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Effect of molecular weight of sodium polyacrylates on the size and morphology of nickel nanoparticles synthesized by the modified polyol method and their magnetic properties

O.A. Logutenko[a,*], A.I. Titkov[a], A.M. Vorob'yov[a], D.A. Balaev[b], K.A. Shaikhutdinov[b], S.V. Semenov[b], Y.M. Yukhin[a], N.Z. Lyakhov[a]

[a] Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Kutateladze, 18, 630128 Novosibirsk, Russia
[b] Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Academgorodok, 50/12, 660036 Krasnoyarsk, Russia

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ABSTRACT

Nickel nanoparticles were synthesized by the reduction of nickel chloride with hydrazine hydrate in a polyol medium in the presence of sodium polyacrylates (Na-PA) having molecular weights (M_w) of 1200, 5100 and 8000. The size and morphology of the resulting nickel nanoparticles were characterized by X-ray diffraction, scanning and transmission electron microscopy. Polymers having lower M_w values were found to be more efficient in reducing the nickel particle size. A decrease in the polymer concentrations yielded the smaller particles. Magnetic measurements showed that the as-prepared powders are ferromagnetic and their saturation magnetization and coercivity are size-dependent. Compared with bulk nickel, the nanoparticles exhibit an enhanced coercivity which is due to their small size and a decreased saturation magnetization resulted from the surface oxidation of the powder. The synthesis procedure offers a simple approach to preparing nickel nanopowders on a large scale which could be used as magnetic recording materials, including high-density memory storage devices.

1. Introduction

Materials based on nanoparticles represent a new class of functional materials with unique properties that are currently of great interest and are widely studied. In recent years, interest in the preparation of nickel nanoparticles has increased substantially, which is caused by the possibility of their application in catalysis and medical diagnostics, as well as in magnetic devices, batteries, superconducting devices, etc. Nickel nanoparticles were shown to be efficient catalysts for the hydrogenation of nitrobenzene and nitrophenol, for the reduction of oxygen and oxidation of olefins [1]. They are also used as biosensors, composites and materials for solar energy usage and as magnetic nanofluids [2,3]. In addition, nickel, being a cheaper alternative to silver, platinum and palladium, is more attractive from a commercial point of view.

To produce nickel nanoparticles, various chemical and physical approaches have been developed. Among them, the chemical reduction of various nickel salts in organic or aqueous solutions with hydrazine hydrate or sodium borohydride is most commonly used. The methods for the synthesis of nanoparticles based on this approach are easy to use, since they do not require special equipment or conditions for their implementation. In addition, they allow control of the size of the resulting particles, their morphology, composition and other properties by changing the reaction conditions, such as temperature and concentration of all the reagents, the nature of the stabilizer and the type of solvent.

When preparing metal nanoparticles in solutions, preventing their aggregation is one of the challenges [4]. Aggregation can be eliminated by coating the particles with a surfactant layer. This is widely used in practice. In the case of nickel, such a surface coating protects the particles from both aggregation and oxidation and it can also affect their size and shape. Polyelectrolytes are one of the most effective and promising nanoparticle stabilizers due to the interaction of the functional groups of the organic macromolecules with the nanoparticle surface. Water-soluble polymers such as polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) were shown to be very good candidates for the stabilization of nanoparticles [5–7]. Using PVP as a surfactant, Singh et al. [8] synthesized nickel nanoparticles in ethylene glycol with an average size of ~3 nm. Roy and Battacharya [9] prepared polymer-protected stable nickel nanoparticles by reducing nickel chloride with sodium borohydride in the presence of both polyvinylpyrrolidone and

* Corresponding author.
E-mail address: ologutenko@solid.nsc.ru (O.A. Logutenko).

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polyacrylic acid. The authors found that the size of the resulting nanoparticles can be easily controlled by changing the type of polymer, as well as its concentration. Thus, a decrease in the nickel to polymer ratio was reported to result in a decrease in the average particle diameter and smaller nanoparticles are formed in the presence of PVP. A comparative study of the effect of molecular weight of polyethylene glycol and polyvinyl alcohol on the size, shape and dispersity of silver nanoparticles was carried out by Diaz-Cruz et al. [10]. The authors showed that the molecular weight of the polymers has no influence on the nanoparticle shape but is directly proportional to their size which decreases as the polymer molecular weight decreases too.

A review of the literature revealed only a limited number of studies on the stabilization of metal nanoparticles with polyacrylic acid and its salts, particularly with regard to nickel nanoparticles. However, there are a number of studies reporting the effect of the concentration of sodium polyacrylate on the size and morphology of platinum nanoparticles and the mechanism of their growth in the presence of this polymer [11,12]. Prucek et al. studied the stabilization of copper and silver nanoparticles using sodium polyacrylates with different molecular weights (1200, 8000 and 15,000) [13–15]. Nano-copper particles, with a size of 20–100 nm, were prepared in an aqueous medium in the presence of sodium polyacrylate with a molecular weight of 1200 by reduction of copper sulfate with sodium borohydride [14]. It was shown that, the growth of the copper nanoparticles is hindered at a higher concentration of sodium polyacrylate. The authors explain this by electrostatic repulsion of the negatively charged anions of sodium polyacrylate adsorbed on the nanoparticle surface.

Thus, using polyacrylic acid and its salts, it is possible to efficiently control the size and morphology of nanoparticles, as well as the degree of their aggregation. However, to our knowledge, no such systematic studies concerning the stabilization of nickel nanoparticles with polyacrylates of different molecular weights have been reported so far. Therefore, the objective of the present study was to investigate the process of the reduction of nickel chloride with hydrazine hydrate in a polyol medium in the presence of the sodium salt of polyacrylic acid as the stabilizing agent. The novelty of this work is that it is the first systematic study on the effect of the polyacrylate-to-nickel ratio and sodium polyacrylate molecular weight on the size and morphology of nickel nanoparticles formed in a polyol medium. The effect of temperature and the type of polyol was also studied which allowed us to determine the optimum reaction conditions under which uniform nickel nanoparticles of less than 20 nm in size were obtained.

2. Experimental

2.1. Materials

Nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) of ≥97.0% purity grade, and ethylene glycol ($HO(CH_2)_2OH$) of 99.8% purity grade, ≥99.7% pure propylene glycol ($CH_3CH(OH)CH_2OH$), 95% pure ethanol, and hydrazine monohydrate of 100% purity, supplied by Sigma Aldrich, were used in the experiments without further purification. Sodium polyacrylates $[-CH_2-CH(CO_2Na)-]_n$ (Na-PA) with molecular masses (M_W) of 1200, 5100 and 8000 (all as 45% aqueous solutions) (Sigma-Aldrich) were used as the stabilizers. Sodium hydroxide (NaOH, 50% aqueous solution) was of a highly pure grade.

2.2. Synthesis of nickel nanoparticles

Nickel nanoparticles were prepared by the reduction of nickel chloride in the presence of sodium polyacrylate, according to the published procedure [16]. The molecular weights of the polyacrylates used were 1200, 5100 and 8000. In a typical experiment, initially, appropriate amounts of nickel chloride and sodium polyacrylate at different molar ratios of nickel ions to monomeric unit of polyacrylate (Ni:Na-PA) were dissolved in ethylene glycol or propylene glycol under stirring by heating in an oil bath to the desired temperature. Then a concentrated solution (100%) of hydrazine hydrate was added to the reaction mixture under continuous stirring at a nickel to hydrazine hydrate molar ratio of 1:14. To accelerate the reduction reaction rate, the process was carried out in the presence of sodium hydroxide (Ni:NaOH = 1:5). After the reaction was complete (the reduction time was 5–10 min), the mixture was air-cooled and the resultant nickel powder was collected by centrifugation, washed several times with ethanol to remove impurities and then it was dried in air at room temperature. The particle sizes and their morphology were investigated using various techniques.

2.3. Characterization of the nickel nanoparticles

XRD patterns were recorded on a D8 Advance powder X-ray diffractometer equipped with a one-dimensional Lynx-Eye detector and a K_β filter using Cu Kα radiation. The crystallite size and lattice parameters were estimated by the Rietveld method [17] using Topas 4.2 software (Bruker AXS, Germany) for the profile and structural analysis. The broadening of the patterns due to the crystallite size was modeled by the "Double-Voigt" function. Analysis of the samples by transmission electron microscopy (TEM) was performed using a JEM 2010 electron microscope (JEOL, Japan) operating at 200 kV and having a resolution of 0.14 nm. The study of the samples by scanning electron microscopy (SEM) was performed using a Hitachi 3400 N scanning electron microscope (Hitachi Ltd., Japan). The magnetization of the samples was measured using a PPMS-6000 vibrational magnetometer within the temperature range of 4.2–300 K [18]. A powder sample of nickel nanoparticles was placed in a paraffin matrix. The variation of the magnetization as a function of the temperature (*M-T* curves) was measured in zero-field-cooled (ZFC) and field-cooling (FC) modes with an applied magnetic field of 1 kOe и 5 kOe.

The nickel concentration in the solutions was determined by complexometric titration using murexide as the indicator.

3. Results and discussion

3.1. Effect of the molecular weight of sodium polyacrylate and its concentration on the particle size

To study the effect of the Na-PA molecular weight and concentration on the size and morphological characteristics of the resulting nickel particles, the reduction of nickel ions was carried out in the presence of sodium polyacrylates of 1200, 5100 and 8000 molecular weights and at a temperature of 130 °C. It was shown that in the absence of Na-PA in the system, the particles formed have a nearly spherical shape and a quite narrow size distribution (Fig. 1). Their average size is

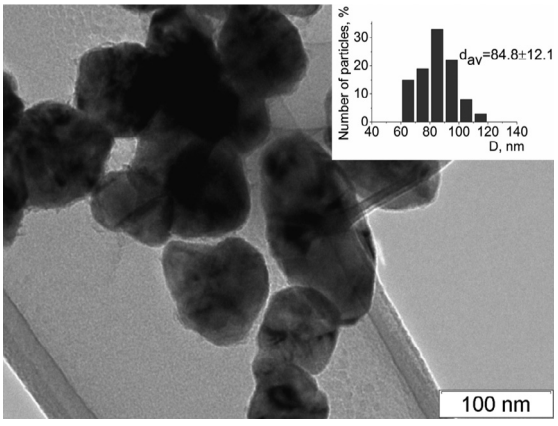

Fig. 1. SEM image of the nanoparticles prepared by reduction of nickel chloride in ethylene glycol with hydrazine hydrate in the absence of sodium polyacrylate at 130 °C.