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Solid-State Synthesis of Molybdenum–Vanadium Mixed Oxide of Tubular Morphology

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Abstract—The thermally stimulated processes in the disperse carbon–V₂O₅ : MoO₃ mixed oxide composite at 400°C were studied by electron microscopy, Raman spectroscopy, and EPR. The mixed oxide phase recrystallized to form tubulene-like structures in the form of rolled lamellae.

Keywords: mixed oxides, vanadium, molybdenum, tubular structures, solid-state synthesis, electron microscopy, EPR, Raman spectroscopy

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INTRODUCTION

Recent interest in the preparation of tubular structures based on transition metal oxides, in particular, vanadium oxide nanotubes, was dictated by prospects for the creation of new heterogeneous catalysts of selective oxidation, electrode materials for high-capacity lithium batteries, and gas sensors and elements of microelectronic devices [1–4]. Vanadium oxide nanotubes are generally prepared by prolonged (for 10 or more days) hydrothermal synthesis at 150–200°C from aqueous organic mixtures containing various vanadium compounds (V₂O₅, VOCl₃, HVO₃, and VO(OPr)₃) [5, 6]. The significant disadvantages of this synthesis include high reaction time, low yield of the desired product (other nanostructured objects are obtained along with nanotubes, namely, nanoparticles, nanoribbons, whiskers with nanometer-sized section, etc.) and the necessity of using additions for selective growth of oxide nanostructures. Various nitrogen-containing substances including ammonia and various amines are used as additions. These additions (generally, mono- or diamines) play the role of a structure-forming molecular matrix and can be incorporated into the interlayer voids of vanadium oxide, thus affecting the internal arrangement of the growing nanotube [5–7]. A complete removal of these template molecules is a hard problem [7]; i.e., vanadium oxide nanotubes are basically hybrid materials with quasi-two-dimensional layers and molecular spacers bonded by noncovalent interactions. Molybdenum–vanadium mixed oxide tubulenes were prepared by the hydrothermal method using hexadecylamine as a structure-forming intercalate. In this case, the hydro-

thermal treatment took a week, and the molybdenum content in the mixed oxide was up to 1 mol % [8].

Synthesis of vanadium oxide tubulenes using carbon nanotubes as a matrix is an alternative to hydrothermal synthesis. The drawbacks of this method include not only the use of expensive structure-forming agents, but also the necessity of their subsequent removal using high-temperature (above 700°C) oxidative annealing [9].

The goal of this study was to develop a method for the synthesis of molybdenum–vanadium oxide nanotubes using the layered oxide V₂O₅ : MoO₃ as a precursor obtained by the recently proposed solvothermal procedure [10, 11]. The introduction of ultradisperse carbon as a gas-generating agent that can be removed during the thermal treatment in an oxygen-containing atmosphere in the oxide should create favorable conditions for the splitting of the oxide matrix into individual monolayers and their rolling into tubular structures.

EXPERIMENTAL

Molybdenum–vanadium oxide dispersions were prepared by thermal treatment of the 0.2 M aqueous solution of mixed molybdenum–vanadic acid (molar ratio V : Mo = 1 : 1) for 4 h at 100°C. The V : Mo mixed acid was obtained from ammonium paramolybdate solutions (the starting compound was the crystalline hydrate (NH₄)₆Mo₇O₂₄ · 4H₂O) and ammonium vanadate NH₄VO₃ by the ion-exchange procedure using cationite KU-2 in the H form. At the start of the solvothermal synthesis, ultradisperse carbon (5 or 50 wt % based

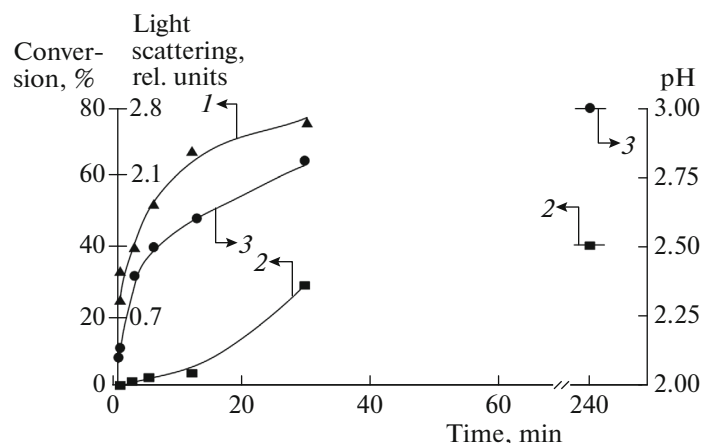


Fig. 1. Kinetic curves of (1) light scattering, (2) degree of conversion of oxo acid into the oxide phase, and (3) pH for the thermo-stimulated polycondensation of the 0.2 M aqueous solution of molybdenum–vanadium oxo acid during treatment at 100°C.

on the mass of the oxide) was introduced in the working solution. According to the electron microscopy data, the carbon particle size was 100–500 nm. The thus obtained carbon-containing dispersion was subjected to ageing in the mother liquor for 1 day and separated; after four washings with distilled water, it was separated by centrifuging at a rate of 13000 rpm, dried at room temperature until its mass became constant, and subjected to thermal treatment in air at 400°C.

The size and morphology of the particles of the disperse phases were studied on a Leo-1420 scanning electron microscope with a Rontec Edwin X-ray microanalyzer (the diameter of the probed region was 3 μ m). The Raman spectra of the samples were recorded with a NANOFINDER TII Raman microscope. The EPR spectra were recorded on a Bruker EMX-8 (X-band) spectrometer at 77 K in quartz ampules with a diameter of 3.0 mm. The modulation frequency was 100 kHz. The parameters of the spin Hamiltonian for V(IV) ions were calculated in accordance with the recommendations given in [12]. The number of paramagnetic centers in the samples was determined by double integration of the spectra while comparing them with the reference spectrum of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ single crystal with the known number of spins.

RESULTS AND DISCUSSION

The carbon nanophase was introduced in the Mo : V mixed oxide matrix by growing a shell of V_2O_5 : MoO_3 on the surface of carbon particles in a molybdenum–vanadium acid solution by the solvothermal method. According to Fig. 1, the thermal treatment of this solution at 100°C leads to a quick increase in light scattering in solution. This is caused by thermostimulated polycondensation, which occurs in it and leads to a symbatic increase in pH of the mother solution. At

the initial stage of the synthesis (within the first 10 min), oligomers accumulate in solution, which do not form oxide–hydroxide species. Centrifuging of these solutions did not lead to isolation of the oxide phase. Further thermal treatment of the solution of the mixed oxo acid led to the formation of oxide particles, which exhibited transformation into perfect micron-sized crystallites during gradual growth, agglomeration, and further recrystallization [11] (Fig. 2).

According to the kinetic curves shown in Fig. 1, the structural units of future particles of the disperse phase accumulate in the reaction solution during the induction period when the formation of nuclei is suppressed. This period takes ~ 10 min. The introduction of particles of the disperse phase which play the role of nuclei in solution during the induction period triggers the epitaxial deposition of the mixed oxide phase on the surface of particles and formation of oxide shells around them. During further agglomeration of the formed particles of the “core–shell” type, ultradisperse carbon is encapsulated inside the mixed oxide matrix.

The heating of the obtained oxide–carbon composite for 4 h at 400°C leads to combustion of carbon and formation of a highly porous cellular structure of mixed oxide, in which the pore size varies from 500 to 700 nm depending on the amount of incorporated carbon (Fig. 3). The greater the carbon fraction in the sample, the higher the degree of porosity of the mixed-oxide structure formed during the calcinations. The resulting porous structures have thin walls (a few dozens of nanometers); this suggests that the mixed-oxide layers are split in the course of the combustion of carbon particles.

The heating is also accompanied by considerable changes in the Raman spectrum (Fig. 4). The bands in the range 695–800 cm^{-1} corresponding to the stretching vibrations of the V–O–V, V–O–Mo, and Mo–O–

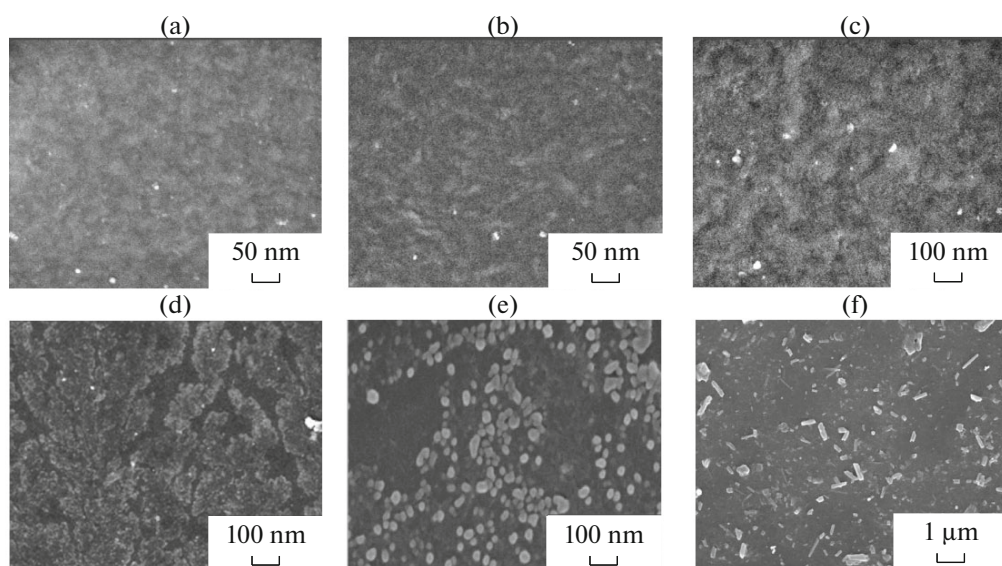


Fig. 2. Electron micrographs of disperse molybdenum–vanadium mixed oxide phases (molar ratio V : Mo = 1 : 1) formed during thermostimulated polycondensation of the 0.2 M aqueous solution of molybdenum–vanadium oxo acid at 100°C. Thermal treatment time: (a) 1, (b) 3, (c) 5, (d) 7, and (e) 10 min; (f) 4 h.

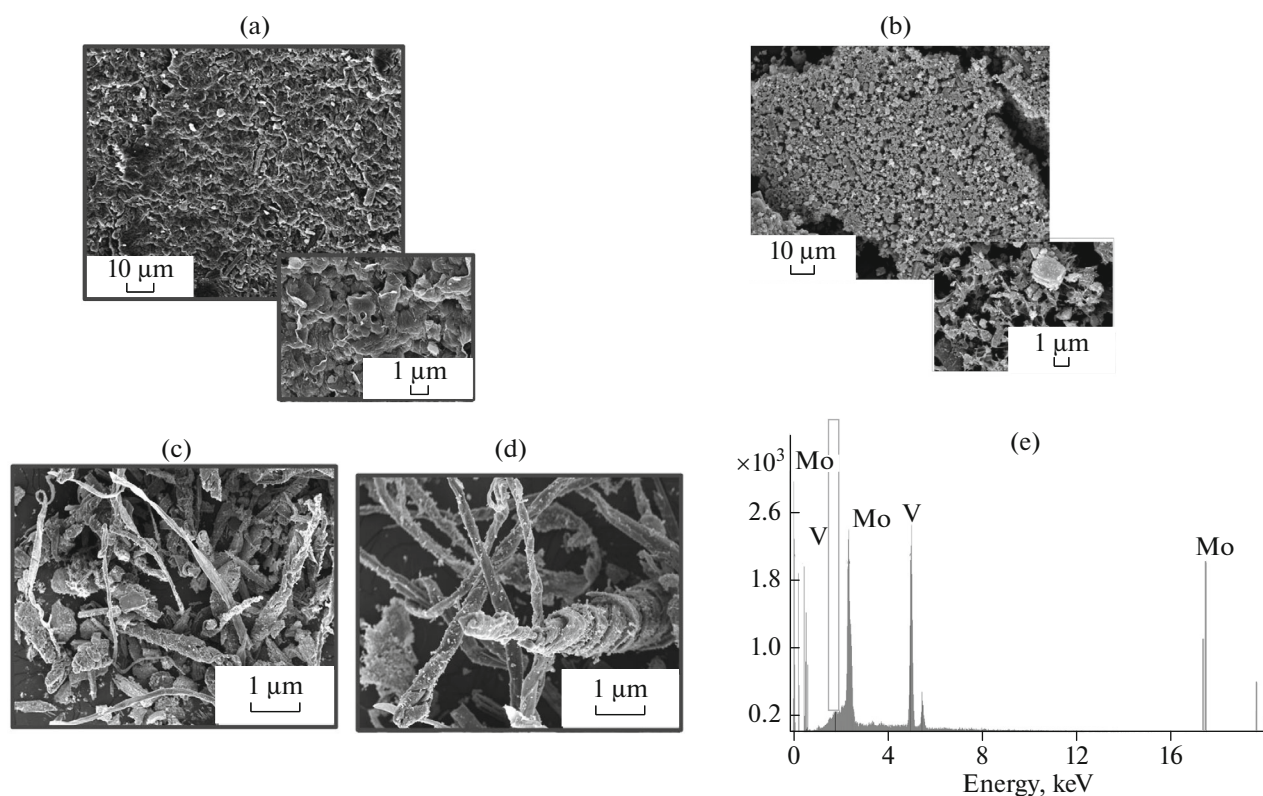


Fig. 3. Electron micrographs of the products of annealing of carbon-containing molybdenum–vanadium mixed oxide for (a), (b) 4; (c) 8; and (d) 12 h at 400°C; the carbon content in the starting composite: (a) 5 and (b)–(d) 50 wt %; (e) X-ray fluorescent spectrum of the $\text{MoO}_3 : \text{V}_2\text{O}_5$ tubular structure.

Mo groups [13, 14] are drastically broadened and shift toward higher frequencies. The 1000-cm^{-1} band corresponding to the stretching vibrations of the V=O

group undergoes a similar shift. The observed changes in the spectrum indicate that the cell-forming lamellae have a disordered structure with strained bonds. The

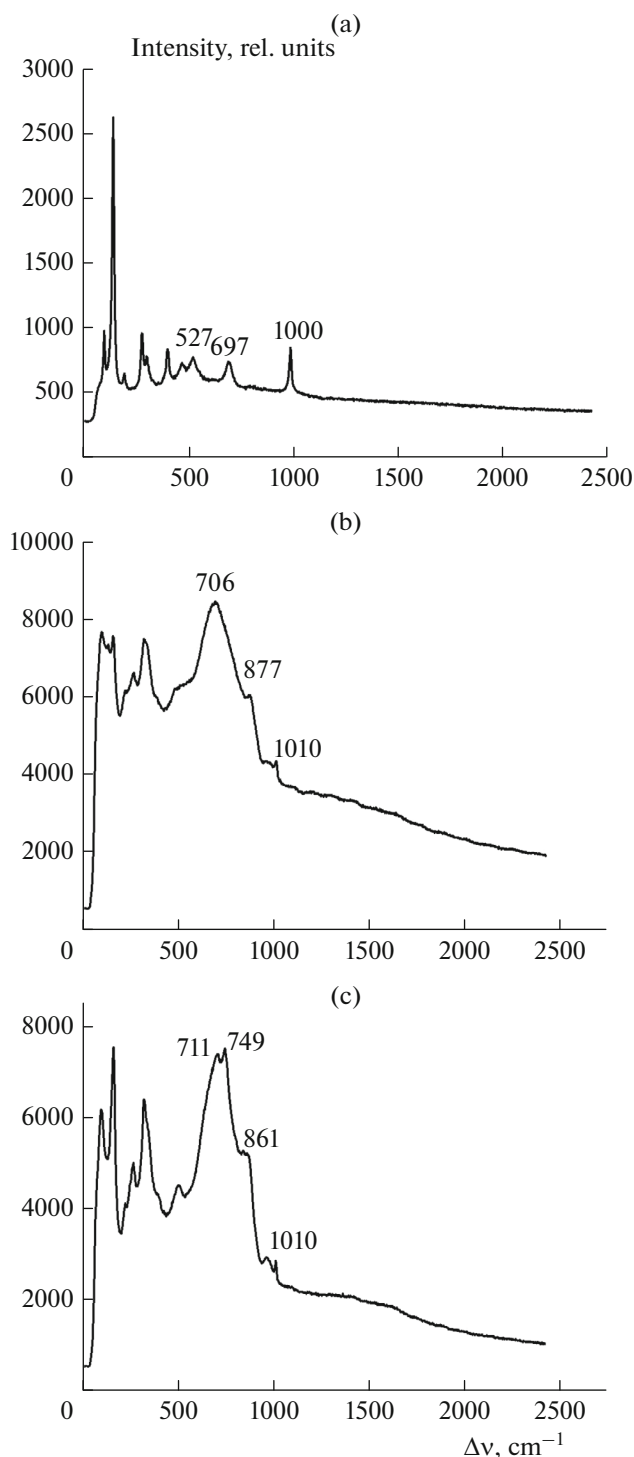


Fig. 4. Raman spectra of (a) freshly synthesized $\text{MoO}_3 : \text{V}_2\text{O}_5$ dispersion; (b) and (c) carbon-containing composite based on $\text{MoO}_3 : \text{V}_2\text{O}_5$ after heating for (b) 4 and (c) 12 h.

obtained Raman spectrum (Fig. 4) is generally similar to the spectrum of vanadium oxide nanotubes [13], and the elements of nanotubular structures start to form already at the stage of the formation of mixed oxide with a cellular morphology.

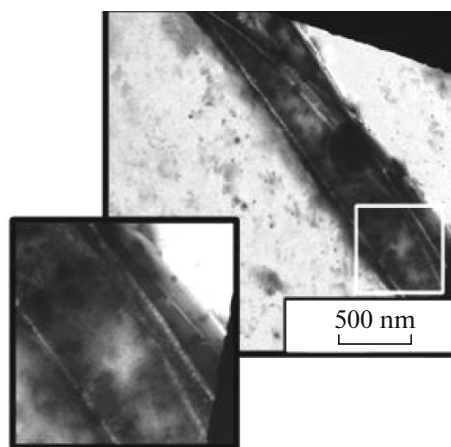


Fig. 5. Electron micrographs of molybdenum–vanadium mixed oxide with a tubular structure. Insert: fragment of nanotube (magnification $\times 2$).

Prolonged thermal treatment of the obtained porous oxide structures leads to extended ribbon formations, which transform into rolled tubulenes with a length of 20–30 μm during calcination. Their form (Figs. 3 and 5) and Raman spectrum (Fig. 4) are characteristic of multilayered vanadium oxide nanotubes obtained by the traditional hydrothermal method [5, 14, 15].

The electron microscopy data suggest that the formed tubes are the result of the rolling of lamellae (Fig. 5). The microprobe analysis data (Fig. 3) indicate that the ions of both metals (molybdenum and vanadium) are included in the structure of the tubulene walls; i.e., no phase segregation is observed in the mixed oxide during heating. The incorporation of molybdenum ions in the VO_x monolayers at the stage of nanotube formation is accompanied by the partial reduction of V(V) to V(IV), as a result of which the samples become dark-colored. Note that the partial reduction of V_2O_5 is considered as a condition for the rolling of the oxide lamella [16]. This mechanism of formation of $\text{VO}_x : \text{MoO}_y$ nanotubes is responsible for their pronounced diversity (Fig. 3).

Additional information about the valence state of vanadium and molybdenum ions and their environment was obtained by EPR. Figure 6 shows the EPR spectra of tubular molybdenum–vanadium mixed oxides (with a molar ratio of V : Mo = 1 : 1) obtained by the solvothermal procedure at 77 K. The EPR spectrum of the tubular structure is a nonuniformly broadened asymmetric line with the effective g factor $g_0 = 1.972 \pm 0.005$ and line width $\Delta H_0 = (7.6 \pm 0.6)$ mT. The spectrum shape and the g_0 and ΔH_0 parameters in the case of tubulenes are in good agreement with the results obtained for mixed oxide of the same composition prepared by the hydrothermal method at a pressure of 10–20 MPa [17].

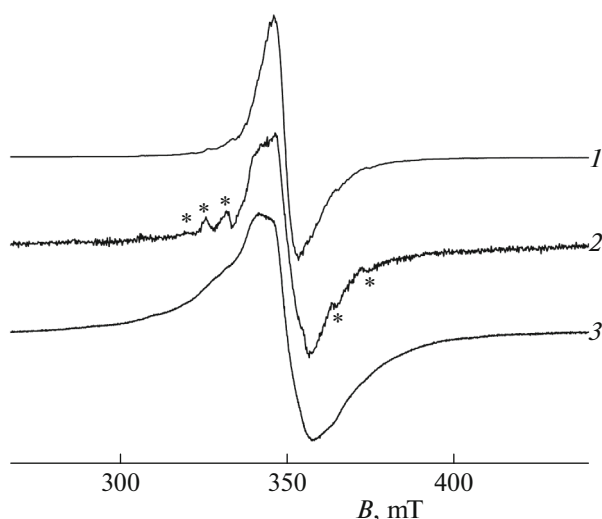


Fig. 6. EPR spectra of molybdenum–vanadium mixed oxides ($V : Mo = 1 : 1$) at 77 K normalized with respect to amplitude: (1) tubular structures; oxides obtained by the solvothermal method: (2) starting and (3) heated at 400°C for 4 h. The asterisks show the lines of the isolated $V(\text{IV})$ ions.

Similar EPR spectra were observed earlier for molybdenum–vanadium mixed oxides prepared by the solvothermal method (spectrum 3, Fig. 6) [18–20]. For $V_2O_5 : MoO_3 = 1 : 1$ prepared by this method, the experimental value of $g_0 = 1.970 \pm 0.007$ almost completely coincides with that for spectrum 1, while

the spectrum shape and $\Delta H_0 \approx 14.0$ mT are substantially different.

These EPR spectra suggest the formation of regions with a very high local concentration C_{loc} of the paramagnetic $V(\text{IV})$ centers—magnetically concentrated associates with a strong static spin-exchange interaction between them, which shows itself as singletization of the EPR spectra [21–23]. The low-intensity lines marked with asterisks in spectrum 2 (Fig. 6) indicate that the solvothermal sample contains a certain number of isolated $V(\text{IV})$ centers before the thermal treatment, whose fraction does not exceed ~ 25 – 30% of the total number of $V(\text{IV})$ ions in this sample. Note that for the tubular sample under study, as well as for the sample prepared by the hydrothermal method [17], the EPR spectrum did not show any signals of isolated $V(\text{IV})$ ions; i.e., their concentration does not exceed 1–5%.

The larger EPR line width for mixed oxide obtained by the solvothermal method relative to that for tubulenes at the same $V : Mo = 1 : 1$ ratio suggests weaker spin-exchange interaction between the paramagnetic $V(\text{IV})$ ions because of the lower C_{loc} value, i.e., larger distance $\langle r \rangle$ between them. Double integration of the EPR spectra of the sample with a tubulene-like structure showed that a significant part (more than 50–70%) vanadium ions in the sample are in the paramagnetic $V(\text{IV})$ state.

Thus, the EPR spectra of molybdenum–vanadium mixed oxides with a composition of $Mo : V = 1 : 1$ and

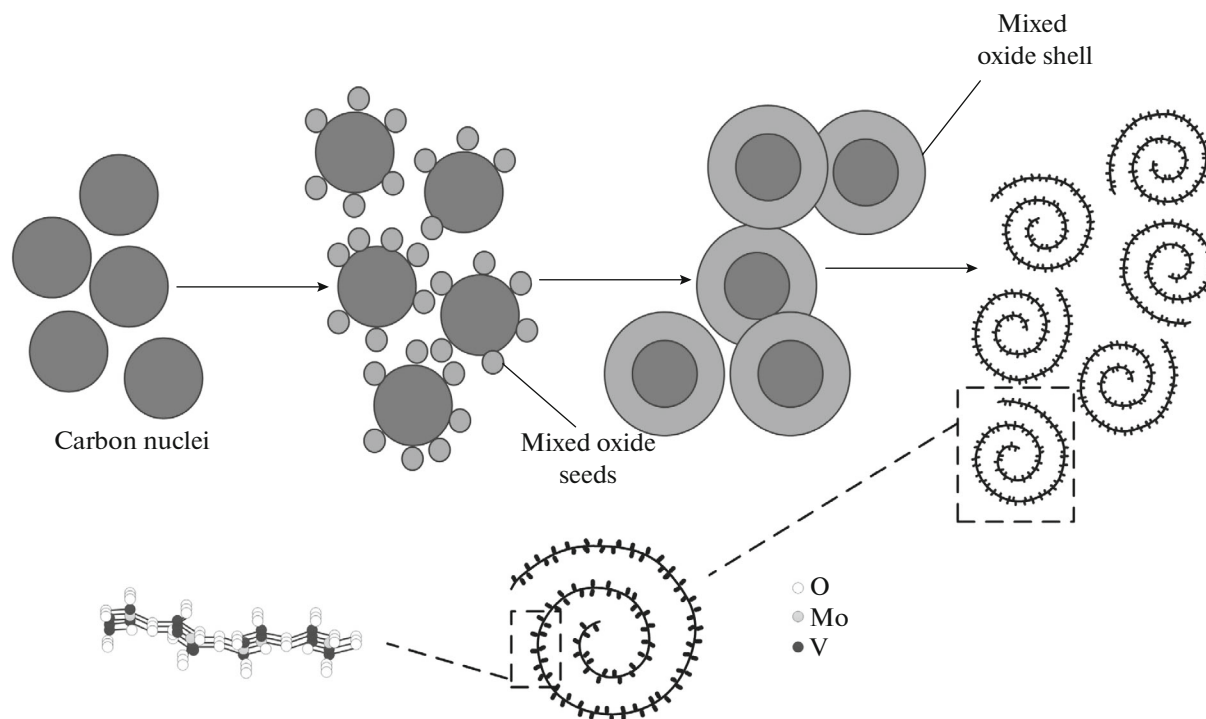


Fig. 7. Scheme of the formation of mixed oxide tubulenes.

with a tubular structure are similar to those of mixed oxides of the same composition obtained by the hydrothermal method at a high pressure, but differ from those of the samples prepared by the solvothermal technique. As in the case of the hydrothermal synthesis, a peculiarity of the formation of mixed oxide with a tubular structure lies in the high local concentration of V(IV) ions in the magnetically concentrated associates. Accumulation of large V(IV) ions in one plane, in turn, leads to lamella bending and rolling.

The synthesis of mixed oxide tubulenes schematically shown in Fig. 7 generally includes the following main stages: (1) formation of oxide–carbon composites due to polycondensation of mixed oxo acid on carbon cores followed by aggregation of oxide–carbon particles; (2) oxidation of carbon accompanied by the splitting of the oxide phase into separate lamellae; (3) rolling of lamellae during prolonged thermal treatment. The main condition for lamella rolling is accumulation of the V(IV) states in the $V_2O_5 : MoO_3$ mixed oxide. This is the result of the isomorphic substitution of a large number of vanadium ions by molybdenum ions.

The thermochemical method of synthesis provides high yields of tubular structures: according to electron microscopy data, the fraction of nontubular elements in the obtained samples is insignificant. Another key feature of the thermochemical method is the fact that the obtained tubular structures do not contain any other template molecules in the interlayer space.

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