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Self-Assembly of Nanoclusters in Molybdenum Blue Dispersions in the Presence of Organic Reducing Agent †

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Abstract: Molybdenum blue dispersions were synthesized by reducing an acidic molybdate solution with glucose, hydroquinone and ascorbic acid. The influence of the H/Mo molar ratio on the rate of formation of molybdenum particles was established. For each reducing agent, the conditions for the formation of aggregative stable dispersion of nanoclusters with the maximum concentration of particles are determined. The dispersed phase is represented by toroidal molybdenum oxide nanoclusters, which was confirmed by the results of UV-Vis, FTIR, XPS spectroscopy, DLS and TEM.

Keywords: molybdenum blue; self-assembly; polyoxometalates; molybdenum oxide; sol-gel method

1. Introduction

Molybdates in aqueous solution can form a variety of structures. Of greatest interest are the self-assembling molybdate nanostructures, one of which is molybdenum blue [1]. Molybdenum blue are oxygen-containing compounds of molybdenum of variable composition in which molybdenum is in oxidation states +5 and +6.

Molybdenum-oxygen clusters represent a large class of polyoxometalates (POM). The modern chemistry of polyoxometalates is very extensive and includes clusters of various chemical composition, size and shape [4–6]. Usually disperse phase of polyoxometalates represent of giant clusters of the order of 1–3 nm, which are formed as a result of self-assembly from the original building blocks, which are Mo_1, Mo_2 and Mo_8 etc. [7].

Polyoxometalates exhibit remarkable physicochemical properties, structural versality and highly reactivity. These systems are considered as the most promising clusters for production of hybrid materials, drug delivery systems, nanoreactors and catalytic materials [2,3,8,9].

Since the synthesis of clusters of polyoxomolybdates is a process of self-assembly the great attention of researchers was focused on the target synthesis of nanoscale structures from various initial building blocks and identification of its structure.

There are various methods of obtaining molybdenum blue and the most common is the reduction of molybdates in an acid solution. As a reducing agent can be used inorganic or organic compounds [2–5].

The most works in the area of molybdenum-oxygen clusters are related to the production of aqueous systems of molybdates, its functionalized or their crystalline precipitation. Water systems

containing molybdenum oxide clusters are often considered within the framework of the chemistry of complex compounds but not objects of colloid chemistry [8,9].

One of the reasons for this approach is that molybdenum oxide clusters can undergo dissociation to form a true solution. Despite this, in many works devoted to molybdenum-oxygen clusters, such characteristics of disperse systems as the sign of the electrokinetic potential and the hydrodynamic radius were determined [5,10–12]. On the other hand, the behavior of these systems under certain conditions, including aggregation in the presence of some electrolytes, allows us to attribute molybdenum blue to disperse systems [13].

In [14–16] were found that the choice of organic compounds as a reducing agent as glucose, hydroquinone and ascorbic acid, allows to obtain colloidal systems. The selection of conditions—the content of the reducing agent and acid makes it possible to create a chemical stable and resistant to sedimentation systems.

A study of the processes leading to the formation of particles in stable colloidal systems would lead to a more complete understanding of the synthesis of molybdenum blue as colloidal systems. The aim of this work was to synthesize stable dispersions of molybdenum blue using organic reducing agents and investigate the process of self-assembly.

2. Materials and Methods

Molybdenum blue dispersions were synthesized at room temperature using the reagents ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, reagent grade), crystalline glucose ($C_6H_{12}O_6$, reagent grade), hydroquinone ($C_6H_6O_2$, reagent grade), ascorbic acid ($C_6H_8O_2$, reagent grade) and hydrochloric acid (HCl, reagent grade).

The pH value was measured on a HI-8314 pH/mV meter (Hanna Instruments, Vöhringen, Germany) by using a combination electrode.

UV-Vis spectra were recorded by Leki SS2110 UV scanning spectrophotometer (MEDIORA OY, Finland) using quartz cells.

The hydrodynamic radii of the particles in the molybdenum blue dispersions was determined via dynamic light scattering by Photocor Compact-Z analyzer (OOO Photocor, Russia). The signal acquisition time was 30 min at a laser power of 20 mW and a wavelength of 658 nm.

The sizes and shapes of the particles were determined by LEO 912AM Omega Carl Zeiss transmission electron microscope.

IR spectra were measured by using Nicolet 380 IR Fourier spectrometer (Thermo Fisher Scientific Inc., MA, USA) in compressed KBr pellets in the range from 350 to 4000 cm^{-1}.

3. Results

3.1. Properties of Molybdenum Blue Properties

It is known that the formation of clusters of molybdenum blue occurs as a result of self-organization (self-assembly) of molybdenum complexes. For the process of self-organization, the presence of certain complexes of Mo^{5+} and Mo^{6+} is required. For the obtaining of Mo^{5+} complexes it is necessary to carry out a partial reduction of the molybdate ions in solutions. In this case the self-organization process is possible only at a certain pH of the dispersion medium (pH < 2). It is in such a medium that polycondensation of molybdate ions is observed with their subsequent organization into large molybdenum oxide clusters (particles of molybdenum blue).

Thus, to obtain dispersions of molybdenum clusters (hereinafter referred to as molybdenum blue), it is necessary to determine the optimal molar ratios of the reagents: reducing agent/Mo (R/Mo), acid/Mo (H/Mo), and also to establish the pH value at which stable molybdenum blue hydrosols are formed. In this work, glucose, hydroquinone and ascorbic acid were used as the reducing agent.

Earlier [14–16] were found that the formation of aggregative stable molybdenum blue occurs at a certain R/Mo ratio, while for each reducing agent there is an optimal ratio. For example, when using glucose, the required ratio R/Mo is 7/1, hydroquinone—4/1 and 1/1 for ascorbic acid. Under these

conditions the maximum number of molybdenum oxide clusters is formed. These parameters were used in this work for the synthesis of stable dispersions

The interaction of ammonium heptamolybdate with reducing agents in the above ratios leads to the formed of stable dispersions of molybdenum blue. The fact of their formation is confirmed by the appearance of an intense blue color and a change in the optical spectrum of electronic absorption. In Figure 1 UV-Vis spectra are given for dispersions synthesized using glucose, hydroquinone, and ascorbic acid.

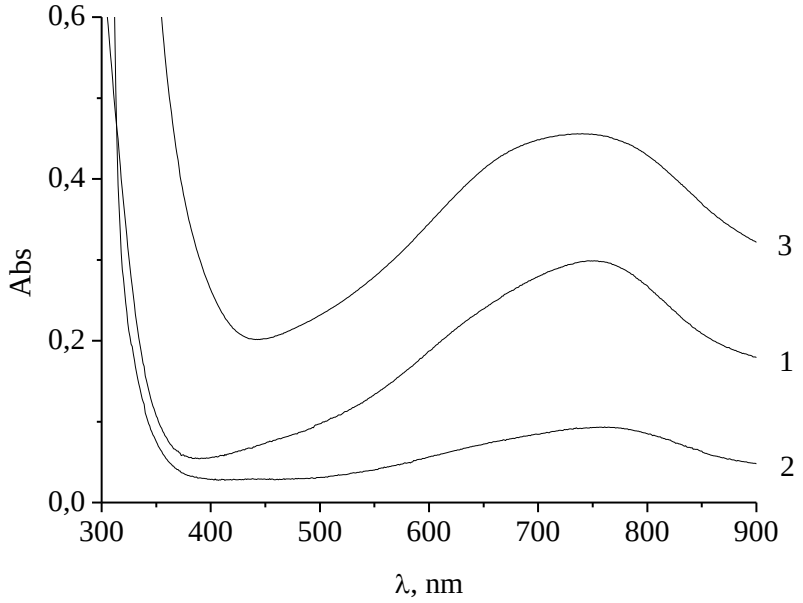

Figure 1. The electronic absorption spectrum of dispersion of molybdenum oxide clusters synthesized using various reducing agents: glucose (1), hydroquinone (2), ascorbic acid (3).

It is known that the self-assembly of molybdenum-oxide clusters proceeds during time [17]. To establish the effect of the H/Mo molar ratio on the rate of the formation of molybdenum blue particles, series of samples were prepared with a constant R/Mo ratio and different acid contents. The absorbance at the wavelength corresponding to the absorption maximum (λ = 745 nm) was used as a controlled parameter. The dependences of the optical density on time for various values of H/Mo are shown in Figure 2.

The formation of molybdenum blue particles occurs already in the first day after mixing the reagents. These results are also confirmed by dynamic light scattering data (see Figure 3).

Over time, for systems prepared with glucose and hydroquinone, an increase in the optical density and hence the number of particles of molybdenum blue is observed. The rate of their formation depends on the molar ratio of H/Mo. There is a range of values in which the rate of formation is higher. For glucose this region is 0.5–0.8 and maximum of particles of molybdenum blue is observed at H/Mo = 0.5. At values of H/Mo less than 0.5 molybdenum blue formation does not occur. For hydroquinone this region is 1.0–5.0 and maximum of particles is observed at H/Mo = 1.5.

Molybdenum blues synthesized under these conditions retain their aggregative stability for a long time.

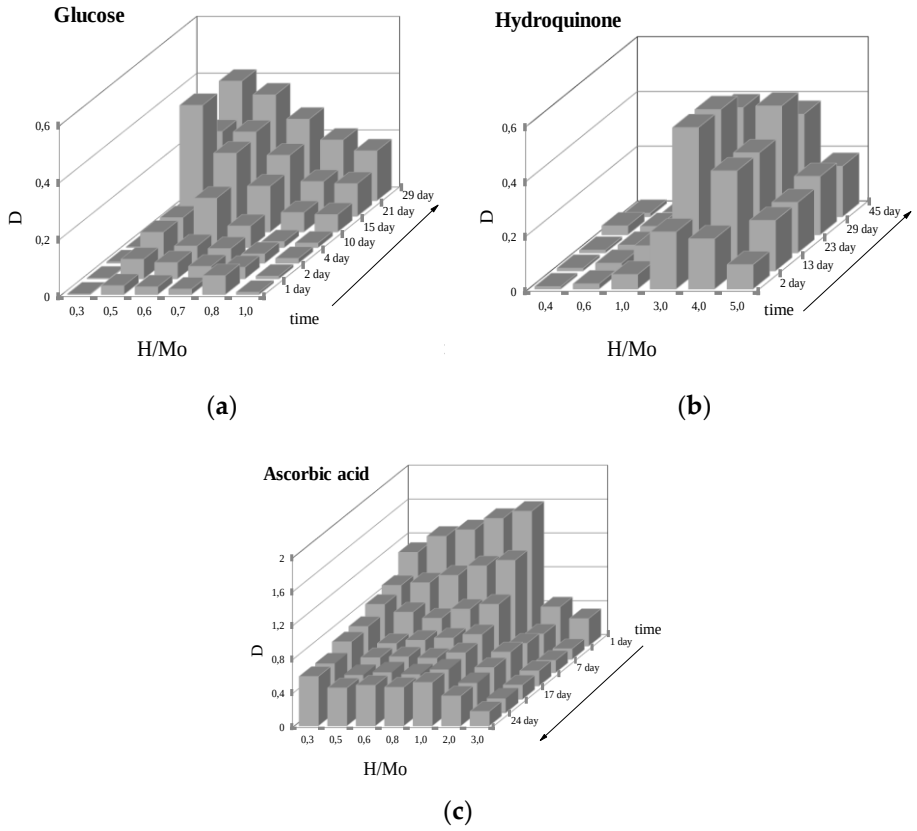

Figure 2. The dependence of the optical density of samples of molybdenum blue on time and molar ratio H/Mo, synthesized by using glucose (R/Mo = 7/1) (**a**), hydroquinone (R/Mo = 4/1) (**b**) and ascorbic acid (R/Mo = 1/1) (**c**).

A different situation is observed in systems synthesized with ascorbic acid. Particle formation occurs on the first day in the entire range of the studied H/ Mo ratios. The largest number of clusters is formed when the ratio H/Mo = 1. However, over time the optical density decreases to a certain value, whereas the character of the spectrum does not change (the absorption maximum is 745 nm). Such behavior can be explained with a long time to establish equilibrium between the formed nanoclusters and the initial building blocks.

Based on DLS measurement the particle-size distribution in molybdenum blues dispersion was established. The predominant radius of the particles (R_h = 1.5 nm) obtained from DLS did not change during the study period.

Transmission electron microscopy was used to determine the particle size of the molybdenum blue. Figure 3 shows TEM images of molybdenum blue particles synthesized using glucose. As can be seen the dispersed phase of the molybdenum blue is represented by particles with diameters not exceed 5 nm.

The image of the particles does not have high contrast, the electron diffraction patterns lack clear reflections, which indicates a low degree of crystallization of the particles. Regardless of the reducing agent used, the particles of molybdenum blue are close in shape to spherical, the presence of toroidal particles is difficult to establish at this resolution.

As can be seen from the presented data, the particles of molybdenum blue have a narrow size distribution, the prevailing diameter (number average) is about 3 nm.

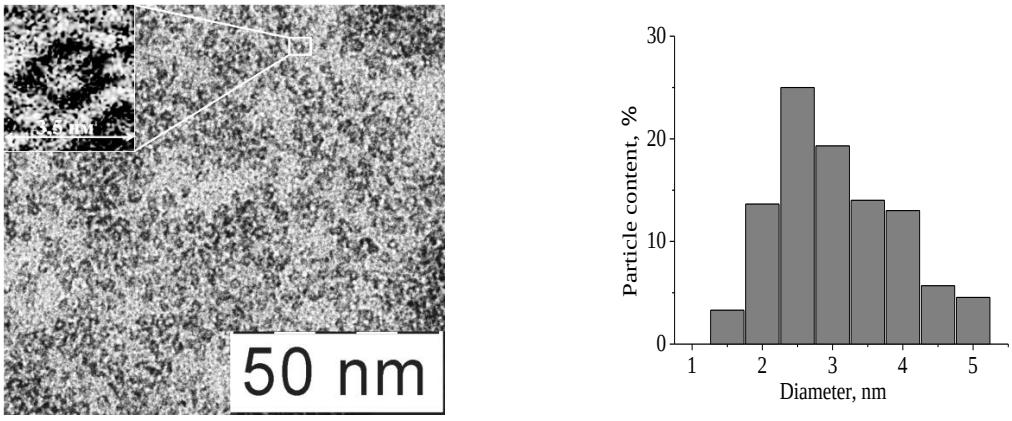

Figure 3. TEM images of particles (**a**) and particle size distribution (**b**) of molybdenum blue synthesized by using glucose.

3.2. Nanoparticles Characterization

UV-Vis and FTIR spectroscopy is used to characterize molybdenum blue particles and its structure [18,19]. Figure 4 shows the UV-Vis spectra of molybdenum blue particles synthesized using various reducing agents.

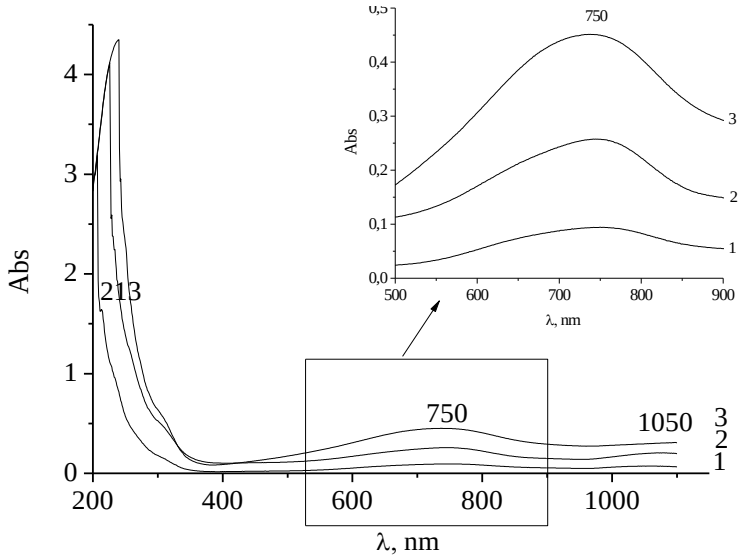

Figure 4. The electronic absorption spectrum of molybdenum oxide clusters isolated from dispersions synthesized using various reducing agents: glucose (1), hydroquinone (2), ascorbic acid (3).

The electronic absorption spectra contain wide absorption bands in the range of 213, 750 and 1050 nm. The observed bands, according to the literature [18], are characteristic of molybdenum blue which contain toroidal clusters (Mo_{138}, Mo_{150}, Mo_{154}, Mo_{176}].

The cluster structure can be determined using IR spectroscopy. The number of absorption bands observed on the spectra of the synthesized samples is in good agreement with the literature data and corresponds to the structure of the Mo_{154} toroidal clusters [18,19].

To confirm the presence of reduced molybdenum Mo^{V} in the analyzed samples, XPS spectroscopy was used. XPS spectroscopy confirmed the presence of reduced molybdenum Mo^{5+} in the composition of molybdenum oxide clusters. The content of reduced molybdenum Mo^{5+} in molybdenum blues synthesized using glucose and hydroquinone is about 12%, with the use of

ascorbic acid—29%. The results obtained agree with the literature data on the degree of reduction of molybdenum in toroidal clusters.

4. Discussion

Methods for the synthesis of aggregative stable molybdenum blue hydrosols using organic reducing agents (glucose, hydroquinone and ascorbic acid) have been developed.

The influence of the H/Mo molar ratio on the rate of formation of molybdenum particles was established. For each reducing agent, the conditions (molar ratios of H/Mo, pH value) for the formation of aggregative stable dispersion of nanoclusters with the maximum concentration of particles are determined.

Based on the UV-Vis, FTIR, XPS spectroscopy, DLS and TEM data it was shown that the particles of the dispersed phase are represented by nanocluster of a toroidal shape.

Author Contributions: Conceptualization, N.G., V.N.; methodology, N.G.; M.M.; investigation, N.G.; M.M.; D.H.; data curation, M.M., N.G.; writing—original draft preparation, M.M.; writing—review and editing, M.M. N.G.; V.N.; supervision V.N. All authors have read and agreed to the published version of the manuscript.

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