co_3O_4 nanostructured microspheres to nanostructured Co, resulting from the Co_3O_4 reduction process, and the structure of metal cobalt, were investigated. It was found that the metal cobalt agglomerates have the same shape and mean diameter (~ 1,5 μm) as those of the cobalt oxide, Co_3O_4. The amount of Co microspheres with smaller diameters decreased with increasing reduction temperature. Also, the β-Co content increased with increasing reduction temperature.

1. Introduction

Nowadays magnetic nanomaterials attract increasing attention due to the fact that, in addition to their magnetic properties, they present unusual electronic, optical, and chemical properties, leading to a broad range of applications in storage, ferrofluid-based and microwave absorption devices, as well as in various medical applications [1–7].

Indeed, cobalt oxide is the choice candidate for a variety of applications due to its semiconducting, magnetic, optical, electrochemical, photocatalytic, and electrocatalytic properties. Also, it is considered as a promising candidate for applications in electrochromic devices, solar energy absorbers, sensors and biosensors, and Li-ion batteries [8]. Different methods have been reported for the Co_3O_4 preparation [9], such as electron beam evaporation, electrochemical and chemical vapor deposition, dip coating and sol-gel processes. Depending on the precursor, different morphologies of Co_3O_4 may be observed, more particularly, spherical nanoparticles [10,11], microplates [12], nanorods [13], nanocrystalline materials [14], nanofibers [15], nanocubes [16], hollow microspheres [17,18], etc… It has been reported [17] that Co_3O_4 samples prepared from cobalt acetate, cobalt chloride, and cobalt nitrate by the ultrasonic spray pyrolysis (USP) method present dimpled and wrinkled surfaces, porous spherical shapes and durian-like shapes, respectively. Thus, it should be expected that the various morphologies of the Co_3O_4 obtained should affect the morphology and the properties of the reduced metal cobalt.

Besides, nanostructured cobalt is an important material which also enters into a variety of applications [19–25] in catalytic [26–28] and battery electrode materials [29], electronic recording devices [30,31], microwave absorbers [24,25], and in the biomedical area [32,33]. Common methods of nanostructured metal cobalt synthesis described in [34,35] include reduction methods [19–21], sol-gel route [36,37], plasma-chemical synthesis [21], pulse evaporation methods [35] and biosynthesis [38]. These different methods allow to obtain nanostructured metal cobalt with a particle size ranging from 10 to 5000 nm (Table 1). This table shows that there is no correlation between the magnetic properties and the material characteristics such as particle size, morphology, and crystal structure. Metal cobalt exists in the α-Co (hcp) and the β-Co (fcc) forms. In the bulk material, the hcp phase is stable at room temperature which transforms into a bcc structure at 422 °C [39], while in the nanostructured material, the β-Co form is observed at lower temperatures than 422 °C [40]. From Table 1 it may be seen also that the saturation magnetization, M_s, of the coexistent face-centered cubic structure (fcc) and the hexagonal close-packed structure (hcp) is smaller than that of the single-hcp cobalt [19].

The main advantages of the ultrasonic spray pyrolysis (USP) method are the simplicity of the production equipment, the scalability and the

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Table 1
Properties of nanostructured cobalt synthesized by different methods.

	Synthesis method	Precursors	Morphology	Structure	Particle size	H_c, Oe	M_s, emu/g
1	Liquid reduction method (Wen et al. [19])	$CoSO_4$	nanostructured microspheres or flowerlike cobalt submicrospheres	hcp or fcc and hcp	2–5 μm	from 90 to 200.92	from 115.41 to 139.4
2	Liquid reduction method (Swain et al. [20])	$CoSO_4$	disc-shaped powder, spherical and non-spherical particles	fcc and hcp	from 100 to 300 nm	521.64	96.97
3	Plasmochemical synthesis (Dzidziguri et al. [21])	$Co(OH)_2$	spherical particles	fcc and hcp	20–200 nm	from 193 to 283	from 88 to 129
4	Liquid reduction method (Dzidziguri et al. [21])	$Co(OH)_2$	agglomerated spherical particles	fcc and hcp	56–83 nm	from 153 to 539	from 121 to 148
5	Infra-red pyrolysis (Dzidziguri et al. [21])	$Co(C_5H_7O_2)_2$	spherical particles in carbon shell	fcc	9–11 nm	from 280 to 677	from 11.0 to 14.7
6	Modified polyol process (Lakhdar et al. [22])	$Co(C_2H_3O_2)_2$	sub-micrometric fibers constituted by spheres and flower-like morphology	hcp	about 2 μm	from 81 to 171.0	from 117.4 to 144.0
7	Liquid reduction method (Fan et al. [23])	$CoCl_2$	hierarchical cobalt dendrites	hcp	lengths of 30–125 μm	133.1	172.0

possibility to control the composition and the particle size by adjusting the production conditions [41–46]. The two-stage method allows to control the properties of both the Co_3O_4 microspheres and the metal cobalt nanostructured microspheres. Indeed, the morphology and particle size of the Co_3O_4 microspheres may be controlled by varying the USP conditions, whereas the particle size and the phase structure of the metal cobalt may be controlled by varying the reduction conditions [47].

This study investigates the impact of the USP and the reduction conditions on the cobalt oxide and the metal cobalt morphology, particle size, and the crystal structure of metal cobalt and its impact on the magnetic properties in view of further potential applications.

2. Materials and methods

2.1. Materials used

The solution (10 wt.%) of analytical grade cobalt nitrate salt $Co(NO_3)_2 \times 6H_2O$ (Labteh, Russia) in distilled water was used as a precursor to synthesize the Co_3O_4 by means of the ultrasonic spray pyrolysis method.

2.2. Experimental procedure

The nanostructured Co_3O_4 microspheres were synthesized using the ultrasonic spray pyrolysis method that was previously described in great detail [47,48]. In brief, the aerosol generated in the frequency range from 1.7 to 2.2 MHz produced droplets with a mean diameter ranging from 0.5 to 10 μm. The aerosol is introduced into an electrical furnace Nabertherm RT 50/250/13 (Naberterm, Germany), which was heated at different temperatures: 800, 900, 1000 or 1100C, where it evaporated and thermally decomposed into droplets of Co_3O_4. The obtained finely divided aerosol was then passed through a filter and pumped out by means of a vacuum pump Vacuubrand MZ 2C NT + AK + EK (Vacuubrand, Germany) in order to collect the nanostructured Co_3O_4 powder.

The obtained powder was reduced to metal cobalt by a thermal treatment in the furnace Carbolite HZS 12/600E (CARBOLITE GERO, Germany) under a continuous flow of hydrogen. All the reduced metallic cobalt particles were then passivated under a nitrogen atmosphere of technical purity (Labteh, Russia).

To investigate the influence of the pyrolysis temperature on the metal cobalt properties, we reduced the temperature of all the samples pyrolyzed from 800, 900, 1000 or 1100 °C to 300 °C. These samples were labeled Co (800_300), Co (900_300), Co (1000_300) and Co (1100_300), respectively, in Figs. 2 and 3. To study the influence of the reduction temperature on the metal cobalt properties, a sample pyrolyzed at 1000 °C was selected and reduced at different temperatures. The reduction temperatures used were 220, 240, 300, and 350 °C. These samples were labeled Co (1000_220), Co (1000_240), Co (1000_300) and Co (1000_350), respectively, in Figs. 2 and 3.

2.3. Sample characterization

The crystal structure was determined by an X-ray phase analysis on a PANanalitical Empyrian (PANanalitical, Germany) with $Cu_{k\alpha}$, $\lambda = 0.154$ nm and Difrey 401(Scientific Instruments, Russia) with Cr, $\lambda = 0.229$ nm. The morphology, dispersion, and elemental composition of the samples were studied on a JEOL JSM-6610LV (JEOL, USA) scanning electron microscope (SEM) with an INCA SDD X-MAX (Oxford Instruments, UK) device for the analysis of the chemical composition (EDX). The thermogravimetric analyses were carried out on a TGA SDT Q600 (TA Instruments, USA). The room temperature magnetic properties were investigated on a VSM Lake Shore-7407 (Lake Shore Cryotronics, USA) vibration magnetometer in magnetic fields up to 10 kOe.

3. Results and discussion

3.1. X-ray analysis

The XRD showed that all the pyrolyzed samples consisted of a pure Co_3O_4 phase (Fig. 1).

According to XRD, all the samples obtained via the USP route, at various temperatures and followed by hydrogen reduction at 300 °C consisted of both α-Co with an hexagonal close-packed structure and β-Co with a face-centered cubic structure (Figs. 2 and 3).

The amount of the β-Co phase was calculated using a quantitative method based on the analysis of the intensity ratios of the two peaks: the first peak (100) corresponding to the pure α-Co and the second peak representing the sum of reflexes (002) from the α-Co and (111) from the β-Co [49]. The amount of the β-Co phase was in a range of 20 to 26% and these amounts did not depend on the pyrolysis temperature (Table 2).

The XDR patterns of all the reduced samples showed the presence of the α-Co and the β-Co. The amount of the β-Co phase ranges from 20 to 29% and depended on the reduction temperature rather than on the pyrolysis temperature. The β-Co content increased with increasing reduction temperature. This increase can be explained by the fact that in bulk cobalt β-Co is the stable phase at temperatures higher than 422 °C [39], whereas for the nanosized material the critical temperatures are lower than 422 °C [36]. However, the rate of the α → β transformation should increase with increasing temperature, but the temperature is still insufficient to complete that transformation.