Materials Proceedings

MDPI

*Proceeding Paper*

# Properties of Molybdenum–Tungsten Blue Nanoparticles as a Precursor for Ultrafine Binary Carbides †

**Maria Myachina *, Natalia Gavrilova, Ksenia Poluboyarinova and Victor Nazarov**

Department of Colloid Chemistry, D. Mendeleev University of Chemical Technology of Russia, Miusskaya sq., 9, 125047 Moscow, Russia; ngavrilova@muctr.ru (N.G.); amalieleon@gmail.com (K.P.); nazarov@muctr.ru (V.N.)

* Correspondence: mmyachina@muctr.ru

† Presented at the 2nd International Online-Conference on Nanomaterials, 15–30 November 2020; Available online: https://iocn2020.sciforum.net/.

**Abstract:** A promising method for the synthesis of ultrafine carbide particles is the sol–gel method using dispersions of molybdenum–tungsten nanoparticles. For further use, the main properties of molybdenum-blue nanoparticles, including the size, structure, and stability, under different conditions must be determined. The synthesis of dispersions of molybdenum–tungsten blue was carried out as a result of the reduction of molybdate and tungstate ions in the presence of hydrochloric acid. Ascorbic acid was chosen as a reducing agent and further acted as a carbon source. Dispersions and nanoparticles were investigated by transmission electronic microscopy (TEM), UV/vis and infrared (FTIR) spectroscopy, and dynamic light scattering (DLS).

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

**Citation:** Myachina, M.; Gavrilova, N.; Poluboyarinova, K.; Nazarov, V. Molybdenum-Tungsten Blue Nanoparticles as a Precursor for Ultrafine Binary Carbides. *Mater. Proc.* **2021**, *4*, 1. https://doi.org/10.3390/IOCN2020-07894

Academic Editors: Ana María Díez-Pascual, Antonio Di Bartolomeo and Guanying Chen

Published: 11 November 2020



## 1. Introduction

The use of highly dispersed transition metal carbides is one of the promising directions in the development of some catalytic processes, including hydrogen evolution reactions and the production of synthesis gas [1–3]. To obtain a carbide with a small particle size and high 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 carbides. The sol–gel method using molybdenum–tungsten blue as a dispersed system can be chosen as such a method.

The nanoparticles of molybdenum–tungsten blue are polyoxometalate complexes or nanoclusters containing molybdenum and tungsten in varying 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 mixed Mo-W carbides will lead to the formation of a carbide phase with a nanometer particle size and high surface area [10]. However, the first stage in the development of a method for obtaining highly dispersed carbides is to establish the conditions for forming the molybdenum–tungsten blue nanoparticles and the way in which to obtain 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 the nanoparticles of molybdenum–tungsten blue.

## 2. Materials and Methods

Molybdenum–tungsten blue dispersions were synthesized using the following 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).

The Leki SS2110 UV scanning spectrophotometer (MEDIORA OY, Helsinki, Finland) was used for UV-vis spectra recording.

The hydrodynamic radius of the molybdenum–tungsten blue nanoparticles was determined by dynamic light scattering using a Photocor Compact-Z analyzer (OOO Photocor, Moscow, Russia). The signal was accumulated for 30 min (laser power of 20 mW and wavelength of 658 nm).

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

The FTIR spectra were recorded using a Nicolet 380 IR Fourier spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) in KBr pellets in the range from 350 to 4000 $cm^{-1}$.

## 3. Results

Molybdenum–tungsten blue hydrosols are formed as a result of the self-assembly process. The self-assembly of nanoparticles or nanoclusters occurs during the reduction of solutions of molybdate and tungstate in the presence of acid. Ascorbic acid was chosen as a reducing agent, because other types of reducing agents, such as glucose or hydroquinone, are not as strong for the reduction of tungstate.

In this work, molybdenum–tungsten blue hydrosols with molar ratios [Mo]/[W] ranging from 100 to 50/50 were synthesized. In the first stage, it was necessary to establish the optimal content of reducing agents in the system. According to the synthesis of molybdenum blue dispersions in the presence of ascorbic acid, the optimal molar ratio [R]/[Mo] ranged from 0.8 to 1 [11]. In addition, this range of ratios was chosen for the synthesis of molybdenum–blue dispersions. It was established that stable molybdenum–blue dispersions can be obtained in the discussed range of [R]/[Mo]. The equimolar ratio [R]/[Mo] = 1 was chosen for the further synthesis of dispersions and their investigation.

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

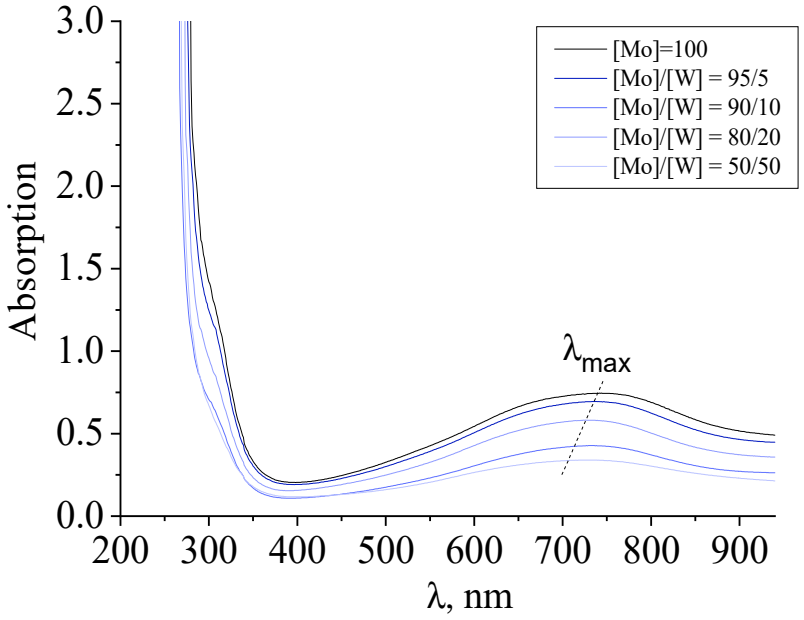


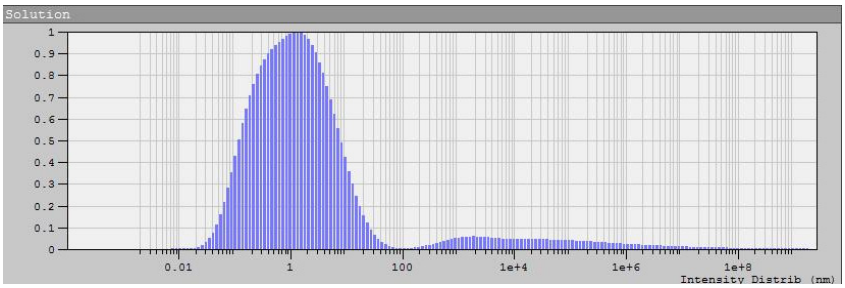

**Figure 1.** The electronic absorption spectrum of the dispersion of molybdenum–tungsten blue synthesized using ascorbic acid ([R]/[Mo] = 1) and with different molar ratios [Mo]/[W].

The increase in the tungsten content caused the absorption maximum to shift from 750 to 680 nm. This shift might be associated with the possible incorporation of tungsten compounds into the structure of the molybdenum blue nanoparticles. Their presence was previously shown in molybdenum blue dispersions, synthesized using ascorbic acid [11].

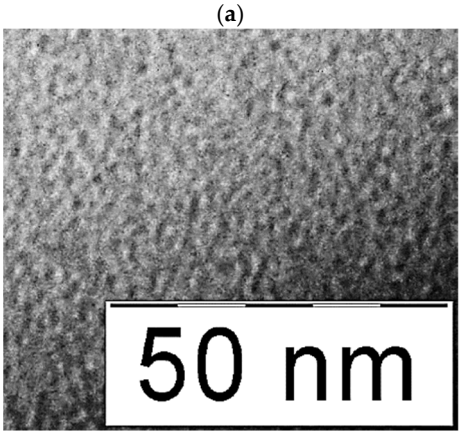
The size and shape of the particles were analyzed by DLS and transmission electron microscopy. Figure 2 shows the hydrodynamic radius distribution of particles and a TEM micrograph.

The predominant hydrodynamic radius was 1.5 nm, which is comparable to the molybdenum oxide nanocluster size given in the literature [7,8].

The micrograph shows that the particles of molybdenum–tungsten blue were toroidal particles with a constant size. The estimation of the particle size showed that the diameter of the tori was on the order of 3–4 nm; however, a more accurate determination of the size was impossible due to the resolution limit being reached. It should be noted that the size distribution and micrographs were the same for all investigated dispersions with molar ratios [Mo]/[W] ranging from 100 to 50/50.




(**a**)




(**b**)

**Figure 2.** DLS distribution (**a**) and TEM image (**b**) of molybdenum–tungsten blue nanoparticles ([Mo]/[W] = 90/10).

FTIR spectroscopy was used to determine the structure of synthesized molybdenum-blue nanoparticles. Figure 3 shows the FTIR spectra for samples with different molar ratios [Mo]/[W]: 95/5, 90/10, 80/20, and 50/50. The spectrum of molybdenum–tungsten blue nanoclusters is similar to that 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 $\delta H_2O$.

Thus, the nanoparticles of molybdenum–tungsten blue have similar properties to the molybdenum blue nanoparticles. They have a narrow particle size distribution and predominant particle size of about 3–4 nm. According to the UV/vis and FTIR spectra, the shape of the nanocluster is more likely to be toroidal.

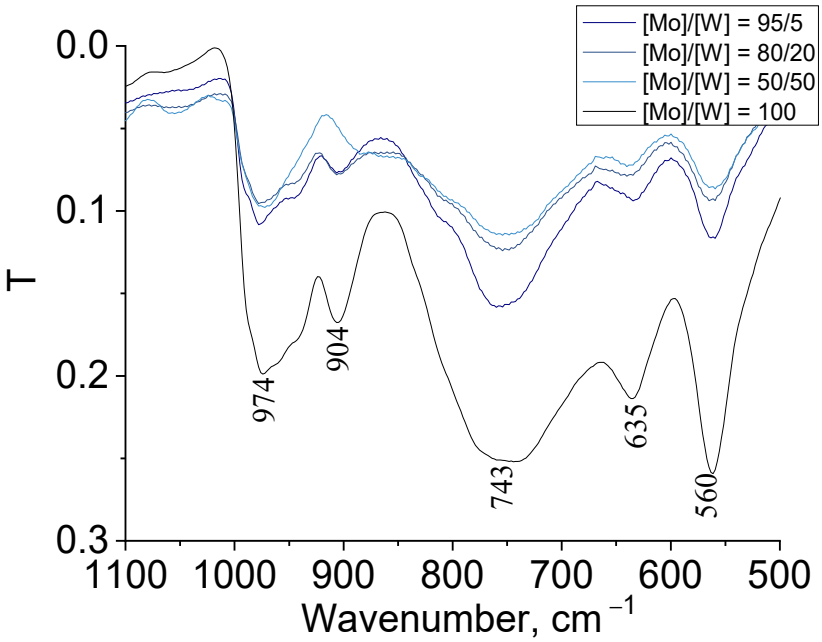



**Figure 3.** FTIR spectra of molybdenum–tungsten oxide nanoclusters with different molar ratios [Mo]/[W] isolated from the dispersions synthesized.

## 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 sizes of about 3–5 nm. The effects of the molar ratio of the reducing agent/metal (molybdenum and tungsten) and the molar ratio of the molybdenum/tungsten on the properties of dispersions were investigated. It was shown that stable nanoparticles were formed at the molar ratios [R]/[Me] = 0.8–1 and at the molybdenum/tungsten molar ratios [Mo]/[W] = 95/5, 90/10, 80/20, and 50/50.

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

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/IOCN2020-07894/s1.

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

**Funding:** This research was funded by D. Mendeleev University of Chemical Technology, grant number 031-2020.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

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

## References


1. Rasaki, S.A.; Zhang, B.; Anbalgam, K.; Thomas, T.; Yang, M. Synthesis and application of nano-structured metal nitrides and carbides: A review. *Prog. Solid State Chem.* **2018**, *50*, 1–15.
2. Lamic, A.F.; Shin, C.H.; Djéga-Mariadassou, G.; Potvin, C. Characterization of New Bimetallic Oxycarbide ($MoWC_{0.5}O_{0.6}$) for Bifunctional Isomerization of n-Heptane. *Catal. Lett.* **2006**, *107*, 89–94.
3. Mehdad, A.; Jentoft, R.E.; Jentoft, F.C. Single-phase mixed molybdenum-niobium carbides: Synthesis, characterization and multifunctional catalytic behavior in toluene conversion. *J. Catal*. **2017**, *351*, 161–173.
4. Peng, X.; Ge, X.; Wang, H.; Liu, Z.; Fisher, A.; Wang, X. Novel Molybdenum Carbide–Tungsten Carbide Composite Nanowires and Their Electrochemical Activation for Efficient and Stable Hydrogen Evolution. *Adv. Fun. Mat*. **2015**, 25, 1520-1526.
5. Bastos, L.; Monteiro, W.; Zacharias, M.; da Cruz, G.; Rodrigues, J.A. Preparation and characterization of Mo/W bimetallic carbides by using different synthesis methods. *Catal. Lett.* **2008**, *120*, 48–55.
6. Mehdad, A.; Jentoft, R.E.; Jentoft, F.C. Single-phase mixed molybdenum-tungsten carbides: Synthesis, characterization and catalytic activity for toluene conversion. *Catal. Today* **2019**, *323*, 112–122.
7. Long, D.L.; Burkholder, E.; Cronin, L. Polyoxometalate clusters, nanostructures and materials: From self-assembly to designermaterials and devices. *Chem. Soc. Rev.* **2007**, *36*, 105–121.
8. Botar, B.; Ellern, A.; Kögerler, P. Mapping the formation areas of giant molybdenum blue clusters: A spectroscopic study. *Dalton Trans*. **2012**, *41*, 8951–8959.
9. Scaffer, C.; Merca, A.; Bogge, H.; Todea, A.M.; Kistler, M.L.; Tianbo, L.; Thouvenot, R. Unprecedented and Differently Applicable Pentagonal Units in a Dynamic Library: A Keplerate of the Type $\{(W)W_5\}_{12}\{Mo_2\}_{30}$. *Angew. Chem. Int. Ed*. **2009**, *48*, 149–153.
10. Zheng, Z.; Yuan, Z.; Li, S.; Li, H. Big to small: Ultrafine $Mo_2C$ particles derived from giant polyoxomolybdate clusters for hydrogen evolution reaction. *Small* **2019**, *15*, 1900358.
11. Gavrilova, N.; Myachina, M.; Harlamova, D.; Nazarov, V. Synthesis of Molybdenum Blue Dispersions Using Ascorbic Acid as Reducing Agent. *Colloids Interfaces* **2020**, *4*, 24–38.