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SYNTHESIS AND X-RAY STUDY OF AMMONIUM POLYVANADOMOLYBDATE XEROGELS

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$(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ ($x = 0$, 1) gels were produced from V_2O_5, NH_4VO_3, 40% H_2O_2, and Mo powder by using sol–gel technology. Synthesized gels were investigated by X-ray photoelectron spectroscopy methods. The shape and position of the complex core photoelectron lines V $2p$, O $1s$, C $1s$, Mo $3p$, Mo $3d$, and N $1s$ were analysed for the gels with different x values. The valences of the V and Mo ions, which have an important role in the electrical conductivity of the compounds, was studied. It has been found that the molybdenum is in the stable Mo^{6+} state. The vanadium ions are in V^{5+} and V^{4+} states. The reduction ratio of vanadium ions is about 0.043 independent of the x value. The position of the N $1s$ peak indicates that the nitrogen is connected with hydrogen in NH_4 ions.

Keywords: vanadium oxides, hydrates, ammonium, XPS

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1. Introduction

Hydrated vanadium compounds $M_2V_{12}O_{31\pm\delta}\cdot nH_2O$, where M is an alkali-metal, possess a number of unusual properties, which make them the candidate materials for many technological applications [1, 2]. When prepared by using sol–gel technology methods [3], they have a very labile structure, where V–O chains are separated by water molecules, and the interlayer distance in such xerogels varies from 8.8 to 40 Å, depending on water content [4]. In addition to water molecules and M^{n+} cations, the polyvanadates readily intercalate organic solvents, N-alkyl ammonium organic ions, and metal complexes [5]. The sol–gel technology was also used to prepare $M_xV_{12-y}Mo_yO_{31\pm\delta}\cdot nH_2O$ xerogels [1]. Such compounds might incorporate H_3O^+, $NH_4{}^+$, hydroquinone, or polyvinyl alcohol in the gaps between V-O-Mo layers [6–9].

The synthesis, structure, and some physical properties of ammonium polyvanadomolybdate xerogels are described in [8]. The aim of this work is the characterization of the states of various elements and chemical bounds between them in the V-O-Mo-NH_4 system xerogels.

2. Experimental

As starting materials, we used V_2O_5, NH_4VO_3, 40% H_2O_2, and Mo powder. V_2O_5 and Mo powders in a suitable proportion were dissolved in H_2O_2 to form mixed solutions of pervanadic (molybdic) acids. Slow heating up to 333 K initiates the decomposition of the peroxide compounds, followed by gelation. The reactions with the participation of V_2O_5 are

$$V_2O_5 + 2\,H_2O_2 = 2\,HVO_2(O_2) + H_2O\,, \qquad (1)$$

$$HVO_2(O_2) + 3\,H_2O = VO(OH)_3(OH_2)_2 + \frac{1}{2}\,O_2\,, \qquad (2)$$

$$2\,[VO(OH)_3(OH_2)_2] \rightarrow V_2O_5\cdot 5\,H_2O\,. \qquad (3)$$

Scheme (3) represents polymerization of the neutral precursor, resulting in a hydrous V_2O_5 gel, which can be regarded as the polyvanadic acid $H_2V_{12}O_{31\pm\delta}\cdot nH_2O$.

Mo ions replace V^{5+} in the resulting compounds, $2\,V^{5+} \rightarrow V^{4+} + Mo^{6+}$ or $2\,V^{5+} + Mo^{6+} + OH^-$. The V^{4+} and OH^- ions increase the degree of polymerization and stability of the gels. Decomposition of the

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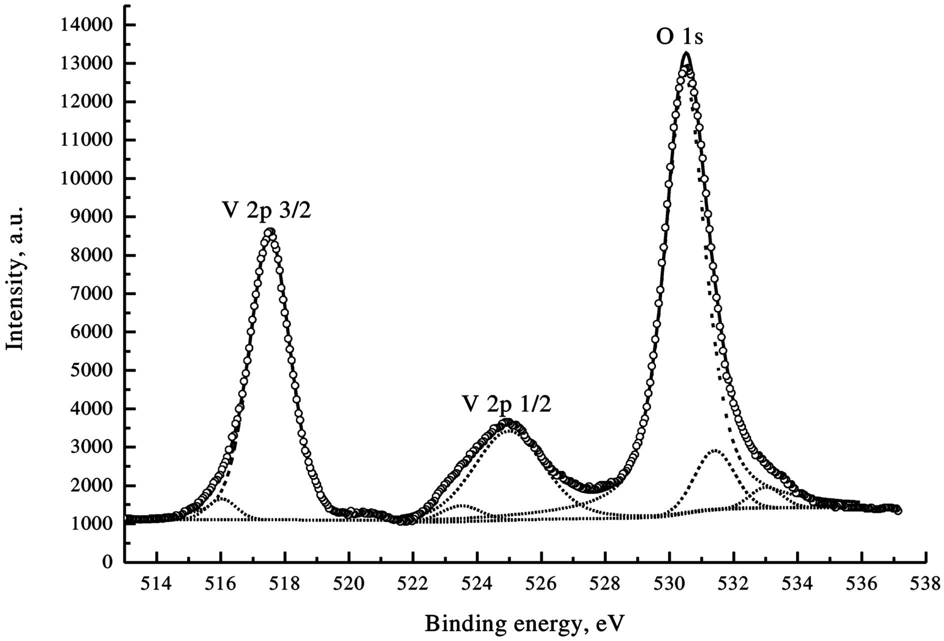


Fig. 1. XPS V–O region spectra of $(NH_4)2V_9Mo_3O_{31\pm\delta}\cdot nH_2O$ xerogel.

peroxide solution of vanadium containing $NH_4{}^+$ is not accompanied by gelation, whereas, in the presence of molybdenum, $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ (x = 0, 1) gels are formed. Obtained gels were deposited on Ni substrates by screen printing method and dried in air. The thickness of prepared films was about 10 μm. The films have layered structure where $NH_4{}^+$ ions and H_2O are incorporated between the V-O-Mo layers [10]. Such structure causes anisotropy of physical properties of the produced films along and across the V-O-Mo layers that is peculiar to the other hydrated vanadium compounds [11].

Surface chemical composition was controlled by using the X-ray photoelectron spectroscopy (XPS) method. XPS spectra were measured with a VG ESCALAB MK II spectrometer (Mg $K_{\alpha1,2}$ source, 1253.6 eV). The working pressue in the analytic chamber was maintained below 10^{-7} Pa during the spectrum analysis. Before the measurement the surface of samples was cleaned using Ar^+ ion bombardement at 3 kV and current density of 10 μA·cm^{-2} for 3 min. The energy scale was calibrated using the Au $4f_{7/2}$ peak (84.0 eV). Charging effects were taken into account using the C $1s$ peak (284.6 eV).

Table 1. V–O region fitting parameters of $(NH_4)2V_9Mo_3O_{31\pm\delta}\cdot nH_2O$ xerogel.

Peak	Binding energy, eV	FWHM, eV	RA[1], %	G/L[2], %
V $2p_{3/2}$ (V^{4+})	516.03	1.50	1.27	70
V $2p_{3/2}$ (V^{5+})	517.53	1.06	28.10	100
V $2p_{1/2}$ (V^{4+})	523.50	1.45	1.36	100
V $2p_{1/2}$ (V^{5+})	524.98	2.59	14.36	80
O $1s$ (O^{2-})	530.48	1.53	49.06	40
O $1s$ (O–C)	531.40	1.46	4.71	100
O $1s$ (H_2O)	533.01	1.18	1.14	100

[1] relative area of the peak

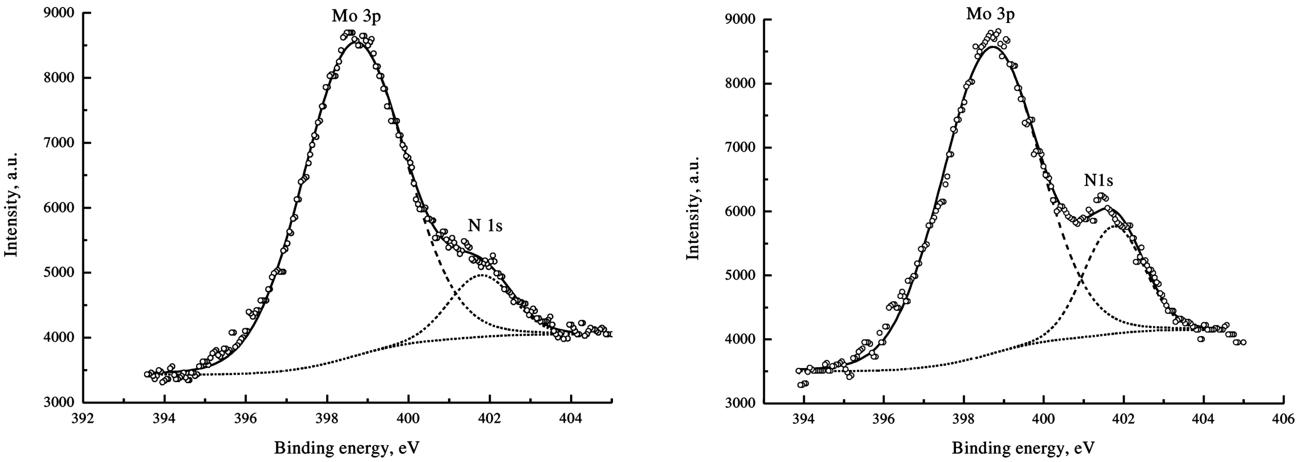
[2] Gaussian and Lorentzian ratio

3. Results and discussion

Figure 1 presents the XPS V–O region spectra of $(NH_4)2V_9Mo_3O_{31\pm\delta}\cdot nH_2O$ xerogel (points are experimental data). V $2p$ and O $1s$ peaks are composed of several components the parameters of which are given in Table 1. V $2p_{3/2}$ and V $2p_{1/2}$ peaks consist of two components and O $1s$ peak consists of three components. It is possible to subsume the V $2p_{3/2}$ peak components with binding energies 516.03 and 517.53 eV under the quadrivalent [12] and quinquivalent [13] vanadium ions in the xerogel. The same is possible to say about the V $2p_{1/2}$ peak components with binding energies of 523.5 and 524.98 eV [14]. Taking the V $2p_{3/2}$ peak area data from Table 1 we may calculate the vanadium ion reduction ratio

$$C = \frac{V^{4+}}{V^{5+} + V^{4+}}\,, \tag{4}$$

where V^{5+} and V^{4+} are corresponding ion concentrations. In our case $C = 0.043$, i. e. quadrivalent vanadium constitutes just 4.3% of vanadium ion content, similar as in other vanadium hydrates [10]. The reduc-



(a) (b)

Fig. 2. XPS spectra of molybdenum (Mo $3p$) and nitrogen region of $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ xerogels, (a) for $x = 0$, (b) for $x = 1$.

Table 2. Mo $3p$–N $1s$ region fitting parameters of $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ xerogels.

Peak	Binding energy, eV		FWHM, eV		RA[1], %		G/L[2], %	
	$x = 0$	$x = 1$	$x = 0$	$x = 1$	$x = 0$	$x = 1$	$x = 0$	$x = 1$
Mo $3p_{3/2}$	398.68	398.65	2.9	2.95	87.78	94.03	44	57
N $1s$	401.76	401.73	1.76	1.57	12.22	5.97	100	100

[1] relative area of the peak
[2] Gaussian and Lorentzian ratio

tion ratio of vanadium ions for $(NH_4)HV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ gel also is about 0.043.

The O $1s$ peak has three components (Fig. 1 and Table 1). The first one, a more intensive peak with binding energy of 530.48 eV matches the O_2- ions [15] linked with vanadium and molybdenum ions. The second one, less intensive (531.4 eV), is possible to ascribe to the relations with carbon [15]. And the last and weakest component with binding energy at 533.01 eV matches the oxygen linked with hydrogen in water molecules [16].

In Fig. 2 the XPS spectra of molybdenum (Mo $3p$) and nitrogen region ((a) for $x = 0$, (b) for $x = 1$) is shown. The fact that Mo $3p$ and N $1s$ binding energies are close to each other makes the analysis of this spectrum more complex, whereas the neglect of nitrogen presence in the gel makes the interpretation of this spectrum quite difficult. The spectrum component parameters are given in Table 2. The component with binding energy 398.68 eV matches Mo^{6+} ions [17] and the component with binding energy 401.76 eV matches nitrogen which is in NH_4^+ ions [18]. Mo $3d$ emission comprises the pair of spin–orbit doublets with Mo $3d_{3/2}$ and Mo $3d_{5/2}$ binding energies of ~236 and ~233 eV respectively that was observed in other vanadium hydrates containing molybdenum [19].

4. Conclusions

The composition and chemical structure of $(NH_4)_{2-x}H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ ($x = 0$, 1) gels synthesized by the sol–gel technology were determined by X-ray photoelectron spectroscopy methods. The vanadium ions are in the V^{5+} and V^{4+} states with reduction ratio of about 0.043 independent on the x value. The investigation of the Mo $3p$ and Mo $3d$ spectra shows that the molybdenum ions are in the stable Mo^{6+} states. The O $1s$ peak consists of three components, where the first one is connected with vanadium and molybdenum ions, the second is possible to subsume under relations with carbon, and the third belongs to oxygen linked with hydrogen in water molecules. The position of the N $1s$ peak indicates that the nitrogen is connected with hydrogen in NH_4 ions.

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References

[1] V.L. Volkov, *Intercalation Phases Based on Vanadium Oxides* (Uralskii Nauchnyi Tsentr Akademii Nauk SSSR, Sverdlovsk, 1978) [in Russian].

[2] J. Livage, Vanadium pentoxide gels, Chem. Mater. **3**(4), 578–593 (1991).

[3] D.R. Ulrich, Prospects of sol–gel processes, J. Non-Cryst. Solids **100**(1–3), 174–193 (1988).

[4] P. Aldebert, H.W. Haesslin, N. Baffier, and J. Livage, Vanadium pentoxide gels: III. X-ray and neutron diffraction study of highly concentrated systems; one-dimensional swelling, J. Colloid. Interface Sci. **98**(2), 478–483 (1984).

[5] P. Aldebert, N. Baffier, J.-J. Legendre, and J. Livage, V_2O_5 gels: A versatile host structure for intercalation, Chim. Miner. **19**(4–5), 485–495 (1982).

[6] R.M. Guseinov and V.D. Prisyazhnyi, Protonic solid electrolytes, Ukr. Khim. Zh. (Russ. Ed.) **58**(10), 823–833 (1992).

[7] A.B. Yaroslavtsev, Proton conductivity of inorganic hydrates, Usp. Khim. (Russ. Chem. Rev.) **63**(5), 449–455 (1994) [in Russian].

[8] V.L. Volkov, G.S. Zakharova, L.V. Kristallov, M.V. Kuznetsov, G. Dai, and M. Tong, Synthesis, structure, and properties of ammonium polyvanadomolybdate xerogels, Inorg. Mater. **37**(4), 408–412 (2001).

[9] V.L. Volkov, G.S. Zakharova, M.V. Kuznetsov, A. Jin, Q. Zhu, and W. Chen, Nanocomposites of $V_{1.67}M_{0.33}O_{5\pm\delta}\cdot nH_2O$ (M = Ti or Mo) xerogels intercalated with hydroquinone and poly(vinyl alcohol), Russ. J. Inorg. Chem. **51**(9), 1339–1344 (2006).

[10] V.L. Volkov, G.S. Zakharova, and V. Bondarenka, *Xerogels of Simple and Complicated Polyvanadates* (Ural Branch of Russian Acad. Sci., Yekaterinburg, 2001) [in Russian].

[11] G.S. Zakharova, V.L. Volkov, V.V. Ivanovskaia, and A.L. Ivanovskii, *Nanotubes and Similar Nanostructures of Metal Oxides* (Ural Branch of Russian Acad. Sci., Yekaterinburg, 2005) [in Russian].

[12] C.D. Wagner, J.F. Moulder, L.E. Davis, and W.M. Riggs, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin–Elmer Corporation, Physical Electronics Division, 1995).

[13] B.F. Dzhurinskii, D. Gati, N.P. Sergushin, V.I. Nefedov, and Ya.V. Salyn, Simple and coordination compounds. An X-ray photoelectron spectroscopic study of certain oxides, Zh. Neorg. Khim. (Russ. J. Inorg. Chem.) **20**, 2307–2314 (1975).

[14] G. Hopfengärtner, D. Borgmann, I. Rademcher, G. Wedler, E. Hums, and G.W. Spitznagel, XPS studies of oxidic model catalysts: Internal standards and oxidation numbers, J. Electron Spectrosc. Related Phenomena **63**(2), 91–116 (1993).

[15] T.L. Barr, An ESCA study of termination of the passivation of elemental metals, J. Phys. Chem. **82**(16), 1801–1810 (1978).

[16] C.-O.A. Olsson and S.E. Hornstrom, An AES and XPS study of the high alloy austenic stainless steel 254 SMO tested in a ferric chloride solution, Corrosion Sci. **36**(1), 141–151 (1994).

[17] G.D. Khattak, M.A. Salim, A.S. Al-Harthi, D.J. Thompson, and L.E. Wenger, Structure of molybdenum-phosphate glasses by X-ray photoelectron spectroscopy (XPS), J. Non-Cryst. Solids **212**(2–3), 180–191 (1997).

[18] C.R. Clayton and K.G. Martin, Evidence of anodic segregation of nitrogen in high nitrogen stainless steels and its influence on passivity, in: *Proceedings of International Conference on High Nitrogen Steel HNS 88, Lille, May 1988*, eds. A. Hendry and J. Foche (London, 1989) pp. 256–260.

[19] V. Bondarenko, S. Kaciulis, A. Plesanovas, V. Volkov, and G. Zacharova, Photoelectron spectroscopy of the poly-vanadium transition metal acids, Appl. Surf. Sci. **78**(1), 107-112 (1994).

AMONIO POLIVANADATŲ–MOLIBDATŲ SINTEZĖ IR RENTGENO FOTOELEKTRONINIŲ SPEKTRŲ TYRIMAS

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Santrauka

Iš V_2O_5, NH_4VO_3, 40% H_2O_2 ir Mo miltelių, naudojant zolių ir gelių technologiją, buvo pagaminti $(NH_4)_{2-x}\,H_xV_9Mo_3O_{31\pm\delta}\cdot nH_2O$ ($x = 0, 1$) geliai. Pateikti minėtų gelių cheminės sudėties bei atskirų elementų būsenų tyrimo Rentgeno fotoelektroninės spektroskopijos (RFS) metodu rezultatai. Analizuoti V $2p$, O $1s$, C $1s$, Mo $3p$, Mo $3d$ ir N $1s$ smailių parametrai bei vanadžio ir molibdeno jonų valentingumas. Nustatyta, kad molibdeno jonai yra stabilioje Mo^{6+} būsenoje, o vanadžio – V^{4+} ir V^{5+} būsenose. Vanadžio jonų redukcijos santykis nepriklauso nuo gelių sudėties ir yra apie 0,043. N $1s$ smailės ryšio energijos vertė rodo, kad azotas geliuose surištas su vandeniliu NH_4 jonuose.