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LETTERS
TO THE EDITOR

Organic Shell Influence on Physicochemical Properties of Nickel Polyol Nanoparticles

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Recently metal nanoparticles attract attention due to their unique properties and potential use in such areas as nanoelectronics and optoelectronics, catalysis, magnetic devices for information storage, and medicine. The polyol synthesis is the most promising method of obtaining such nanoparticles due to two factors: first, reduction of metal salts occurs upon their heating in a medium of polyatomic alcohols, which function simultaneously as solvents and reducing agents; second, when carrying out the reaction it is possible to use so-called surfactants, substances adsorbed on a surface of a formed solid phase, to limit further growth of the particles. At present the most widespread surfactants are lauric and oleic acids, however, the search for surfactants of other types is of scientific and practical importance.

Adsorption of surfactant molecules leads to the formation of an organic shell on the surface of nanoparticles, which influences the complex of their physical and chemical properties. The study of this influence is necessary both for understanding the mechanism of the adsorbed substance action and for the elucidation of a possibility of practical application of resulting nanoparticles.

In this work we have studied the morphology of nickel nanoparticles prepared under polyol process conditions without a surfactant introduction (“”pure“ nickel) and also in the presence of paraffins or oxyethylidenediphosphonic acid (1-hydroxyethane-1,1-diphosphonic acid) and also have studied the surface shell of nanoparticles and its influence on the behavior of nickel powders in aqueous solutions and on their magnetic characteristics.

The X-ray phase analysis of the obtained samples has shown presence of reflexes from metal nickel and an organic phase. For all samples they are shifted in the region of shorter interplanar spaces, which is a typical manifestation of the size effect of metal nanoparticles.

According to the data of transmission electron microscopy (TEM), all powders consist of spherical nanoparticles (diameter of 14−20 nm) covered by an organic phase, which was confirmed by IR spectroscopy data. However, the composition of the organic shell covering the nanosize metal is variable in the studied series. For the samples prepared in the surfactant presence the existence of a shell is connected with its adsorption on the surface of particles, whereas in the case of “pure” nickel the shell apparently consists of polyethylene glycol molecules, which is indirectly confirmed by the data of the thermogravimetric analysis. Furthermore, a spectrum inversion was observed for this sample, which points to incomplete covering of the nanoparticles. Samples of “pure” nickel and nickel obtained in the presence of paraffins have similar IR spectra, which is attributable to close structures of the molecules forming their shells.

A region of sharp weight loss (40%) was found in a range of 320–360°C by thermogravimetric studying the sample of “pure” nickel, which apparently is connected with the removal of the organic phase consisting of polyethylene glycol molecules from the surface of nanoparticles, as it is known that this is the temperature range where the decomposition of this polymer occurs. To study the morphology of the sample after removal of the surface shell, we carried out its heat treatment at 350°C in an inert atmosphere. The TEM method has shown that nanoparticles of 30–70 nm in diameter free from a shell are present in the heat-treated product. Hence, the heat treatment results not only in the removal of a surface shell, but also in an insignificant coarsening of nanoparticles.

Influence of a surface shell of nickel nanoparticles on their behavior in aqueous solutions was studied by the light scattering method. The fulfilled experiments have shown that nanoparticles are in the form of aggregates, whose size depends on a surface shell type. The results obtained also point to similar compositions of the surface shells of "pure" nickel and nickel with paraffin-covered nanoparticles.

The magnetic behavior of nickel nanoparticles was studied by the vibration magnetometry method. Characteristics of a hysteresis loop of magnetic properties of the powders (the maximal and residual magnetization, coercive force, and hysteresis-loop squareness ratio) were determined. The maximal magnetization for all samples lies in a range of 0.49–1.13 A m^2 kg^{-1}, which is essentially less than for a massive material (54.39 A m^2 kg^{-1}). The same behavior is observed also for residual magnetization (0.17–0.46 A m^2 kg^{-1}). As the values for samples of both "pure" nickel and nickel obtained in the surfactant presence are very small and close to each other within the limits of experimental error, in fact these powders are not magnetic. The values of coercive force (210, 159, and 101 Oe for "pure" nickel and for nickel with oxyethylidene-diphosphonic acid and with paraffin, respectively) and of hysteresis-loop squareness ratio (0.339, 0.355, and 0.475, respectively) apparently are connected with the occurrence of a magnetic dipole–dipole interaction. It can be caused by the fact that nanoparticles forming a powder are additionally structured by means of the interaction of surface shell hydrocarbon "tails" with each other, which leads to overlapping magnetic fields of the particles. The hysteresis-loop squareness ratio values point to a single-domain state of the particles, which have associated in chains. For the sample having undergone heat treatment a sharp increase in specific magnetization is observed, which can be connected with both the removal of an organic phase and the additional increase in the size of particles due to a high-temperature crystallization.

Thus, the introduction of different-type surfactants in the course of the polyol nickel synthesis leads to the fact that organic shells of various compositions are formed on the nanoparticles surface to affect magnetic properties and aggregate stability of the resulting nanopowders.

Nickel nanoparticles were prepared by the polyol method in an ethylene glycol medium on heating in a surfactant presence. The measurements were carried out on a Jeol JEM-107 microscope. The X-ray measurements of powders were fulfilled on a DRON-3M device using a copper monochromatic radiation (CuK_α). Phase compositions of the synthesized products were determined with the use of the PDF card file. The thermogravimetric analysis was carried out on an STA 429 CDs NETZSH derivatograph in an argon atmosphere in a temperature range from 20 up to 1000°C at a heating rate of 20 degree/min. Magnetic measurements of hysteresis loop parameters were carried out on a Vibrating Sample Magnetometer in a field of 0.1 T. The behavior of particles in aqueous solutions was studied by the light scattering method using a Zetasizer Nano ZS laser analyzer (Malvern Instruments). The IR spectra were recorded on a Bruker IFS 88 spectrophotometer.