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LETTERS TO THE EDITOR

Features of Reduction of Nickel, Cobalt, and Copper Ions in Polyol Processes

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In the last decades much attention is attracted by the synthesis of metal nanoparticles, which is caused by their unique properties and a wide applicaton as optical, electronic, catalytic, and magnetic materials. Of special interest is the study of methods for obtaining metal nanoparticles with specified properties and of the synthesis condition influence on the final product characteristics.

Physical and physicochemical properties of metal nanopowders are basically defined by the morphology of their particles and also by their polydispersity coefficient. It should be pointed out that the majority of practical applications require a narrow particle size distribution. Among actively progressing methods of generation of metal nanoparticles with specified characteristics a great attention is given to the polyol synthesis, which is based on the reduction of metal compounds in a medium of a polyhydric alcohol acting simultaneously as a solvent and a reducing agent.

One of widely discussed problems of the polyol synthesis is the control over metal ions reduction, which, as was found earlier [1], significantly affects the size, shape, and phase composition of the final product.

When nanoparticles are synthesized from solutions, their morphology is defined by kinetic (rates of reduction, nucleation, and crystal growth processes) and thermodynamic (ability of metal ions to be reduced in specified conditions) factors.

The kinetic factor can be controlled during the synthesis by varying the process duration and also by using agents limiting crystal growth and (or) crystal-nucleating agents. These approaches are fairly actively developed [2], including in our works [3, 4].

The situation with the thermodynamic factor is much more complicated, as its action is defined directly by the nature of a reduced ion and, in some cases, by the nature of the applied polyol alcohol. Calculated values of free energy for the reduction of various metals in ethylene glycol at 200°C are presented in [5].

We have chosen three types of metal ions for the experimental study: copper (most easily reduced metal ion), nickel (taking the intermediate position), and cobalt (one of the most difficultly reduced metal ions). The aim of the work was to compare characteristics of products of the polyol synthesis of these metals.

As it was expected, the reduction rate decreases in the series copper-nickel-cobalt. It was found that in all three cases the reduction proceeds by different mechanisms with the formation of various intermediates. It was shown by the UV-spectroscopy method that the mother compound is a complex of a corresponding metal with ethylene glycol.

In the case of copper, on heating copper(II) hydroxide is formed, which remains stable up to 120°C. Further in the range 140–180°C copper(I) oxide is formed, which then rapidly turns to metal copper. To reduce completely the initial reagent, at the standard temperature of the synthesis (198°C) an exposure for 5 min is sufficient.

In the case of nickel, immediately after injection of alkali in a cold reaction mixture nickel(II) hydroxide is formed, which begins to be reduced only after reaching the temperature of the synthesis, the reduction process being rather slow. No less than 40 min are required for the complete reduction.

In the case of cobalt, the metal formation is impossible without application of additional reducing agents. In the ethylene glycol medium cobalt alcoholates/hydroxoalcoholates of various compositions are formed on heating. They are crystalline, have color from pink up to violet, the cubic shape of particles, and the minimal edge size of 3 μm. Long-term exposure of a reaction mixture at the final temperature does not result in changes of the shape, size and phase composition of the product. When sodium borohydride is added, which is an additional reducing agent, the metal is formed. In this case, the reduction process proceeds successfully only on addition of sodium borohydride into the reaction mixture heated up to the final temperature of the synthesis. An obligatory stage in this case (as well as for nickel) is maintaining the reaction mixture after adding reducing agent for a certain time. The mechanism of the sodium borohydride action consists in the decomposition with the gaseous hydrogen formation, which acts as the reducing agent. It should be noted that in an alkaline medium sodium borohydride is more stable than in acidic medium, however the final temperature of the synthesis leads to its immediate decomposition with the gas evolution. Taking into account the fact that the target product is formed not earlier than within 15 min after the reaction beginning, we can assume that the role of sodium borohydride consists in stimulating the reducing process by formation of a significant amount of nuclei, on which metal phase grows further with the participation of ethylene glycol only. This conclusion is indirectly confirmed by our experiment on the reaction of nickel ions reduction. In the case of a direct reduction, the particle size of the product is about 600 nm and, when the reducing agent is added, the size decreases to approximately 200 nm, which clearly points to point nucleation of metal nickel upon addition of sodium borohydride. It should be noted that when the synthesis duration is extended, no further nanoparticle growth occurs in all three cases, their size being about 600 (nickel) and 300 nm (copper and cobalt).

One of polyol synthesis features is the protection of formed nanoparticles from agglomeration due to adsorption of polyethylene glycol (PEG) formed in the reaction medium on their surface, as we have detected by the gel-permeation chromatography and NMR methods. It was found by the TGA and differential scanning calorimetric methods that the weight content of the polymeric envelope depends on the nature of particles and is maximal for nickel. It seems to be caused by the above-mentioned difference in the reduction processes. Copper and cobalt, the first one by its nature and the second because of sodium borohydride addition, are reduced fast, which does not allow a great quantity of PEG to react with the surface of nanoparticles. In the case of nickel, the reduction occurs slowly, and nanoparticles are evenly distributed in the polymeric matrix. Therefore, the faster the nucleation process occurs, the less PEG is formed and sorbed on the surface of nanoparticles during the synthesis.

Thus, our experimental results point to the dependence of the reduction of metal ions on their nature, however certain general regularities were found in nanoparticle growth after their independent or forced nucleation.

We generated copper, nickel, and cobalt nanoparticles in an ethylene glycol medium at 198°C in an inert atmosphere. Reaction mixtures were stirred with a Heidolph RZR 2020 top-driven stirrer. We used ethylene glycol and copper and cobalt nitrates (“analytically pure” grade) and nickel acetate (“chemically pure” grade) as the initial reagents. It should be pointed out that the use of these salts is caused by a high solubility of the sodium salts with the above anions in ethanol that is extremely important for the removal of admixtures by washing. Duration of the process was varied from 5 min up to 2 h. The product was cooled, separated on a Sigma 2-16P centrifuge, washed with ethanol, and subjected to lyophilic drying.

Phase composition was studied with the use of a Bruker D2 Phaser instrument with a cobalt anode and a Hitachi S-3400N scanning electron microscope with an AzTec Energy 350 analytical attachment for quantitative energy-dispersion microanalysis. Sizes and shapes of nanoparticles were determined by means of Hitachi S-3400N, JEOL JEM 107, and ASAP 2020MP Micromeritics microscopes. NMR spectra were taken on a Bruker 500 Avance III spectrometer. Gel-permeation chromatography experiments were carried out with the use of an LC-20 Prominence (column TSKgel

G4000PWxl, eluent – water, detector RID-10A) liquid chromatograph. UV spectra were recorded on a UNICO 2800 UV/VIS spectrophotometer.

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