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Synthesis of Cu and Co metal oxide nanoparticles from thermal decomposition of tartrate complexes

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ABSTRACT

Cu and Co metal oxide nanoparticles were obtained from the thermal decomposition of the corresponding tartrate complexes ($[M(C_4H_2O_6)_n]_m$, M = Cu(II), Co(II)). The complexes were prepared by metathesis reactions in water and characterized by Fourier transform infrared spectroscopy, Thermal gravimetric analysis and high resolution mass spectrometry. The metal complexes were calcined at 500 °C for 5 h and the metal oxides obtained were characterized by FTIR, X-ray diffraction, scanning electron microscopy, transmission electron microscopy and selected area electron diffraction. XRD analysis showed that the obtained oxides are crystalline and corresponded to the CuO and Co_3O_4 phases. Crystal size, shape and crystallinity were determined by SEM and TEM.

1. Introduction

Synthesis of materials at nanometric scale with controlled size and shape is one of the main challenges of nanotechnology research. There are many reports discussing different conditions of synthesis of nanostructured materials, such as chemical vapor deposition, sol–gel, microemulsion, reduction–precipitation, laser pyrolysis, solution-based synthesis, etc. [1–15]. Thermal decomposition, as a technique broadly employed in nanotechnology [16,17], is an endothermic chemical disintegration caused by heat. Heat is required to break chemical bonds in the compound undergoing decay. This is a promising and easy "top down" technique to prepare nanometric metal oxides and it is essentially based in the breakdown of the material into smaller units. It can be assumed that the initial crystalline ordering of the selected precursor will have a strong influence on the crystal structure of the thus obtained metal oxide [18–21].

Typically, thermal decomposition methods make use of high boiling point solvents such as octadecene, oleic acid, kerosene, octyl ether, oleylamine, polyethylene glycol, among several others, with working temperatures among 100–350 °C. Under those conditions, carbon-based ligands decompose easily, allowing homogenous nucleation of the metal oxide particles. Uniform growth of the nanoparticles may be achieved by controlling time, temperature, concentration of reagents and kind of surfactant employed. Many times, purification of the products requires further steps in order to remove residual solvent molecules from the surface and may require chemical substitution or functionalization in order to obtain water soluble nanoparticles [18,22–26]. Besides, several metallic compounds such as coordination complexes [27–29], organometallic compounds [39] and alkoxides [40] can be used as precursors of metal oxide nanoparticles. However, large scale synthesis requires the use of low cost precursors, a simple process and no extra purification steps. So, solventless methods are attractive as they result easier to operate, have higher yields, produce less by-products and after careful control of temperature and decomposition conditions, may result in smaller sizes without aggregation of nanoparticles. Despite its simplicity and potential, this technique has not been widely explored; there are some examples reported in the literature on the direct calcinations of metal complexes as precursors for the preparation of metal oxide nanoparticles [33–37], some of them employing metal carboxylates and coordination compounds resulting on the formation of composite materials containing metal nanoparticles and indicating that the organic matrix provides protection to oxidation of the nanomaterials synthesized [32]. The method has been also explored for the preparation of mixed Nb–Ta oxides from thermal treatment of peroxo-tartrate complexes

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and copper sulfide nanostructures from the solventless thermolysis of a copper alkylthiolate precursor [38].

Copper and cobalt oxide nanoparticles (NPs) are attractive due their properties as metal oxides [4,44]. It has been reported that copper oxide NPs have antimicrobial and cytotoxic activities, and cobalt oxide NPs can be applied as contrast agents in MRI, drug carriers and in thermal therapy due their magnetic properties [45]. However, in medical applications it is necessary to use NPs with uniform size and shape and chemical stability [18–32,39–43]. For that reason, thermal decomposition of metal carboxylate precursors offers a good alternative to control size and uniformity in shape. We report here our results on the exploration of a simple, economical, one step method for the preparation of CuO and Co_3O_4 nanoparticles by the thermal decomposition of metal tartrate precursors.

2. Experimental

2.1. Materials and physical measurements

$CuCl_2 \cdot 2H_2O$ (CAS 10125-13-0), $CoCl_2 \cdot 6H_2O$ (CAS 7791-13-1) and disodium L-tartrate dibasic dihydrate (CAS 6106-24-7) ($NaO_2CCH(OH)CH(OH){-}CO_2Na \cdot 2H_2O$) were analytical grade and purchased from Sigma–Aldrich. All reagents used in our experiments were used as received without further purification.

2.2. Synthesis of copper (II) and cobalt (II) tartrate complexes

Copper (II) and cobalt (II) tartrate complexes were prepared by simply mixing the corresponding metal salts and the disodium salt of L-tartaric acid ($Na_2C_4H_4O_6 \cdot 2H_2O$) according to the molar ratio 1:2 (metal:ligand) in an appropriate amount of distillated water. In a typical synthesis, $Na_2C_4H_8O_8$ was dissolved in 50 mL of distilled water at room temperature and it was maintained under magnetic stirring until the ligand was completely dissolved. A stoichiometric amount of the metallic salt ($CoCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$) was added as powder and the mixture was stirred during two hours. During that time, a precipitate (blue for copper tartrate, pink for cobalt tartrate) was obtained and recovered by gravity filtration. The products were dried at room temperature during two days and characterized by FT-IR, MS and TGA. *$Cu(C_4H_4O_6)_2 \cdot 3H_2O$:* m.p. 275 °C (d); FAB^+–MS {m/z (%) [fragment]} = 413 (24) [M^+], 391 (33) [$M^+ - H_2O - 2H$], 329 (7) [$M^+ - 3H_2O, -O_2$], 307 (15) [$M^+ - 2CO_2$], 148 (84) [$M^+ - CuC_4H_4O_6$]. *$Co(C_4H_4O_6)_2 \cdot 2H_2O$:* m.p. 408 °C (d); FAB^+–MS m/z (%) [fragment]} = 391 (6) [M^+], 329 (8) [$M^+ - O_2$], 307 (14) [$M^+ - 2CO_2$], 289 (13) [$M^+ - 2CO_2 - O$], 176 (22) [$M^+ - CoC_4H_4O_6$].

2.3. Synthesis of CuO and Co_3O_4 nanoparticles

The as prepared dried metal–tartrate complexes (300 mg) were grinded and loaded into a previously dried and weighted ceramic crucible. The crucible was placed inside a blast furnace previously set to a temperature of 500 °C (±20 °C) and calcined during four hours, in presence of air. After this time, the sample was slowly cooled to room temperature and a black powder was collected, weighed and characterized by FT-IR, XRD, SEM and TEM. These products could be easily re-dispersed in polar solvents such as ethanol, water or acetone by ultrasonication.

2.4. Details of the instruments

Fourier transform infrared (FT-IR) spectra were recorded as grinded solids on a Varian-Scimitar FTIR-800 spectrophotometer equipped with an ATR detector, and recorded in the region 4000–400 cm^{-1}. Positive-ion fast atom bombardment mass spectrometry (FAB^+–MS) spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a 3-nitrobenzyl alcohol matrix using 3 keV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material. Thermogravimetric-differential scanning analysis (TGA-DSC) were carried out on grinded samples in Al containers, using a thermal gravimetric analysis instrument Netzsch STA 409PC/4/H/Luxx under a nitrogen atmosphere (60 ml/min) with a heating rate of 20.0 K/min and in the range from 30 to 500 °C. X-ray diffraction (XRD) measurements were taken on a Bruker-AXS D5000 diffractometer on grinded powders in a quartz sample holder using the Cu Kα line source (κ = 1.5418 Å) in 2θ mode (measuring interval: 10–80°); step scan = 0.02; step time = 0.6 seg. Scanning electron microscopy (SEM) images were obtained using a Tescan VEGA-II microscope, with an accelerating voltage of 20 kV. SEM specimens were dispersed in ethanol by ultrasonication and a few drops deposited on a graphite film adhered on an Al pin. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analyses were performed in a JEOL Model JEM2010 electron microscope operated at 200 kV accelerating voltage. The powder samples were ultrasonically dispersed and supported on carbon membrane coated copper grids. High resolution TEM imaging was used to observe the crystallinity of single powder grains.

3. Results and discussion

3.1. Infrared spectroscopy analysis of metal oxide nanoparticles

Fig. 1a shows the FT-IR spectrum of the disodium L-tartrate dibasic dihydrate, while Fig. 1b–e correspond to the FT-IR spectra of $CoL_2 \cdot 2H_2O$, Co_3O_4, $CuL_2 \cdot 3H_2O$ and CuO, respectively (L = $C_4H_4O_6$). FT-IR spectroscopy of the cobalt (II) tartrate showed the characteristics $\nu_{asym}(C{=}O)_{COO}$ and $\nu_{sym}(C{=}O)_{COO}$ bands at 1591 and 1375 cm^{-1}, respectively. In the other hand, the copper (II) tartrate complex, has a strong signal corresponding to the ν_{asym} at about 1614 cm^{-1}, and the $\nu_{sym}(C{=}O)_{COO}$ is detected at 1330 cm^{-1}. Shifts and changes of the peaks from the FT-IR spectra of the sodium salt of tartaric acid (free ligand showed the $\nu_{asym}(C{=}O)_{COO}$ band at 1620 cm^{-1} and the $\nu_{sym}(C{=}O)_{COO}$ band at 1412 cm^{-1}) with those listed before of the metal complex, are unequivocal signals of the formation of the desired precursors, which probably form a coordination polymer or metal organic framework (MOF) due to the existence of two opposite coordination sites on the ligand structure. The values found are in agreement with those previously reported for a series of tartrate metal complexes and reported by Rodrigues et al. [51]. For the FT-IR spectra of the calcination prodcalcinationucts, no relevant peaks indicating the presence of an organic ligand or fragment are present, which is in agreement with what is expected for a pure metal oxide.

3.2. Mass spectrometry

In the high resolution mass spectra (MS) of the metal complexes in a matrix of 3-nitrobenzyl alcohol (NBA), the molecular ion for the cobalt (II) tartrate complex was found at a value of m/z = 391, which corresponds to one cobalt atom bounded to two ligands and two water molecules. Evidence of the formation of an uni-dimensional coordination polymer was found, as small peaks with m/z ratio of 413, 492, 522, 562 and so on, corresponding to the addition of water, metal ion or tartrate fragments were also located in the MS spectrum, which is in agreement with what