Preparation of bimetallic Co–Ag and Co–Cu nanoparticles by transmetallation of tetrakis(pyridine)silver(II) peroxydisulfate and tetrakis(pyridine)sulfatocopper(II) monohydrate complexes

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ABSTRACT

Co–Cu and Co–Ag bimetallic nanocrystallites were prepared by transmetallation of tetrakis(pyridine)silver(II) peroxydisulfate and tetrakis(pyridine)sulfatocopper(II) monohydrate complexes by metallic cobalt nanoparticles. In this work, cobalt nanoparticles were reacted as a reducing agent in a chemical reduction of metal complexes. Due to the complex formation constant and the reduction potential of Ag^{II} and Cu^{II} complexes, bimetallic Co–Ag and Co–Cu nanoparticles in aqueous solution are formed. These nanoparticles were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM) and EDX analysis. The percentages of phases were calculated by the Rietveld method. Besides, strain and crystals size were calculated by the Williamson–Hall method and the profile coefficients were obtained in the GSAS software.

1. Introduction

Magnetic nanoalloys and bimetallic nanoparticles are used in different areas such as refrigeration applications, optoelectronic, catalysis and biological applications. Bimetallic catalysts due to the relationship between electronic structure and catalytic activity of metals have been extensively investigated [1]. Transition metal complexes, especially the metal compounds of group IB, are such as Fe, Ni, and Co varying the composition of the alloy, due to electronic factor, can alter their catalytic activity [2]. Magnetic nanoalloys, are a class of materials used in stealth technology. The radar absorbing materials reduce the energy reflected back to the radar by means of absorption. Radar energy is absorbed through one or more of several mechanisms, which may involve the dielectric or magnetic properties of the materials. One of the most commonly known types of RAM is metallic iron ball paint. The iron particles in the paint are obtained by decomposition of iron pentacarbonyl. The interesting radar absorption properties of magnetic alloys attracted much interest during the last decades [3,4]. On the other hand, the

dilute magnetic alloys such as the transition metals dissolved in a simple metal show a unique magnetic property. In these alloys the oscillating long-range interactions appear via the conduction electrons, and the spin glass state in which the local magnetic moments are randomly oriented forms due to the competition between long range ferromagnetic interactions. Among magnetic alloy systems a major role is played by the so-called granular magnetic, consisting of nanometer-sized particles of a magnetic metal (e.g. Fe, Co, Ni) dispersed in a nonmagnetic metallic matrix (e.g. Ag, Au, Cu). This is mainly the consequence of the discovery of giant magnetoresistance (GMR) effects in such materials, made more than a decade, that represented a breakthrough in the frontier of research on magneto transport properties. Subsequently, the phenomena of tunneling magnetoresistance and extraordinary Hall effects have been discovered in magnetic nanogranular systems. These materials, commonly termed nanogranular magnetic materials, reveal unique physical properties and offer an excellent opportunity to study fundamental magnetic interactions in highly controlled physical systems. Nanostructured materials have had an important technological impact on the development of new magnetic devices, on magnetic recording and, more recently, on biotechnology [5].

These nanoparticles can be generated in a variety of ways. The

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methods are included molecular beams, chemical reduction, thermal decomposition of transition-metal complexes and electrochemical synthesis. The mentioned methods can be performed in the gas phase, in solution, in a matrix or supported on a substrate [6]. Chemical reduction method is highlighted in the literature than other ways. During the reduction process, the metal species with the highest redox potential precipitates first, forming a core on which the second component is deposited as a shell [7]. In the second approach, nanoalloys are synthesized by replacing the surface layer of a metal species with the low redox potential by a metal species with the high redox potential using the transmetallation reaction [8–10]. In this work, cobalt nanoparticles were reacted as a reducing agent in a chemical reduction of metal complexes. The chemistry of coordination compounds and metal complexes is a wide area of inorganic chemistry and an enormous number of reactions are known to occur in these compounds [11]. The numerous types of reactions including ligand exchange reactions, isomerization reactions, redox reactions and reactions of coordinated ligands have been reported in the literature [12]. Consequently, intermolecular electron transfer involving metal and complex take place between coupled redox centers. In many cases, the reaction of metal with complex is associated with the reduction of the complex and oxidation of the metal. Transition metal complexes have several unique features in reactions. The most important feature is the pattern of reduction of complexes. The preparation of tetrakis(pyridine)silver(II) peroxydisulfate and tetrakis(pyridine)sulfatocopper(II) Monohydrate complexes have been reported [13,14]. The cobalt particles gradually reduce silver and copper in the solution of the complexes and nanoparticles are formed in which the core is cobalt and the shell is silver and copper. Appropriate chemical analysis confirmed the formation of the particles. Our goal in this work is investigation on the ability of metallic cobalt particles in the destruction of the complex. The reduction of copper(II) and silver(II) complexes, provide a method in the preparation of bimetallic nanoparticles and study the morphologies of particles, and determine the percentage of phase in these particles open new horizons in the research.

2. Experimental

All chemical reagents used in this experiment were pure grade and used without further purification. Potassium peroxydisulfate, silver(I) nitrate, copper(II) sulfate pentahydrate, cobalt(II) chloride hexahydrate, hydrazine monohydrate solution and sodium hydroxide were purchased from Merck. The water used throughout this work was doubly distilled. The complex of hexaminecobalt(III) chloride was synthesized using the method described in the literature [15]. Copper and silver nanoparticles (to compare the XRD patterns in Fig. 1) have been prepared using the method mentioned in the literature [16,17].

2.1. Preparation of cobalt nanoparticles

A 0.4 g sample of $[Co(NH_3)_6]Cl_3$ is dissolved in a mixture of 10 ml ethanol and 10 ml of water. To this solution are added 50 ml of 6 M NaOH solution and 6 ml of hydrazine and then heated to 45 °C for about 2 h. The product is filtered and washed with water and dried in air [18].

2.2. Preparation of tetrakis(pyridine)silver(II) peroxydisulfate

A 2.5 g of potassium peroxydisulfate is dissolved in 25 ml water contained in a 250 ml beaker. 5 ml of pyridine (0.1 mol) is added to a solution of 0.5 g of silver(I) nitrate in 10 ml of water, and the resulting solution is slowly added with stirring to the potassium

peroxydisulfate solution. The resulting solution soon becomes yellow, then orange, and a precipitate of fine, orange crystals soon begins to deposit. The beaker and contents are allowed to stand in an ice bath until precipitation appears completely (about 15 min). The product is filtered and washed with 10 ml of ice-cold water and 95% ethanol and then air-dried [13].

2.3. Preparation of tetrakis(pyridine)sulfatocopper(II) monohydrate

Hot, freshly distilled pyridine in a large excess was added to a boiling aqueous solution of $CuSO_4$, saturated at 293 K. The compound crystallizes readily from the hot solution. The crystals were filtered from the hot solution and washed several times with cold ether. Recrystallization was carried out from a 3:1 mixture of pyridine and water at room temperature [14].

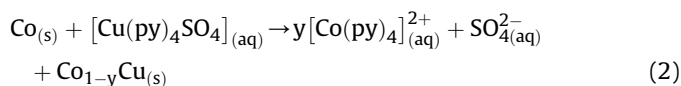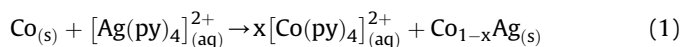### 2.4. Preparation of Co−Ag nanoparticles

For preparation of Co−Ag nanoparticles, a 0.15 g (0.2435 mmol) of tetrakis(pyridine)silver(II) peroxydisulfate were poured in a beakers and were added 10 ml of water and 0.05 g of Co particles and were stirred using a magnetic stirrer for about 10 min. After completion of the reaction, the particles were washed and then dried in air. A similar procedure was used to prepare Co−Cu nanoparticles except the amount which was used 0.120 g (0.2435 mmol) of tetrakis(pyridine) sulfatocopper(II) Monohydrate.

3. Characterization

X-ray diffraction patterns of the products were taken in a Philips X'Pert PRO X-ray diffractometer (XRD) equipped with graphite monochromatized Cu-K$_\alpha$ radiation from 0 to 80 (2θ) at room temperature. The morphology and microanalysis of the ground mixture were obtained using a scanning electron microscope (MIRA3 FEG-SEM) that equipped with detectors of LVSTD (Low Vacuum), BSE (Back-Scattered Electrons) and SE (Secondary Electrons). FT-IR spectra of the products were obtained in a Magna 550 IR spectrophotometer using KBr pellet technique from 400 cm^{-1} to 4000 cm^{-1}. The vibrating sample magnetometer (VSM, Maghnetis Daghigh Kavir Co.) was used to research the magnetic parameters.

4. Results and discussion

In the reaction, cobalt particles reduce copper and silver ions in complexes. The reaction can be expressed as the following equations:

$$Co_{(s)} + [Ag(py)_4]^{2+}_{(aq)} \rightarrow x[Co(py)_4]^{2+}_{(aq)} + Co_{1-x}Ag_{(s)} \quad (1)$$

$$Co_{(s)} + [Cu(py)_4SO_4]_{(aq)} \rightarrow y[Co(py)_4]^{2+}_{(aq)} + SO_4^{2-}_{(aq)}$$
$$+ Co_{1-y}Cu_{(s)} \quad (2)$$

The reduction potential for Ag^{2+} is +1.39 V and for Cu^{2+} is +0.34 V, whereas for Co^{2+} it is −0.28 V. This leads to replacement of each Co atoms with Ag and Cu atoms at the surface, thereby forming a core−shell structure. However, the reduction potential in the complexes are different than the values listed above, and the complexation of silver and copper ions can interfere with the transmetallation reaction which depends on the stability of the complex and the metal-ligand interactions. As the interaction of the ligand - metal increases and the stability of the complex increases, the possibility of replacement of Co atoms and reduction of Ag^{2+} and Cu^{2+} ions decrease. We examined this relation by entering