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Colloidal Characteristics of Molybdenum Blue Nanoparticles Dispersion for Catalytic Applications †

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Abstract: The nanosized clusters of molybdenum blues and their monodispersity make it possible to consider as promising precursors for the synthesis of molybdenum carbides. For the synthesis of supported catalysts using dispersions of nanoparticles (sols) it is necessary to know their main colloidal-chemical properties (electro-surface characteristics, rheological properties and the conditions of aggregative stability). The paper presents the results of a study of the colloidal-chemical properties of molybdenum blue, the dispersed phase of which is represented by toroidal particles of Mo_{154-x} family. It was found that aggregate stable sols exist in the pH range from 0.8 to 2.0. In this range molybdenum blue particles are negatively charged, the electrokinetic potential does not exceed 30 mV. Molybdenum blues have high aggregate stability and can be concentrated to a high concentration of the dispersed phase (20–30 wt%); at concentration more than 30 wt.%, a transition of the sol into a gel is observed. In a wide range of concentrations molybdenum blues are Newtonian liquids, the viscosity of which mainly depends on the concentration of the dispersed phase. The results obtained can be used as a basis for the development of a sol-gel method of supported catalysts based on molybdenum blue.

Keywords: molybdenum blue; molybdenum oxide nanocluster; aggregative stability

1. Introduction

In recent years, the development of catalysts based on transition metal carbides has become increasingly important in chemical technology, since transition metal carbides are similar in catalytic properties to noble metals. One of these promising objects is molybdenum carbide Mo_2C. Molybdenum carbideshows high efficiency in the reactions of hydrazine decomposition [1], cellulose conversion [2] and hydrogenation [3–5], as well as in reactions involving hydrogen (methane conversion [6–8], water gas shift reaction [9,10], isomerization [11] etc.).

The most widely used heterogeneous catalysts are supported catalysts. To synthesize supported catalysts sol-gel method can be used, which allows varying the properties of the catalyst in a wide range. The sol-gel method of preparation Mo_2C catalysts can be carried out using dispersions of molybdenum blue synthesized with organic reducing agents, this avoids an additional stage of catalyst activation [12,13]. To develop the main stages of the sol-gel method, knowledge of the main colloidal-chemical properties of dispersions, such as electro-surface and rheological characteristics, conditions of aggregate stability is needed.

The purpose of this work is to study the aggregative stability, electro-surface and rheological characteristics of dispersions of molybdenum blue synthesized using ascorbic acid.

2. Materials and Methods

2.1. Materials

Ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, ascorbic acid $C_6H_8O_6$, and hydrochloric acid HCl were purchased in CT Lantan, Moscow, Russia. All chemicals were used without further purification.

2.2. Synthesis of Molybdenum Blue Dispersion

Molybdenum blue were synthesized by reducing a solution of ammonium heptamolybdate (0.07 M, calculated on monomolybdate) by ascorbic acid in the presence of hydrochloric acid The synthesis was carried out at room temperature and the following conditions: molar ratios [R]/[Mo] = 0.2–5.0, molar ratios [H]/[Mo] = 0.8. The details of the synthesis can be found in [14].

2.3. Molybdenum Blue Dispersion Characterization

Particle size distribution of the molybdenum blue dispersion was measured using the DLS technique. The measurement were performed with a Photocor Compact-Z instrument (Photocor LLC, Moscow, Russia) at a wavelength of 658 nm.

The particle size of the molybdenum blue was studied using a LEO 912AB Omega (Carl Zeiss) transmission electron microscope. Images were acquired at 100 kV accelerating voltage. The analysis of the microphotographs and the calculation of particle sizes were carried out using the Image Tool UTHSCSA V.3.00.

Electronic absorption spectra were obtained using Leki SS2110 UV scanning spectrophotometer (MEDIORA OY, Helsinki, Finland) and quartz cuvettes with an optical path length of 10 mm. For spectrophotometric studies, the samples were preliminarily diluted with hydrochloric acid solutions with the same pH values.

The electrophoretic mobility of hydrosol particles was evaluated using Photocor Compact-Z (LLC Photocor, Moscow, Russia). The value of the applied electric field strength during analysis ranged from 3 to 15 V cm^{-1}. The analysis error of the electrophoretic mobility was of ± 1 10^{-9} m^2 $(s\cdot V)^{-1}$.

Since the particle sizes of hydrosols are comparable to the thickness of the diffuse part of the double electric layer (DEL), the Henry formula was applied to calculate the electrokinetic potential [15]:

$$\zeta = \frac{3\eta U_{эф}}{2\varepsilon\varepsilon_0}\cdot\frac{1}{f_1(\kappa r)} \qquad (1)$$

where Uef is electrophoretic mobility, ε is the dielectric constant of the medium, ε_0 is the electric constant, η is the sol viscosity, r is the particle radius, and κ is the reciprocal of the Debye length. To calculate the function f1 (κr), we used the relation proposed in reference [16]:

$$f_1(\kappa r) = 1 + \frac{1}{2}\left[1 + \left(\frac{2{,}5}{\kappa r[1+2\exp(-\kappa r)]}\right)\right]^{-3} \qquad (2)$$

The rheological properties of diluted hydrosols were studied using a Brookfield LV DV II rotational viscometer (Brookfield Engineering Laboratories Inc, Middleboro MA, USA) with an ULA adapter. The measurements were carried out at a constant temperature of 20 °C, which was maintained with an accuracy of ± 0.1 °C using a Brookfield TC-502 thermostat (Brookfield Engineering Laboratories Inc, USA). Temperature control was carried out using a thermocouple connected to the measuring cell.

3. Results

3.1. pH Region of Aggregative Stability

The pH range in which dispertions retain aggregate and chemical stability is one of the most important properties of sols as dispersed systems. To determine this region a series of molybdenum blue samples were prepared, which differed in the pH value of the dispersion medium. Optical density at the maximum absorption (760 nm) corresponds to the concentration of particles in the dispersed phase. The constancy of its value, as well as the hydrodynamic radius, indicates the stability of the dispersions.

In Figure 1 shows the dependence of optical density on the pH value of the dispersion medium 1 and 7 days after synthesis.

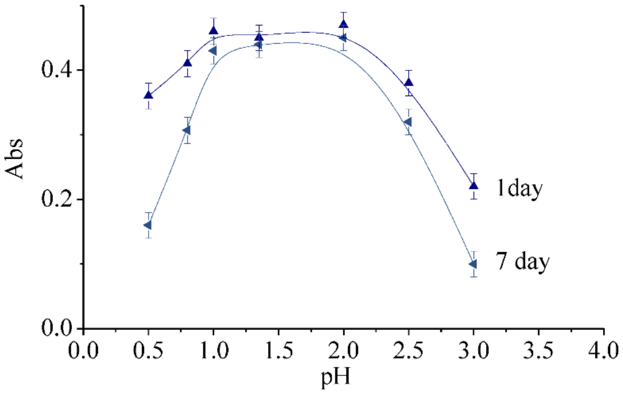

Figure 1. The dependence of optical density of molybdenum blue on the pH value of the dispersion.

At pH values of 0.8 or less, a drop in the optical density of dispersions is observed. At the same time, coagulation of particles and precipitation is observed. In the region of pH 2.5 and more, a decrease in optical density is also observed, but this is due to a different reason. With increasing pH, destruction of molybdenum oxide clusters occurs. Molybdenum blue particles dissolve to form molybdate ions (Mo^{VI}).

Thus, molybdenum blues synthesized using ascorbic acid are aggregative and chemical stable in a narrow pH range from 0.8 to 2.0.

3.2. Electrokinetic Potential

The electrokinetic potential was used as a characteristic of the electrosurface properties of dispersions. molybdenum blue with different pH values are shown in Figure 2.

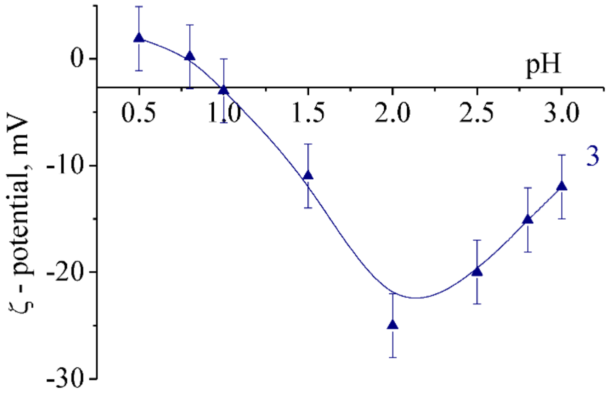

Figure 2. Dependence of the electrokinetic potential of molybdenum blue particles on the pH of the dispersion medium.

As shown in Figure 2 data, in the range of pH values from 3.0 to 0.8 molybdenum blue particles are negatively charged. The maximum (in absolute value) value of the electrokinetic potential (−28 mV) corresponds to the pH range of ~2.0–2.5.

In the range of pH values from 2.0 to 0.8, the absolute value of the ζ-potential decreases, accompanied by a change in sign at a pH value of 0.5. The obtained value is close to the position of the isoelectric point for molybdenum trioxide MoO_3, which, according to the literature, is in the range of pH values from 0.5 to 2.0 [17].

3.3. Rheological Properties

Rheological properties are of great importance for the synthesis of deposited materials by the sol-gel method. To determine the rheological properties of molybdenum blue, a series of samples with different concentrations of the dispersed phase and different pH values of the dispersion medium (in the region of aggregate stability of systems) were prepared.

Experiments have shown that the dispersions of molybdenum blue synthesized using ascorbic acid are Newtonian liquids. As an example, Figure 3 shows the flow curves and the dependence of the viscosity on the shear stress.

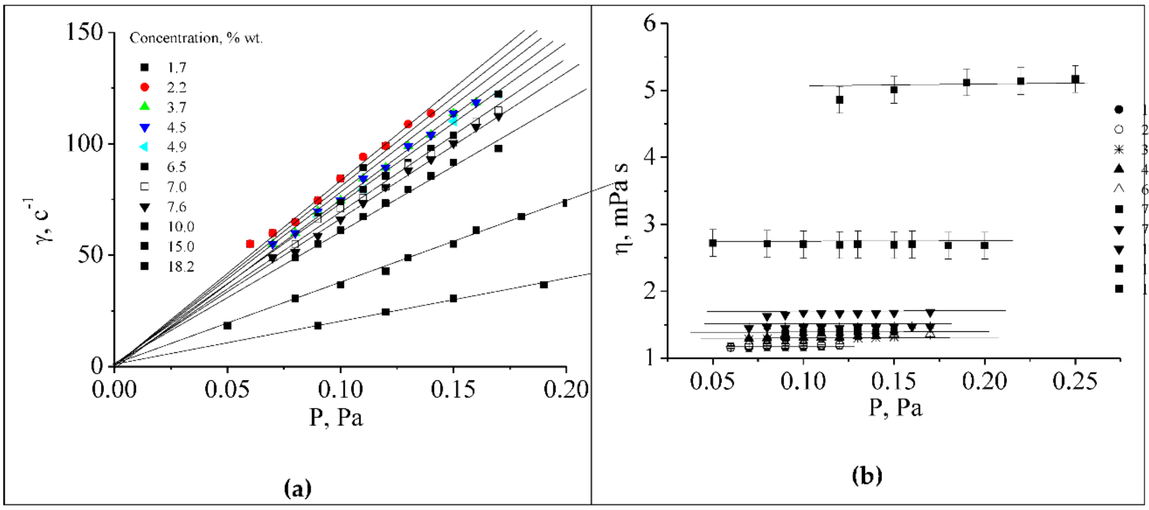

Figure 3. (**a**): Flow curves and (**b**): dependence of viscosity on load for molybdenum blue with different concentration of the dispersed phase. (pH = 1.5).

From the data obtained, it follows that the flow curves in the studied concentration range are linear dependences, which indicates that these hydrosols are Newtonian liquids with low viscosity. Figure 4, and the same data are presented in the coordinates of the Einstein equation. A more distinct increase in viscosity (compared to what the Einstein equation predicts) with increasing concentration of the dispersed phase is related to electro-viscous effects, which are associated with the presence of DELs on the particle surfaces. The strongest effect on viscosity is caused by the diffuse parts of the DEL overlap, i.e., the occurrence of a secondary electro-viscous effect.

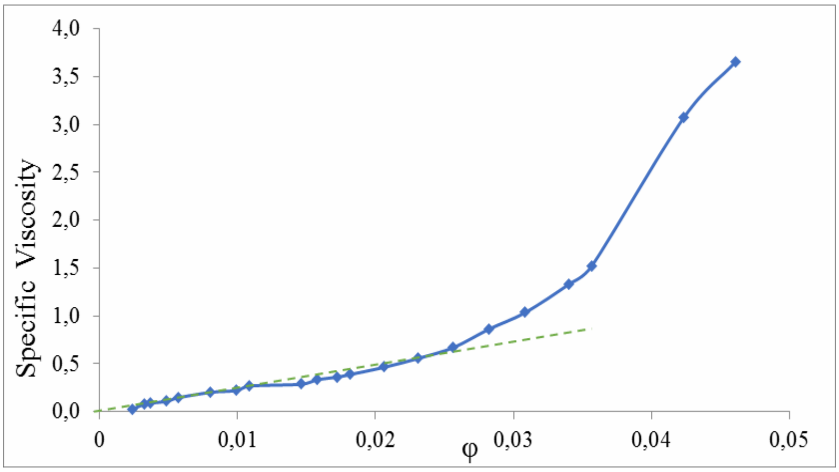

Figure 4. The dependence of the specific viscosity on the concentration of molybdenum blue (pH = 1.5).

4. Discussion

The presented results of the study of the colloidal-chemical properties of molybdenum blue are a continuation of the work [14] in which the features of the synthesis of molybdenum blue in the presence of ascorbic acid were considered. This dispersion is of undoubted interest, since it allows one step to synthesize highly dispersed molybdenum carbide [13], which is a catalyst for many reactions. The data on the basic colloidal-chemical characteristics are very important in the transition from the synthesis of powdered to supported Mo_2C catalysts.

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