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Molybdenum–Vanadium Mixed Oxides Synthesized by the Hydrothermal Method

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Abstract—The effect of pressure (5–20 MPa) on the process of hydrothermal synthesis of a molybdenum–vanadium mixed oxide from a molybdenum–vanadium mixed poly(oxyacid) is studied. It is shown that the synthesis product is a solid solution of isomorphically substituted vanadium pentoxide with a pressure-independent composition. With increasing pressure, the degree of crystallinity of the synthesized products increases, concentration of isolated V(IV) ions decreases, habitus of the crystals changes from prismatic to needlelike, and overall dispersity increases. This makes it possible to regard the pressure as a dispersing factor for the synthesis of nanostructured molybdenum–vanadium oxides.

Keywords: mixed oxides, vanadium, molybdenum, hydrothermal synthesis, EPR, phase analysis by X-ray diffraction, electron microscopy, infrared spectroscopy

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INTRODUCTION

An upsurge of interest in recent years in methods for controlled synthesis of mixed molybdenum–vanadium oxides is largely motivated by their high catalytic activity in the oxidation of organic compounds with molecular oxygen, which opens the possibilities for developing new low-temperature processes of partial oxidation of various hydrocarbons [1–6] and of desulfurization of hydrocarbon raw materials [7]. In this regard, a promising method for synthesizing molybdenum–vanadium (Mo : V) oxides is the joint polycondensation of the corresponding oxoacids in an aqueous medium, which makes it possible to prepare dispersed phases with a strictly predetermined structural, dimensional, and morphological characteristics [7–9]. For example, carrying out the polycondensation under atmospheric pressure (i.e., under solvothermal conditions) yielded isomorphically substituted oxide phases exhibiting a high activity in the reaction of selective oxidation of thiophene in organic solvents [7].

The purpose of this study was to establish the peculiarities of the formation of mixed Mo : V-oxides during the co-polycondensation of molybdic acid and vanadium in the aqueous medium at an elevated pressure.

EXPERIMENTAL

The Mo : V Mixed oxides were synthesized by hydrothermal method at different pressures (5, 10 and 20 MPa) from a 0.2 mol/L aqueous solution of a molybdenum–vanadium acid (with a V : Mo molar ratio of 1 : 1) prepared by ion exchange. The obtained oxide particles were examined using a LEO-1420 scanning microscope and a LEO 906E transmission microscope. X-Ray diffraction analysis was performed on a Carl Zeiss HZG-4A diffractometer (Cu(K_α) radiation). The IR spectra were recorded on a Thermo Nicolet Avatar 330 FTIR spectrometer. The assignment of the bands of the IR spectra was carried out based on the data from [2, 10–12].

The EPR spectra were recorded in 3.0-mm-diameter quartz ampules at 77 using a Bruker EMX-8 X-band spectrometer operated at a modulation frequency of 100 kHz. The parameters of the spin Hamiltonian for the V(IV) ions were calculated as recommended in the monograph [13]. The number of paramagnetic centers in the samples was evaluated by double integration of the spectra with subsequent comparison of the results with a reference, the spectrum of a $CuCl_2 \cdot 2H_2O$ single crystal with known number of spins.

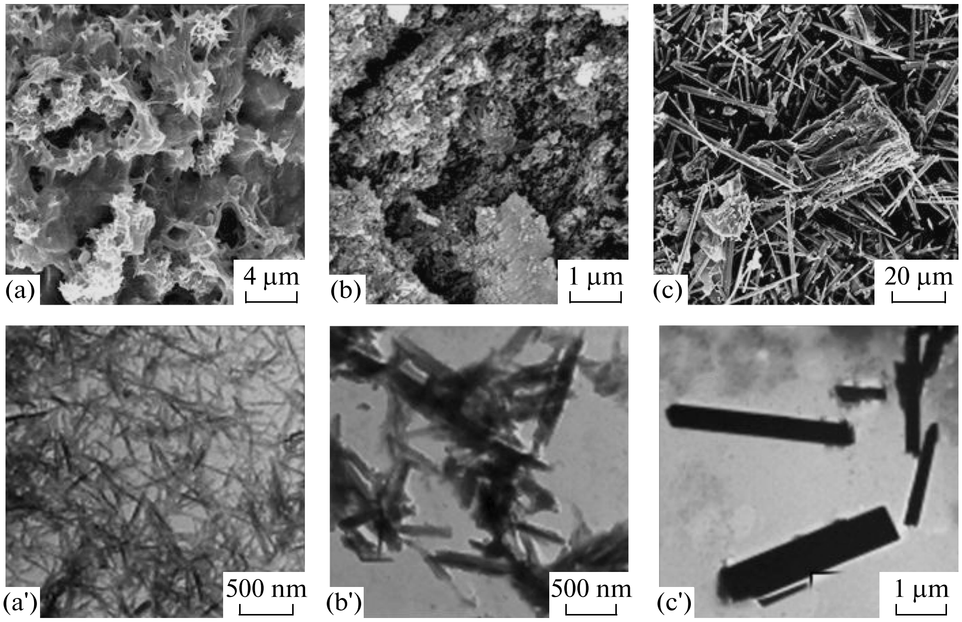

Fig. 1. SEM (top) and TEM (bottom) images of vanadium–molybdenum mixed oxide phases produced by hydrothermal synthesis at a pressures of (a, a') 5, (b, b') 10, and (c, c') 20 MPa.

RESULTS AND DISCUSSION

According to electron microscopy analysis (Fig. 1), at elevated pressures, the formation of homogeneous highly porous structures with pore size up to several microns occurs in the reaction medium containing mixed molybdenum-vanadium acids. When the pressure increases to 20 MPa, these structures tend to degenerate into well-faceted needlelike structures with an average length of 30 μm, which only rarely combine into agglomerates. The major structural elements of both highly porous cellular structures formed at 5 and 10 MPa and extended formations arising at 20 MPa are needles 0.5–5.0 μm in size (Fig. 1).

The results of X-ray analysis show that the oxide phases formed are solid solutions based on a xerogel of hydrated vanadium pentoxide with an admixture of hexagonal molybdenum trioxide; i.e., they have the same phase composition as mixed Mo : V oxides prepared by solvothermal method at atmospheric pressure [7, 9] (Fig. 2). With increasing pressure, the degree of crystallinity of the mixed-oxide phase increases sharply, while manifestations of the separation of the individual MoO_3 phase become more pronounced (Fig. 2).

According to IR spectroscopy, all the dispersed phases formed during the hydrothermal synthesis are characterized by a high content of physically and chemically bound water and by a large number of terminal hydroxyl groups (Fig. 3), as is indicated by the absorption peaks in the frequency ranges 1405–1620 and 3495–3580 cm^{-1}. We can conclude that the oxalation processes responsible for the formation of the xerogel remain largely uncompleted. IR absorption peaks within 480–500 cm^{-1}, corresponding to the bending vibrations of the –V–O– bond, and peaks within 680–740 cm^{-1} (frequencies lower than that of the –V–O–V– bridge bond (756 cm^{-1})), which presumably belong to the stretching vibrations of the –V–O–Mo– bond, are indicative of the presence of a large number of molybdenum atoms isomorphically substituting vanadium atoms in the V_2O_5 xerogel. Note that, when vanadium atoms in the V_2O_5 structure are substituted by molybdenum atoms, part of the vanadium atoms change their valence state from V(V) to V(IV), as evidenced by the presence of a shoulder of the 967-cm^{-1} absorption peak, which belongs to the stretching vibration of the V(IV)=O bond. That the tested samples contain hybrid structures formed by a partial substitution of cationic positions in the V_2O_5 structure by molybdenum atoms is also seen from the splitting of most of the bands in the IR spectra. This effect observed for the mixed oxide phases synthesized at low pressure (5 MPa), but practically undetectable for the samples prepared at high pressure (20 MPa).

As the pressure of hydrothermal synthesis is raised, the manifestations of individual MoO_3 (through absorption bands at ~970 cm^{-1}, Mo=O stretching vibration; ~900 cm^{-1}, –Mo–O–Mo– stretching vibration; and ~500 cm^{-1}, –Mo–O– bending vibration) become increasingly pronounced (Fig. 3). This separation of the hexagonal MoO_3 phase upon pressure rise, which is also clearly seen from diffractograms (Fig. 2), can be explained by the fact that the solid solutions of oxides produced by isomorphic substitution are thermodynamically less stable (due to a weakening of the

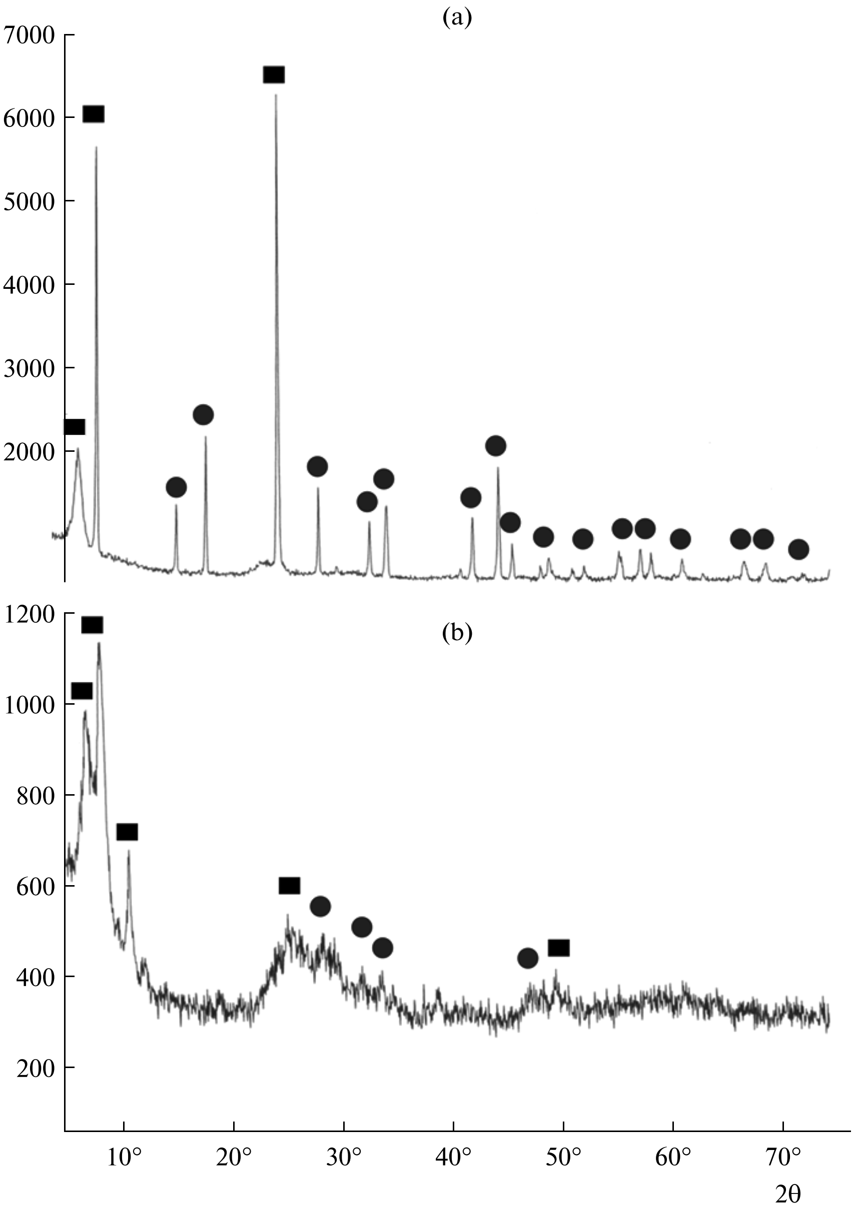

Fig. 2. Diffractograms of molybdenum–vanadium mixed oxide phases synthesized at (a) 5 and (b) 20 MPa; (●) MoO_3 and (■)V_2O_5 xerogel.

bonds), and therefore, they degenerate at harsher synthesis conditions.

Further information on the valence state of the molybdenum and vanadium ions and their spatial organization in the samples was obtained by the EPR method. Figure 4 shows typical EPR spectra at 77 K of mixed molybdenum–vanadium oxides (V : Mo = 1 : 1) prepared at 5 and 20 MPa by using the hydrothermal method. Both spectra are inhomogeneously broadened asymmetric singlet lines with an effective g-factor of $g_0 = 1.975 \pm 0.005$ and a line width ΔH_0 of (8.6 ± 0.7) mT at 5 MPa and (6.5 ± 0.5) mT at 20 MPa. Similar EPR spectra were previously observed for mixed Mo : V oxides synthesized by the solvothermal method (Fig. 4, spectra *3*, *4*) [7, 9, 14] and by the thermal decomposition of coprecipitated ammonium metamolybdate and metavanadate (Fig. 4, spectra *5*, *6*), [5, 15, 16]. It was shown [7, 9, 15] that, even at relatively low vanadium concentrations, the EPR spectra of mixed Mo : V oxides (Fig. 4, spectrum *5*) exhibit no features belonging to Mo(V) or Mo(III) paramagnetic ions. Thus, vanadium ions oxidize the reduced states of molybdenum formed during the synthesis, for example, due to photochemical processes [17].

The EPR spectra in Fig. 4 indicate that, at a sufficiently high concentration of vanadium in the sample, areas with very high local concentrations of V(IV) paramagnetic centers (magnetically concentrated

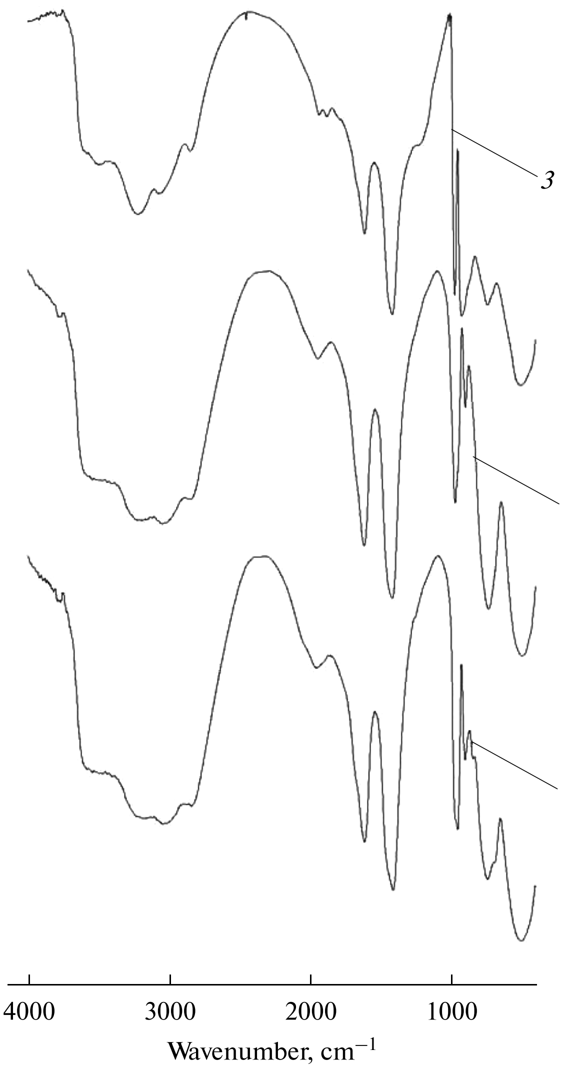

Fig. 3. IR spectra of molybdenum–vanadium mixed oxide phases synthesized at (*1*) 5, (*2*) 10, and (*3*) 20 MPa.

associates) arise, which being involved in a strong static spin–exchange interaction with each other, produce a singletization of the EPR spectra [18–20]. That the shape of the EPR spectrum is different and ΔH_0 is smaller for the sample prepared at a pressure of 20 MPa, as compared to the sample of the same composition prepared at 5 MPa (Fig. 4, spectra *1* and *2*) is indicative of a stronger spin-exchange between V(IV) paramagnetic ions in the sample synthesized at 20 MPa, which can be accounted for by a higher local concentration of V(IV) ions and, accordingly, a smaller average distance between them.

The low-intensity lines observed in spectra *3* and *4* (Fig. 4) suggest that these samples, along with areas with a high local concentration of V(IV) ions, contain isolated V(IV) centers (~25–30% of the available V(IV) ions) (Fig. 4, spectra *3*–*5*). In the studied samples, more than 80% of the vanadium ions are paramagnetic. Note that, in the oxides synthesized by the hydrothermal method (Fig. 4, spectra *1* and *2*), the fraction of isolated V(IV) ions is even smaller, 5%.

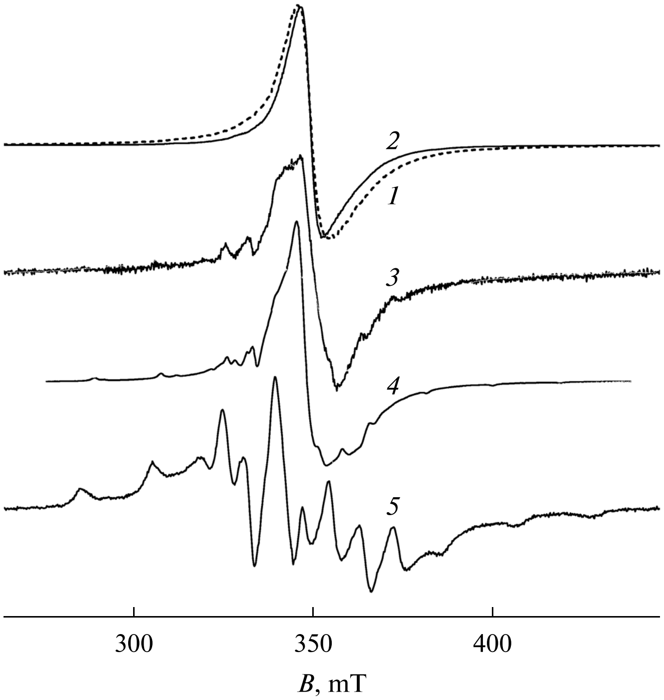

Fig. 4. EPR spectra at 77 K (normalized in amplitude) of molybdenum–vanadium mixed oxides (V : Mo = 1 : 1) synthesized by the hydrothermal method at (*1*) 5 and (*2*) 20 MPa; (*3*, *5*) by the solvothermal method, and (*4*) by the thermal decomposition of coprecipitated salts. For sample *5*, V: Mo = 1 : 10.

The results of the present study suggest that carrying out the polycondensation synthesis at an elevated pressure produces only a negligible effect on the structural features of the resulting oxide phases, which appears to be an isomorphically substituted V_2O_5 xerogel with a MoO_3 admixture unsolved in the V_2O_5 matrix. At the same time, increasing the pressure significantly affects the habitus of synthesized crystals by inhibiting their two-dimensional growth (i.e., suppressing the formation of layered crystals with low aspect ratio), so that one-dimensional growth begins to dominate, thereby producing needlelike structures. This effect, in turn, leads to the formation of mixed oxide phases with a high surface-to-volume ratio, so that increasing the pressure of hydrothermal synthesis of Mo : V oxides can be regarded as a specific dispersing factor.

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