Research Article

Investigation of the Formation of Layered Nanostructure of Vanadium Xerogel

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The paper presents the results of a study of vanadium xerogel synthesized by sol-gel method. It shows that, during the aging process in gel formation, a layered fibrous chain structure of V–O occurs at the nanoscale. Highly anisotropic particles, similar in size to the “tapes” of vanadium oxide gel, were found on the surface of partially ordered layers. IR spectroscopic analyses of groups of V=O and of V–O bonds suggest that the high degree of order in the films is related to the fact that one of the water molecules is found to be short in double bonded V=O. Consequently, the growth chains take place predominantly in the plane equivalent to OH groups. Most of the VO–H consist of twisted (spiral) vanadium oxygen layers and have the morphology of tubes, the ends of which are open. Owing to such morphology of VO–H, significant structural flexibility is observed, which distinguishes them not only from carbon, but also from most other nanotubes.

1. Introduction

The level of current research in the area of advanced nanomaterials is increasing not only by the evolution of new methods for their synthesis, but also by the accurate testing of their physicochemical properties. An important characteristic that determines the properties of nanomaterials is the structure of nanocrystalline phases. One of the primary means of structural investigation of nanomaterials for their composition and structural features of constituent phases is by the X-ray diffraction method [1].

Phase transition of metal-semiconductors in compounds of d- and f-metals, mainly oxides, has been intensively studied by the X-ray diffraction method over the past forty years due to many different possibilities of its practical application [2–4]. It is found that in vanadium-oxygen system there are, according to different sources, about twenty compounds, beginning with suboxide of V_9O to higher oxide of V_2O_5 . Some of them, in particular, V_2O_3 and VO_2 , show a pronounced phase transition in commercial devices.

Intercalation compounds based on a layered structure of vanadium hydrate of $V_2O_5 \cdot nH_2O$ have found industrial applications in recent years in the production of unique composites. These compounds have remarkable flexibility, high strength, and thermal and corrosion resistance. Researchers are paying special attention to the study of physical and chemical properties and the practical use of superfine powders and films of nanomaterials obtained by the sol-gel method [4]. The relevance of this layered material is that it may find application in such areas as catalyst, membranes for sewage treatment, cathode materials of the current source, the switching devices, and antistatic coating.

2. Experimental Procedure

Vanadium-containing gel has been synthesized by sol-gel method using ammonia as the precursor template [5]. The synthesis was carried out as follows. Vanadium pentoxide powder is melted in a muffle furnace at a temperature of

TABLE 1: X-ray diffraction of the gel dried in air for 5 min.

670°C. Next, melt is heated to a temperature of 850°C and this temperature is maintained for 30 min. The material was then removed from the oven without precooling and is introduced into distilled water. The contents were stirred until complete dissolution of the solid. The resulting homogeneous brown solution turned out at a V₂O₅ concentration in the solution of approximately 25 g/L and a pH value of 2.2. Then, at a temperature of ±22°C and constant stirring, a vanadium solution is added to a 30% ammonia solution. Upon reaching pH of 3.4, the solution was slowly solidified to form a sol with a vanadium compound with ammonia and then passed into solid gel by drying it in air at room temperature for 24 hours.

Synthesized gel has been examined by X-ray analysis. For this purpose the gel was predried in the air and was subjected to XRD analysis at intervals of five minutes. The analysis was performed on a diffractometer with high temperature attachment up to 1200°C in X'Pert MPD Pro (PANalytical) equipment using the detection of Bragg-Brendon tube mode under conditions of 30 KV and 40 mA.

Microscopic analysis was performed with a scanning probe microscope with an attachment of Tape Integra Prima. Micrographs have been taken in the atomic force mode. Thermogravimetric studies have been conducted on the DTA/DSC NETZSCH STA 409 PC/PG system.

IR analysis of samples of vanadium-containing gel was performed on FT-IR spectrometer "Avatar 370" in the spectral range 4000–250 cm⁻¹ of the drug from 200 mg to 10 mg of CsI samples, used in the analysis of the prefix—Avatar diffuse reflectance. Gel was observed in the spectral range of 4000–400 cm⁻¹ capillary layer in windows of KRS-5. The attachment used for the experiment was Transmission E.S.P.

3. Results and Discussion

It was found that X-ray diffraction patterns of samples of vanadium-containing gel, taken within the range from 5

to 25 minutes, are identical. X-ray diffractions show amorphous component of the gel which by heating the sample is retained, but the intensity of the corresponding peak in X-ray decreases.

On X-ray diffraction sample (Table 1), aged in the air for 5 min, it is seen that the intensity of the amorphous component decreases by decaying into separate reflexes, and in a little corner area the intensity of a new phase begins to appear.

On the X-ray diffraction (Table 2) for gel dried in air for 30 minutes, vanadium hydroxide peaks (peaks numbers 4, 5) appear [5]. New noncrystalline phases appear in the region of 6–8° with decreased amorphous constituents.

In the process of gel aging in air for 40 minutes, there is a reduction in its water content, at the expense of evaporation and the resulting sample (Table 3); intensity redistribution in the diffraction maxima is observed on the XRD plot.

Due to the reduction of amorphous compounds, there is an increase in the intensity of the spacing boundaries plane in a small corner area of 5–12°. This dependence, as noted earlier, is, probably, due to the formation of V₂O₅·nH₂O, as well as nonstoichiometric vanadium-containing compounds. There is also the appearance of diffraction lines corresponding to the emerging forms of vanadium oxides of V₂O₅ and VO₂ in the X-ray diffraction (Table 3) in a small region.

As a result of further removal of moisture, about 30% of vanadium hydroxide was present in the sample. Against this background, the crystallization and transition distribution of various forms of vanadium oxides occur and show the presence of V₂O₅·H₂O (30%), V₂O₅ (13%), V₃O₇ (45%), and V₂O₅ (11%) [5].

To observe dynamic changes of the curves, depending on the time of gel drying in air and accordingly the occurrence of phase components, collected X-ray diffractions have been superimposed on each other (Figure 1) and have been displayed in the 3D format. From the results obtained, one

TABLE 2: X-ray diffraction of the gel dried in air for 30 min.

TABLE 3: X-ray diffraction of the gel dried in air for 40 min.

can see how the birth of the phases and their distribution occur as the water evaporates. The gel dries completely and uniformly; a transition linkage from crystallization water to OH groups occurs. Thus the composition of substance is changed, and the content of V₂O₅·(H₂O) is reduced from 30% to 8% [5].

In the process of sample drying, the layers of gel are depleted from water and phase transitions occur. As a result, the formation of a layered gel structure is observed. It is well observed on X-ray diffractions presented in Figure 2.

The results are in good agreement with the data of thermogravimetric studies. Isothermal effect corresponds to each

FIGURE 1: The results of superimposed X-ray diffraction of the gel vanadium as a function of aging time.

FIGURE 2: Topographical 3D presentation of X-ray diffraction plots during sequential removal of water from the xerogel.

stage at a constant temperature, as process of crystallization of compounds from amorphous component of the gel takes place. The fibers in the gel have some kind of a chaotic molecular structure which, with removal of water, leads to ordering.

On thermogram of the gel, vanadium-containing (Figure 3) endothermic peaks at 82.3, 140, 277.2, 355.9, and 382.6°C are fixed. Partially hygroscopic and partially water-including components of the crystalline hydrate and some oxide compounds are removed up to 300°C. Communication between layers occurs by converting water of crystallization to OH groups. In addition, phase transitions occur at temperatures of 80, 277, and 355°C and are associated with the formation of $V_2O_5 \cdot nH_2O$, as well as nonstoichiometric vanadium-containing compounds. The results of the first derivative differential thermal curve (DDTA) and X-ray

analysis for measuring plane spacing and the process of crystallization of $V_2O_5 \cdot nH_2O$ at 150°C are confirmed [5, 6].

The method of scanning probe microscopy (Figure 4) also confirmed the formation of the layered structure xerogel of vanadium, formed by conversion of fibers with V–O chains and water molecules.

Absorption valence bands (Figure 5) of $\nu(OH)$, 3400 cm^{-1} , deformational band of δHOH , 1651 cm^{-1} , and librational band of $\nu_L H_2O$, 739 cm^{-1} , fluctuations of molecular water were observed on the IR spectrum of the gel [7, 8]. The absorption band with a maximum, at a wave number of 1013 cm^{-1} , falls in the range of manifestations of the stretching vibrations of V=O [8]. Stretching vibrations of V–O at 747 cm^{-1} and of $[V_2O_8]^{2-}$ at 503 cm^{-1} were found.

FIGURE 3: Thermogravimetric analysis of the vanadium-containing gel.

FIGURE 4: 3D image of the gel photographed on the probe microscope.

FIGURE 5: IR spectra of the vanadium xerogel. (a) IR spectrum of the gel; (b) IR spectrum of the gel with subtraction spectrum of water.

Fibers present themselves as flat ribbons of 100 nm length and width of 10 nm, the structure of which corresponds to the orthorhombic structure of vanadium pentoxide of V_2O_5 [9, 10].

4. Conclusion

Synthesis of vanadium gel has been carried out using ammonia as the template and the study of its structure confirms the formation of porous layered surface of different compounds containing vanadium. Delaminated structural fibers with disordered muddled filamentous particles were obtained.

Highly anisotropic particles, similar in size to the “tapes” of vanadium oxide gel, were found on the surface of partially ordered layers. IR spectroscopic analyses of groups of $V=O$ and of $V-O$ bonds suggest that the high degree of order in the films is related to the fact that one of the water molecules is found to be short in double bonded $V=O$ [5].

The results of X-ray analysis additionally proved that the synthesized vanadium-containing gel is a nanoscale material.

Thus, in the process of removing moisture by air-drying of the synthesized vanadium-containing gel, transition linkages occur from water of crystallization to OH groups, thus forming the layered structure fibers of VO chains and water molecules. Orthorhombic crystal ribbons are not located in a common plane but form as a relief nanoscale structure.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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