Influence of synthesis conditions on the crystal and local structures of WO$_3$ powders.

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Abstract. Influence of synthesis conditions on the crystal and local structures of WO$_3$ powders prepared by thermal decomposition of ammonium paratungstate and precipitation of tungstates aqueous solutions in strong acid conditions has been investigated. Combination of X-ray powder diffraction, X-ray absorption fine structure spectroscopy, IR- and Raman-spectroscopy, and scanning electron microscopy was used. The calcination of all initial compounds at temperatures $\geq 500^\circ$C led to formation of the monoclinic $\gamma$-WO$_3$ single phase. It was concluded that the neutral octahedral complex $[\text{W}=\text{O}(\text{OH})_4(\text{H}_2\text{O})]$ can be a structural unit of the precursors prepared in acidic suspensions. The local structure of synthesized tungsten oxides consists of edge-shared and corner-shared distorted octahedral WO$_6$ species linked together.

1. Introduction
Transition element oxides are of great interest for both fundamental science and technological applications due to their multifunctional properties. Tungsten oxides WO$_x$, where $2 \leq x \leq 3$, are among the most important substances from this large group. Nowadays they are commonly used as photocatalysts, gas sensors, and electrochromic materials. There are also some new applications of WO$_x$ for dye-sensitized solar cells, optical data storage and field-emission displays. Besides, cation-doped WO$_x$ is considered as high-$T_c$ superconductor [1].

Oxides WO$_3$ and their hydrates can be synthesized using various chemical and physical methods, such as wet chemical precipitation, sol-gel hydrolysis of tungsten alkoxide, ion exchange and thermal decomposition of tungsten salts. Films of WO$_3$ can be deposited on various substrates using various vacuum techniques [1-4]. Different crystalline structures as well morphologies occur depending on the processing conditions. The WO$_3$ phase transitions are rather complex.
The aim of the present work is to study the influence of synthesis conditions on the crystal and local structures of WO₃ powders prepared by wet chemical precipitation and thermal decomposition of tungsten salts by means of X-ray diffraction, X-ray absorption fine structure spectroscopy, IR- and Raman-spectroscopy, and scanning electron microscopy.

2. Experimental

The starting materials were sodium tungstate (ST) Na₂WO₄·2H₂O (98.5%), ammonium paratungstate (APT) (NH₄)₁₀W₁₂O₄₁·5H₂O (99.0%). Precursors (tungsten trioxide hydrates or tungstic acids) were prepared by acidification of tungstates salts solutions with hydrochloric HCl (analytical grade) or nitric HNO₃ (analytical grade) acids until the final pH ~ 0 [2]. Tungsten trioxide WO₃ powders were prepared by calcination of synthesized precursors or APT at 300 - 1000°C for 2 - 6 h in air.

Crystal structures of synthesized powders were studied by X-ray powder diffraction at “Center for X-ray structural research and diagnostics of materials” MISiS using a Rigaku MiniFlex 600 diffractometer with Cu Kα radiation. The Rietveld full-profile analysis of X-ray diffraction patterns was performed with the Jana2006 software [5].

The Raman spectra were collected on a lab inVia Reflex confocal Raman microscope (Renishaw) (laser λ₁=532 nm and λ₂=785 nm) and a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific Inc.) with Thermo Scientific iS50 Raman module (λ=1064 nm) at room temperature. Infrared (IR) spectra of the synthesized powders were recorded on Nicolet iS50 FT-IR spectrometer with built-in all reactive, mid- and far-IR diamond iS50 ATR module in the range of 400-4000 cm⁻¹.

X-ray absorption fine structure (EXAFS) spectra were measured above W L₁₋ and L₂₋ edges at “Structural Materials Science” beamline of the Kurchatov synchrotron radiation source in transmission mode at room temperature. The processing and simulation of the EXAFS spectra were performed using IFEFFIT [6] program packages. The back scattering amplitudes and phases were calculated with FEFF-8.20 [7] based on the known crystal structure parameters and the diffraction data. The XANDA program [8] was used to fit the near-edge region of X-ray absorption spectra.

The particle morphology and elemental composition of synthesized powders were studied by Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM/EDS) using an X-Act energy dispersive detector Oxford Instruments with a spectral resolution of 125 eV mounted on a Vega 3 Tescan scanning electron microscope. The characteristic X-ray radiation was automatically processed with the AZteC program.

3. Results and discussion

It was found that acidic precipitation (pH 0; 80°C) of both ST and APT leads to formation of bright lemon yellow powders of tungsten trioxide monohydrates (tungstic acid) WO₃·H₂O with orthorhombic structure (JCPDS № 43-0679). Particles of all synthesized precursors (both ST and APT) had size up to several tens of microns and were aggregates of smaller particles (Figure 1).

Figure 1 SEM images of (ST+HCl) (a) and (APT+HNO₃) (b) precursors
In the precursor samples annealed at 300°C we observed the appearance of the monoclinic phase \( \gamma\)-WO\(_3\) (JCPDS № 43-1035) and probably some amount of residual precursor (Figure 2a, 2b). In the sample prepared by APT at 300°C, we can see the presence of some amorphous phase and hexagonal ammonium tungsten oxide bronze (\(\text{NH}_4\))\(_{0.25}\)WO\(_3\) (JCPDS № 73-1084) (Figure 2c). Further increase of calcination temperature above 500°C led to formation of the \( \gamma\)-WO\(_3\) single phase (Figure 2). This is in a good agreement with data reported in [2, 4]. The XRD study showed that increase of calcination temperature in the range of 500-1000°C leads to increase of crystallite sizes (from tens nm at 300°C to a several hundreds nm at 700°C) and decrease of microstrains in the WO\(_3\) powders.

Figure 2 XRD patterns of powders prepared by calcination of (APT+HNO\(_3\)) (a), (ST+HCl) (b) precursors and APT (c)

Figure 3 shows SEM images of WO\(_3\) particles prepared by calcination at 500°C for 2 h in air. Agglomerates with sizes in the range from a few to tens microns were observed. These agglomerates consist of primary particles with dimensions of a few hundreds nm which is close to the crystallite sizes determined from XRD data.

Figure 3 SEM images (at different magnification) of the WO\(_3\) particles prepared by calcination of APT at 500°C for 2 h in air

It was found that the IR spectra of WO\(_3\)\_H\(_2\)O precursor powders, synthesized from both ST and APT, contain a strong band corresponding to the stretching vibrations of OH groups (3406 cm\(^{-1}\)) and structural water molecules (1620 cm\(^{-1}\)), an IR band at 947 cm\(^{-1}\) corresponding to stretching vibrations of \(\nu(\text{W}=\text{O})\) and very strong and broad band at 667 cm\(^{-1}\) indicating the presence of stretching vibrations of \(\nu(\text{O}-\text{W}-\text{O})\) [3] (Figures 4a and 4b). The FT-IR spectrum of APT (Figure 4c) indicates N-H bending and stretching vibrations from \(\text{NH}_4^+\) at wavenumbers of 1429 and 3163 cm\(^{-1}\), respectively; O-H bond vibrations at 1640 and 3434 cm\(^{-1}\), stretching vibrations of \(\nu(\text{W}=\text{O})\) at 952 cm\(^{-1}\) and W-O bond vibrations at 878, 719 and 522 cm\(^{-1}\) [4]. It should be noted that calcination of all initial compounds led to a significant decrease the intensity of the IR bands of both OH and N-H groups.
However their presence in the IR-spectra at 300°C indicated that both WO$_3$H$_2$O → WO$_3$ and APT → WO$_3$ phase transitions are incomplete. It should be noted that calcination of precursors (prepared from solutions) above 300°C caused the appearance of additional IR bands at 811 cm$^{-1}$ and 730 cm$^{-1}$ corresponding to the stretching vibrations of the W=O and O-W-O bonds, respectively, and indicating the formation of γ-WO$_3$ phase [3] (Figures 4a and 4b). A further increase of the temperature to 500°C led to complete disappearance of IR bands of both OH and N-H groups (Figure 4). IR spectra containing only W-O bond vibrations indicate completion of WO$_3$ formation. This is in a good agreement with the XRD data.

![Figure 4 IR spectra of powders prepared by calcinations of (APT+HNO$_3$) (a), (ST+HCl) (b) precursors and APT (c)](image)

The structural information was confirmed by Raman spectroscopy. As seen in Figure 5a, the precursor (APT + HNO$_3$) contained a sharp mode at wavenumber of 942 cm$^{-1}$ (corresponding to the stretching vibrations of W=O) and strong broad band at 630 cm$^{-1}$ (corresponding to the stretching vibrations of O-W-O). The calcination of the precursor at 300°C led to the appearance of additional intense modes at 718 and 807 cm$^{-1}$, which indicates the presence of stretching vibrations υ(O-W-O), as well as mode at 274 cm$^{-1}$ mode indicating bending vibrations δ(O-W-O) in γ-WO$_3$ [3]. It should be noted that the mode at 630 cm$^{-1}$ was still visible in the sample prepared at 300°C for 2 h. This indicates the presence of the residual WO$_3$H$_2$O phase, which practically disappeared after annealing at the temperature of 700°C (Figure 5a). The Raman spectra of powders prepared by calcinations of (ST+HCl) precursor were similar (Figure 5b). The presence of W=O and O-W-O bonds as well as the formation of an intermediate substance at 300°C and γ-WO$_3$ at ≥ 500°C was found upon calcination of APT (Figure 5c).

![Figure 5 Raman spectra of powders prepared by calcinations of (APT+HNO$_3$) (a), (ST+HCl) (b) precursors and APT (c)](image)
An analysis of IR- and Raman-data made it possible to conclude that the neutral octahedral complex \([W=\text{O(OH)}_2\text{H}_2\text{O}]\) may be a structural unit of the precursors (both APT+HNO\(_3\) and ST+HCl) prepared in acidic suspensions.

We performed XAFS-spectra measurements to understand the local atomic structure realignment during the heat treatment of precursors and prepared WO\(_3\) powders. The W L\(_3\)-edge white line mostly is derived from electron transitions from the 2p\(^{3/2}\) state to a vacant 5d state [9]. The W L\(_3\)-edge XANES spectra of the WO\(_3\) powders synthesized from (APT+HNO\(_3\)) precursor are shown in Figure 6a. There is some splitting of W L\(_3\)-edge white line (Figure 6b), which indicates the presence of distorted octahedral structure units (WO\(_6\)) in investigated samples.

The W L\(_1\)-edge XANES spectrum provides information on the electronic state and the geometry of the tungsten species. The pre-edge peak is mainly attributed to forbidden electron transitions from 2s orbitals to 5d orbitals [9]. Figure 6c shows W L\(_1\)-edge XANES spectra of (APT+HNO\(_3\)) precursor and the synthesized WO\(_3\) powders. The observed moderate pre-edge peaks confirms the presence of distorted octahedral WO\(_6\) species.

![Figure 6 XANES of powders prepared by calcinations of (APT+HNO\(_3\)) precursor W L\(_3\)-edge (a), second derivation (b) and W L\(_1\)-edge (c)](image)

The FT-EXAFS spectra of W L\(_3\)-edge of (APT+HNO\(_3\)) precursor, initial APT and the synthesized WO\(_3\) powders are shown in Figure 7. The peak in the range of 1-2 Å, which is due to the W-O shell [9, 10], appeared in all FT spectra. In Figure 7 one can see that the peak of W-O shell for the precursor consists of a few components, which may be attributed to W=O, W-O and W···OH\(_2\). Conary, for WO\(_3\) samples, the W-O shell had only single peak corresponding to W-O distance in WO\(_6\) unit. These results are in a good agreement with IR (see Figure 4) and Raman spectroscopy data (see Figure 5).

The group of peaks in the range of 3-4 Å is due to W-W shell [9, 10]. One can see in Figure 7 that the W-W shell consists of a few components, which can be attributed to the edge-shared octahedral (shorter distance ~ 3.2 Å) and to the corner-shared octahedra WO\(_6\) (longer distance ~ 3.7 Å). This is in a good agreement with published data [10].

![Figure 7 FT-EXAFS of powders prepared by calcinations of (APT+HNO\(_3\)) precursor (a) and APT (b)](image)
4. Conclusion
A combination of X-ray powder diffraction, XAFS spectroscopy, Raman spectroscopy, IR-spectroscopy, and scanning electron microscopy was used for investigation of the influence of synthesis conditions on crystal and local structures of WO₃ powders prepared by thermal decomposition of ammonium paratungstate and precipitation of tungstates aqueous solutions in strong acid conditions. The calcination of all initial compounds at temperatures above 500°C led to formation of single phase of monoclinic I γ-WO₃. It was concluded that the neutral octahedral complex \([\text{W}=\text{O(OH)}_4(\text{H}_2\text{O})]\) can be a structural unit of the precursors prepared in acidic suspensions. The local structure of synthesized tungsten oxides consist of edge-shared and corner-shared distorted octahedral WO₆ species linked together.

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