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Molybdenum-Tungsten Blue Nanoparticles as a Precursor for Ultrafine Binary Carbides †

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Abstract: The promising method for synthesis of ultafine carbide particles is sol-gel method using dispersions of molybdenum-tungsten nanoparticles. For further use it is necessary to know main properties of molybdenum-blue nanoparticles, including size, structure and stability under different conditions. The synthesis of dispersions of molybdenum-tungsten blue was carried out as a result of the reduction of molybdate and tungstate ions in an acidic medium. Ascorbic acid was used as a reducing agent and further can act as a carbon source. Dispersions and nanoparticles were investigated by UV/Vis and infrared (FTIR) spectroscopy, transmission electronic microscopy (TEM) and dynamic light scattering (DLS).

Keywords: molybdenum-tungsten blue; polyoxometalate complex; sol-gel method; binary carbide

1. Introduction

The use of highly dispersed molybdenum and tungsten carbides is one of the promising directions in the development of some catalytic processes, including hydrogen evolution reaction and production of synthesis-gas [1–3]. To obtain a material with a small particle size and high specific surface area, various methods are used, including solid-phase and liquid-phase methods [4–6]. The main requirement for the method is the ability to obtain highly dispersed carbide. As such method the sol-gel method using as a disperse system—molybdenum-tungsten blue can be chosen.

Nanoparticles of molybdenum-tungsten blues are polyoxometalate complexes or nanoclusters containing molybdenum and tungsten in variable oxidation states. Polyoxometalate complexes have a constant size of the order of 3–5 nm [7–9]. The use of such a highly dispersed precursor of molybdenum and tungsten carbides will lead to the formation of a carbide phase with a small particle size and high specific surface area [10]. However, the first stage in the development of a method for obtaining highly dispersed carbides is to establish the conditions for the formation of molybdenum-tungsten blue nanoparticles and the possibility of obtaining stable dispersions based on them.

The aim of this work was to select the conditions for the synthesis of dispersions of molybdenum-tungsten blue and to determine the main characteristics of nanoparticles of molybdenum-tungsten blue.

2. Materials and Methods

Molybdenum-tungsten blue dispersions were synthesized using the reagents: ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, reagent grade), ammonium tungstate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$, reagent grade), crystalline ascorbic acid ($C_6H_8O_6$, reagent grade) and hydrochloric acid (HCl, reagent grade).

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

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

The sizes of particles were determined by LEO 912AM Omega (Carl Zeiss, Oberkochen, Germany) transmission electron microscope.

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

3. Results

Dispersions of molybdenum-tungsten blue are formed as a result of a self-assembly process. Self-assembly of nanoparticles or nanoclusters occurs during the reduction of solutions of molybdate and tungstate in an acidic medium. Ascorbic acid was used as a reducing agent, because another type of the reducing agent, for example glucose or hydroquinone, are not so strong for the reduction of tungstate.

In this work, samples of molybdenum-tungsten blue with different molar ratios [Mo]/[W] were synthesized. At the first stage it was necessary to establish optimal content of reducing agent in the system. According to the synthesis of molybdenum blue dispersion, using ascorbic acid, the optimal molar ratio was [R]/[Mo] from 0.8 to 1 [11]. So, this range of ratios was chosen for synthesis of molybdenum-blue dispersions. It was established, that stable molybdenum-blue dispersions can be obtained in the discussed range of molar ratio [R]/[Mo]. The molar ratio [R]/[Mo] = 1 was used for further synthesis of dispersions and their investigation.

Figure 1 shows the absorption spectra of the molybdenum-tungsten blue dispersions synthesized at molar ratio [R]/[Me] = 1 and molar ratio molybdenum- tungsten [Mo]/[W] = 95/5; 90/10; 80/20; 50/50. The spectrum of molybdenum blue dispersion ([Mo]/[W] = 100 is shown for comparison.

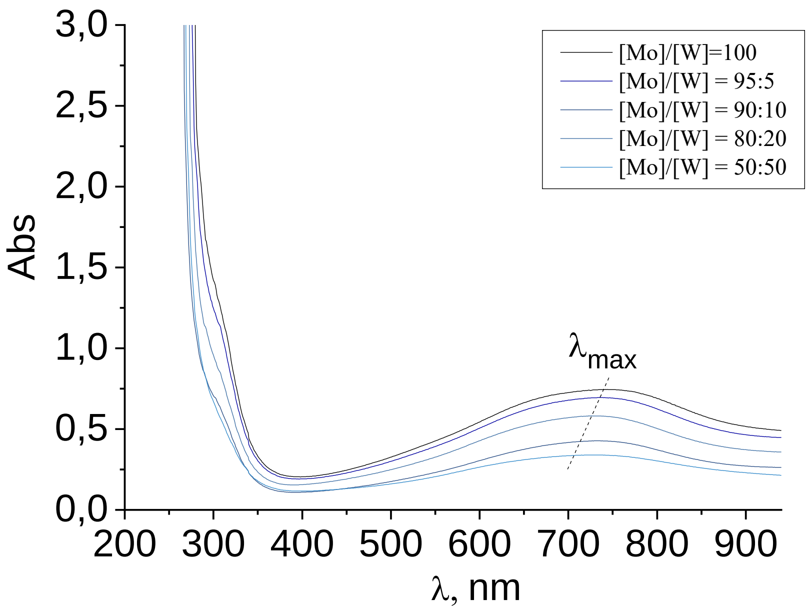


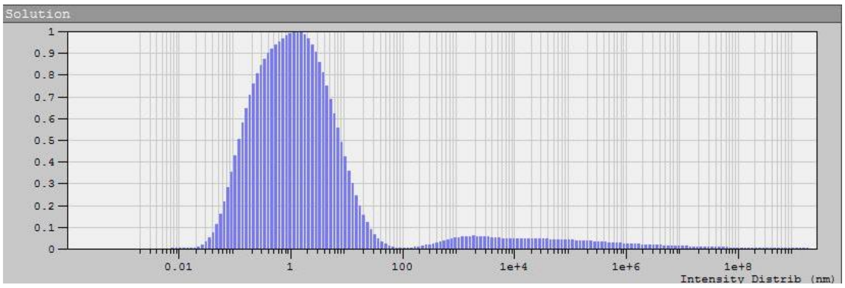
Figure 1. The electronic absorption spectrum of dispersion of molybdenum-tungsten blue synthesized using ascorbic acid ([R]/[Mo] = 1) and with different molar ratio [Mo]/[W].

As can be seen, with an increase in the tungsten content, the absorption maximum shifts from 750 nm to 680 nm. This shift may be associated with the possible incorporation of tungsten compounds into the structure of molybdenum oxide nanoclusters, the presence of which was previously shown in molybdenum blue dispersions, synthesized using ascorbic acid [11].

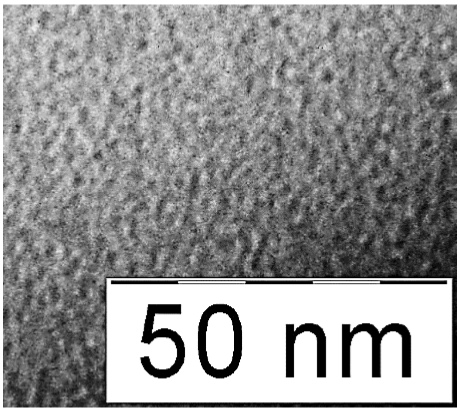
The size and shape of the particles were analyzed by DLS and transmission electron microscopy. Figure 2 shows the hydrodynamic radius distribution of particles and a TEM micrograph.

The predominant hydrodynamic radius is 1.5 nm, which is comparable to the sizes of molybdenum oxide clusters given in the literature [7,8].

The micrograph shows that the particles of molybdenum-tungsten blue are toroidal particles with a constant size. The estimation of the particle size showed that the diameter of the tori is on the order of 3-4 nm; however, a more accurate determination of the size is impossible due to reaching the limit of the resolution. It should be noted, that size distribution and micrographs are the same for all investigated samples with different molar ratio [Mo]/[W].



(**a**)



(**b**)

Figure 2. DLS distribution (**a**) and TEM-image (**b**) of molybdenum-tungsten blue nanoparticles, synthesized with molar ratio [Mo]/[W] = 90/10.

FTIR spectroscopy was used for determining the structure of synthesized molybdenum-blue nanoparticles. Figure 3 shows the FTIR spectra for samples with different molar ratio [Mo]/[W]: 95/5; 90/10; 80/20; 50/50. The spectra of molybdenum-tungsten blue nanocluster are similar to the spectrum of molybdenum blue, especially toroidal molybdenum oxide nanoclusters. The particles have the same high hydration as molybdenum blue, as evidenced by the bands corresponding to hydrogen bonds ν (OH…H) and bending vibrations of water molecules δH_2O.

Thus, the nanoparticles of molybdenum-tungsten blue have the similar properties with the molybdenum blue nanoparticles. They have narrow particle size distribution and predominant particle size about 3–4 nm. According to the Uv/Vis and FTIR spectra, the shape of nanocluster is more possible to be toroidal.

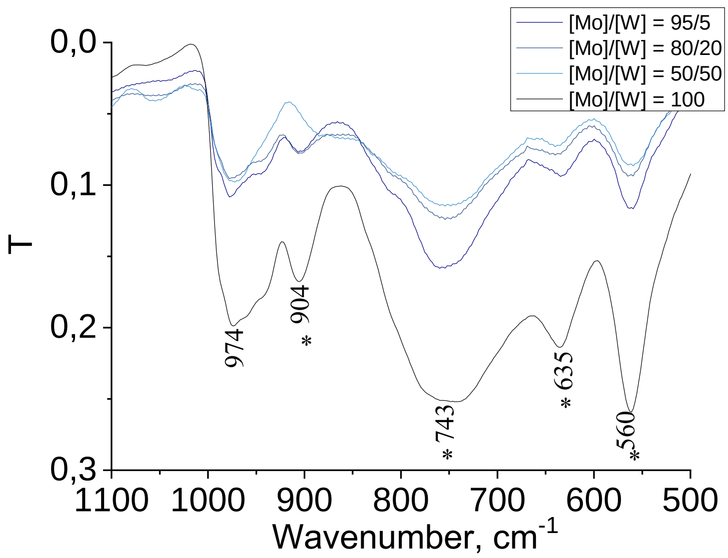


Figure 3. FTIR spectra of molybdenum-tungsten oxide nanoclusters with different molar ratio [Mo]/[W] isolated from dispersions synthesized.

4. Discussion

It was shown, that molybdenum-tungsten blues are highly dispersed systems based on polyoxometalate complexes of molybdenum and tungsten. A unique property of POM is monodispersed particles with size about 3–5 nm. The effect of molar ratio reducing agent/ metal (molybdenum and tungsten) and molar ratio molybdenum/tungsten on the properties of dispersions was investigated. It was shown, that stable nanoparticles were formed at the molar ratio [R]/[Me] = 0.8–1 and at the molar ratio molybdenum/tungsten [Mo]/[W] = 95/5; 90/10; 80/20; 50/50.

The developed method for the synthesis of molybdenum-tungsten dispersions make possible to obtain highly dispersed precursor for ultrafine binary carbides of molybdenum and tungsten.

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Conflicts of Interest: The authors declare no conflict of interest.

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