



Amorphous iron–chromium oxide nanoparticles with long-term stability



Mihail Iacob^{a,b}, Maria Cazacu^{a,*}, Constantin Turta^b, Florica Doroftei^a, Martin Botko^c, Erik Čižmár^c, Adriana Zelenáková^c, Alexander Feher^c

^a “Petru Poni” Institute of Macromolecular Chemistry, Iasi 700487, Romania

^b Institute of Chemistry of ASM, Academiei str. 3, Chisinau 2028, Republic of Moldova

^c Institute of Physics, Faculty of Science, P.J. Šafárik University, Park Angelinum 9, SK-04154 Košice, Slovakia

ARTICLE INFO

Article history:

Received 24 June 2014

Received in revised form 3 November 2014

Accepted 25 January 2015

Available online 28 January 2015

Keywords:

Iron–chromium oxide

Amorphous

Nanoparticles

Morphology

Magnetic properties

ABSTRACT

Iron–chromium nanoparticles (NPs) were obtained through the thermal decomposition of μ_3 -oxo heterotrinnuclear $[\text{FeCr}_2\text{O}]$ acetate in the presence of sunflower oil and dodecylamine (DA) as surfactants. The average diameter of the NPs was 3.5 nm, as estimated on the basis of transmission electron microscopy and atomic force microscopy images. Both techniques revealed the formation of roughly approximated spheres with some irregularities and agglomerations in larger spherical assemblies of 50–100 nm. In hexane, NPs with diameters in the 2.33–4.85 nm range are individually dispersed, as emphasized by dynamic light scattering measurements. The amorphous nature of the product was emphasized by X-ray powder diffraction. The study of the magnetic properties shows the presence of superparamagnetic state of iron–chromium oxide NPs and the diamagnetic contribution from DA layer forming a shell of NPs.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Amorphous iron-oxide nanoparticles (NPs) are of high interest for catalysis as well as sensors, owing to their large surface area [1–4]. They can be synthesized by various methods such as electrochemical [5] or sonochemical techniques [2,6–8], microwave heating [9], hydrothermal treatment [10], thermal decomposition in the solid state or in solution [11], and in the presence or absence of some organic components, for example, in a mixture of polyethyleneglycol and urea [8] or with citric acid as a fuel [11]. In general, the used procedures started from iron salts (e.g., chlorides [10], nitrates [11], or chloride–nitrate [8]). Amorphous phase formation requires special conditions such as a high cooling rate, the sonochemical technique being one that could permit the creation of such conditions [4,12]. But as is known [4], the amorphous state is metastable and changes to the crystalline state through a crystallization process, during which long-range order can be formed and the physical and chemical properties of materials change accordingly, thus affecting the stability of the materials under ambient conditions. The crystallization process depends on temperature and time. Therefore, aging effects can be

prevented by a material synthesis procedure and by keeping it at a low temperature. Nguyen et al. [4,8] introduced different amounts of chromium into amorphous iron oxide NPs to slow down the aging effect. Based on thermal analysis, it has been showed that the chromium presence leads to increasing in activation energy of the phase transition, which could slow the ageing effect of the amorphous state during practical use [8]. Pt supported on Fe–Cr mixed oxides, prepared by the solid thermal decomposition reaction, proved to be an effective catalyst. By adding chromium compounds, Pt dispersion was improved and, as a result, the catalytic performance increased. Moreover, the addition of Cr_2O_3 to Fe–Cr mixed oxides increased their Brunauer–Emmett–Teller (BET) surface area, but also the amount of magnetite in the composition [11]. $(\text{Fe,Cr})_2\text{O}_3$ systems proved to have other applications as pigments as well as mineralogical, magnetic, abrasive, sensor, and refractory materials in the ceramic industry [13].

Iron–chromium oxide NPs, both in crystalline [10,11,14] and amorphous [4,8] states, were obtained using the same procedures as used to obtain single iron oxide, such as ultrasonic radiation [4,8], hydrothermal methods [10], and thermal decomposition [11,14], using physical mixtures of salts as metals sources. According to previously published reports [4,8], amorphous iron–chromium oxide NPs have been prepared using iron chloride and chromium nitrate in different molar ratios as precursors.

* Corresponding author. Tel.: +40 232217454; fax: +40 232211299.

E-mail address: mczacu@icmpp.ro (M. Cazacu).

However, in the case of amorphous materials, a precise determination of the two nuclei cannot be determined by X-ray diffraction, thus their characterization is quite difficult. In our recent work [14], we reported obtaining crystalline iron–chromium oxide NPs starting from a mixed metal complex with a pre-established iron/chromium ratio.

In this paper, using the same metal source (iron–chromium acetate clusters, $[\text{FeCr}_2\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot\text{NO}_3$) and the same procedure (thermal decomposition) in the presence of dodecylamine (DA) and trichloroacetic acid (TCAA), but replacing oleic acid with a cheap and easily accessible surfactant (sunflower oil, SO), which is added in a high excess without any special conditions (cooling for example), we obtained amorphous and well-defined iron–chromium oxide, which exhibited long-term stability. The formation of the NPs was demonstrated by transmission electron microscopy (TEM), atomic force microscopy (AFM), and dynamic light scattering (DLS). The amorphous nature was proven by X-ray powder diffraction (XRPD), whereas the co-existence of iron and chromium was verified by energy-dispersive X-ray (EDX) spectroscopy. Magnetic measurements performed in the 1.8–300 K temperature range and in magnetic fields up to 50 kOe confirmed presence of superparamagnetic state. The existence of an organic surface layer on NPs is responsible for the diamagnetic contribution to the total magnetization of the system.

2. Experimental

2.1. Materials

Heteronuclear iron–chromium acetate (also known as $[\text{FeCr}_2\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot\text{NO}_3$), $\{\text{FeCr}_2\text{O}\}$, and ICA, with a Cr/Fe molar ratio of 2:1 (as determined by EDX; Fig. 1S) [14], was prepared following a previously reported procedure [15], using $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Sigma–Aldrich) and $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Sigma–Aldrich) in a 1:2 molar ratio and calcium acetate monohydrate, $[\text{Ca}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}]$ (Sigma–Aldrich), glacial acetic acid (chemical company), and distilled water. TCAA (CCl_3COOH ; Fluka), DA [$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$; Fluka], SO (“Sorica” brand by Argus S.A. Constanta, Romania), hexane, and ethanol (chemical company) were used as received.

2.2. Equipment

An EDX system available on a Quanta 200 environmental scanning electron microscope (ESEM) was used for qualitative analysis and elemental mapping.

The infrared spectra were registered on a Bruker Vertex 70 FT-IR instrument in transmission mode, in the $300\text{--}4000\text{ cm}^{-1}$ range (resolution 2 cm^{-1} , 32 scans), at ambient temperature.

TEM investigations were carried out with a Hitachi High-Tech HT7700 transmission electron microscope operated at a 100 kV accelerating voltage in high-contrast mode. The samples were prepared on carbon-coated copper grids with 200-mesh size. Microdroplets of the NPs dispersed in hexane (0.1%) were placed on the grids, and then the solvent was removed under vacuum.

Wide-angle X-ray diffraction (WAXRD) was performed on a Bruker-AXS D8 ADVANCE diffractometer, with a Bragg–Brentano para-focusing goniometer. Scans were recorded in step mode using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541\text{ nm}$). The working conditions were 40 kV and 30 mA tube power. The Bruker computer software packages Eva 11 and Topaz 3.1 were used to plot and process the data.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA-SDTA851e type derivatograph (thermogravimetric analyzer) under a flow of nitrogen (20 mL/min), within $25\text{--}800\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C min}^{-1}$ for samples of 2–5 mg each. Alumina crucibles ($70\text{ }\mu\text{L}$) were used as sample holders. Each experiment was repeated three times and exhibited a good reproducibility. The data were processed using Mettler Toledo STAR software.

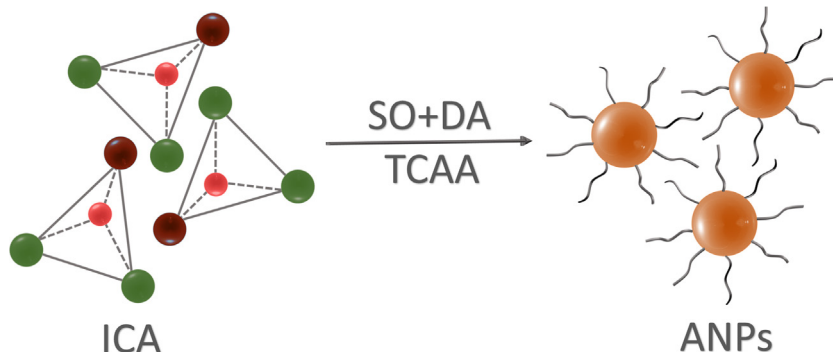
Magnetic measurements were performed on powdered samples placed inside inert gelatin capsules using a Quantum Design SQUID magnetometer. The raw data were corrected for the background signal resulting from the gelatin capsule, which was obtained from a separate measurement. The magnetic moment was measured in a direct-current (dc) magnetic field in the $2\text{--}300\text{ K}$ temperature range within zero-field-cooled (ZFC) and field-cooled (FC) regimes.

AFM measurements were made on a SPM Solver Pro-M platform (NT-MDT, Russia) instrument in air, using semi-contact mode with a rectangular NSG10/Au cantilever and a nominal elasticity constant of $K_N = 11.5\text{ Nm}^{-1}$. Drops of the particle dispersion were placed on glass slides and slowly dried at room temperature prior to analysis.

The average particle-size diameter and distribution (polydispersity index) were determined by DLS on a Malvern Zetasizer NS (Malvern Instruments, UK) instrument, which uses noninvasive backscatter detection (NIBS) (173°) and a laser wavelength of 633 nm. The particles were dispersed in hexane. The autocorrelation signal was analyzed by the cumulant method, giving the z-average diameter of the particles and the polydispersity index according to ISO13321, part 8.

2.3. Preparation of iron–chromium oxide NPs

A mixture of iron–chromium acetate (0.4 g, 0.63 mmol), dodecylamine (2 g, 10.79 mmol), trichloroacetic acid (2.5 g, 15 mmol) and sunflower oil (4 mL) was heated stepwise in a three-necked flask equipped with a condenser, thermometer, and heating mantle until a temperature of $320\text{ }^\circ\text{C}$ was reached; the



Scheme 1. A graphical representation of the process of forming the amorphous NPs (ANPs).

Download English Version:

<https://daneshyari.com/en/article/1487686>

Download Persian Version:

<https://daneshyari.com/article/1487686>

[Daneshyari.com](https://daneshyari.com)