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K.V. Luskan,
A.O. Gyrenko, PhD, Assoc.Prof.,
O.P. Musov, PhD, Assoc.Prof.,
O.P. Klimenko, PhD, Assoc.Prof.
Ukrainian State University of Chemical Technology, 8 Gagarin Ave., Dnipropetrovsk, Ukraine, 49005; e-mail: katerynalu16@gmail.com

INFLUENCE OF THE CONDITIONS FOR THE PREPARATION AND THERMAL DESTRUCTION OF AMMONIUM TETRAVANADATE ON THE COMPOSITION OF OXIDE-VANADIC ELECTRO-FUNCTIONAL MATERIALS

К.В. Лускань, А.О. Гиренко, О.П. Мисов, О.П. Клименко. **Вплив умов отримання та термодеструкції амоній тетраванадату на склад оксиднованадієвих електро-функціональних матеріалів.** Присвячено дослідженню впливу технологічних стадій отримання амоній тетраванадату на кінцевий склад продуктів оксидів ванадію. Метою експериментальних досліджень є визначення технологічних параметрів отримання високодисперсних оксидів ванадію з різним ступенем окислення (V_2O_3, VO_2, V_2O_5). Процес отримання амоній тетраванадату включає три основних стадії: взаємодію 3 г V_2O_5 і 8,32 г $H_2C_2O_4{\cdot}2H_2O$ в 100 мл води з осадженням амоній тетраванадату 30 % розчином аміаку, відділення осаду центрифугуванням або сублімаційною сушкою. Оксиди ванадію утворюються на четвертій стадії термічного розкладання амоній тетраванадату. Рентгенофазовий аналіз виконано на дифрактометрі «ДРОН-3». Деференціально термічний аналіз проводили на дериватографі «Q-1500». Встановлено вплив умови виділення та термічного розкладання осаду на склад кінцевих продуктів (V_2O_3, VO_2, V_2O_5). Рентгенофазовим аналізом визначено, що виділення осаду методом центрифугування призводить до отримання VO_2 в інертній атмосфері, тоді як сублімаційною сушкою – до V_2O_3, високодисперсний V_2O_5 утворюється в окисній атмосфері. Високодисперсні оксиди ванадію з різним ступенем окиснення можуть бути отриманні за розробленною технологією.

Ключові слова: оксид ванадію, амоній тетраванадат, центрифугування, сублімаційна сушка

K.V. Luskan, A.O. Gyrenko, O.P. Musov, O.P. Klimenko. **Influence of the conditions for the preparation and thermal destruction of ammonium tetravanadate on the composition of oxide-vanadic electro-functional materials**. The work represents the investigation of the influence of technological stages of ammonium tetravanadate preparation on the final composition of vanadium oxide products. The purpose of experimental studies is to determine the technological parameters for the production of highly dispersed vanadium oxides with different degrees of oxidation (V2O3, VO2, V2O5). The synthesis of ammonium tetravanadate comprises three main steps: the reaction of 3 g of V2O5 and 8.32 g of H2C2O4 · 2H2O dissolving in 100 ml of water, followed by product precipitation with 30 % ammonium hydroxide, separation of the precipitate by centrifugation or sublimation. Vanadium oxides are formed in the fourth stage of thermal decomposition of ammonium tetravanadate. X-ray diffraction analysis samples was performed on "DRON-3". Differential thermal analysis (DTA) samples was carried out on a derivatograph "Q-150". The influence of separation conditions and thermal decomposition of the sediment on the composition of the final products (V2O3, VO2, V2O5) was studied. With the X-ray analysis it was determined that when using the centrifugation the final product of thermodestruction in an inert atmosphere is VO2, while sublimation drying leads to V2O3, and highly dispersed V2O5 is formed in an oxygen atmosphere. Highly dispersed vanadium oxides with different degrees of oxidation can be synthesized according to the introduced manufacturing scheme.

Keywords: vanadium oxides, ammonium tetravanadate, synthesis, centrifugation, freeze drying

Introduction. Vanadium salts (IV) have properties that open up great opportunities for using them as a precursor for the synthesis of highly dispersed vanadium oxides of varying degrees of oxidation (V_2O_5, V_2O_3, VO_2).

The final synthesis products are widely used in optical switches, memory elements, energy-saving coatings for glass, surfaces of optical media information, catalysts, cathode materials in lithium batteries [1 – 3].

The analysis of recent researches and publications presented in the scientific literature on methods of synthesis of vanadium oxides has shown that in the last decade the authors devote considerable attention to high-temperature decomposition of precursors – nano dispersed salts of vanadium (IV) [2, 4 – 6].

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It should be noted that this method allows to carry out the process of synthesis in optimal conditions in terms of the effectiveness of management of the properties of the final product, energy costs and productivity. It is likely that the composition and quality of the final products of vanadium oxides will depend from the conditions of synthesis and thermal decomposition of the precursor. In this regard, it is relevant to conduct comprehensive research on the choice of the salt of vanadium (IV), the methods of its synthesis and thermal decomposition.

A number of papers have been published on the use of the following precursors: ammonium vanadite $NH_4H_3V_2O_6$[4], ammonium hexavalentate $(NH_4)_2V_6O_{16}$ [6], tetravanadienate ammonium $(NH_4)_2V_4O_9$ [7]. The use of the first two compounds leads to the production of initial products with impurities of other compounds, which requires additional treatment of vanadium salts before thermal decomposition. Application of the latter contributes to obtaining finite nanocrystalline vanadium oxides with a high degree of chemical purity.

Thus, based on the analysis of the disadvantages and features of various vanadium salts, the choice of tetravanadate ammonium as the precursor for the most effective synthesis of vanadium oxides is theoretically justified.

One of the first studies on the properties and composition $(NH_4)_2V_4O_9$ was published in 1876 [8]. Despite the high interest in this topic until recently full research of physical and chemical properties and the development of technology for the production of ammonium tetravanadate was not conducted.

The purpose of the study is to determine the technological parameters for the production of oxides of vanadium with different degrees of oxidation (V_2O_3, VO_2, V_2O_5).

To achieve the goal you need to solve the following tasks:

– to establish the physical and chemical properties of the precursor;

– to determine the influence of sedimentation $(NH_4)_2V_4O_9$ on the composition of final products V_2O_3, VO_2;

to establish conditions for the thermal decomposition of the precursor.

Materials and methods. The process of obtaining salt of vanadium (IV) includes three main stages: obtaining an aqueous solution of oxovanadium (IV), precipitation of the product with a solution of ammonia, separation of the precipitate.

The solution was obtained by dissolving 2.4…3 g of V_2O_5 (reagent grade) and 8.32 g $H_2C_2O_4$ (reagent grade) corresponding to the molar ratio of V_2O_5:$H_2C_2O_4$ from 1: 4 to 1: 5 in 100 ml. Water under heating to a temperature of 330…340 K. The product was precipitated from a solution of oxyanodium (IV) with 25 % ammonium hydroxide to pH = 10.2 with form a dark brown precipitate separated by two methods: centrifugation and sublimation drying.

At the final fourth stage of technology, the dried salt of tetravanadate ammonium was thermally decomposed in air and in a neutral atmosphere of argon.

To determine the phase composition of ammonium powders of tetravanadate and vanadium oxides, an X-ray diffraction analysis performed on the DRON-3 installation in monochromatized copper radiation of CuKa was used.

He differential-thermal analysis of vanadium dioxin was carried out on the derivatograph “Q-1500” of the system F. Paulik, I. Paulik, L. Erdey of the MOM company.

Results. As a research object, salt of ammonium tetravanadate was selected. This choice is due to the fact that when regulating the conditions of salt synthesis and its thermal decomposition, chemically pure products of vanadium oxides of different phase composition are obtained. That is why it is important to determine the physical and chemical properties, the influence of sedimentation methods and the conditions for the thermal decomposition of tetravanadate ammonium in order to create the bases for the technological process of obtaining V_2O_3, VO_2, V_2O_5.

The product obtained after the interaction of the solution of oxovanadium (IV) with ammonium hydroxide is a dark brown precipitate $(NH_4)_2V_4O_9$, which shows high solubility with decreasing pH and is characterized by high oxygen oxidation rate.

To obtain vanadium dioxide, the precursor should contain a minimum amount of compounds of vanadium, 5-oxide and oxalate ions. There is an assumption that the high-temperature treatment of ammonium tetravanadate salt, the presence of impurities of oxalate ions can lead to the formation of V_2O_3.

Taking into account the above, an important stage in the technology for the production of tetravanadate ammonium is the separation of the precipitate. For this purpose, it was advisable to use two methods – centrifugation and sublimation drying which, unlike filtration, aimed at minimizing the contact of a precipitate with oxygen, which prevents oxidation of V (IV) to V (V), and, more likely, helps to remove impurities of oxalate ions.

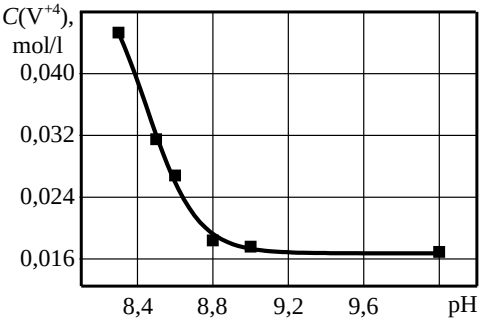

Fig.1. The curve of solubility of freshly deposited $(NH_4)_2V_4O_9$ in water, depending on the pH at a temperature of 293 K

The first method is aimed at separating the excess of oxalate ions by three to four rinsing operations with distilled water, minimizing contact with oxygen in the air. The solubility $(NH_4)_2V_4O_9$ in water is significantly dependent on pH (Fig. 1).

When the pH approaches up to 8.8, the solubility of the ammonium salt of tetravanadate increases dramatically, so that in order to avoid costs, it is necessary to rinse with a weak solution of ammonium hydroxide. The precipitate is dried in an atmosphere of argon at a temperature of 453...473 K for a further 120...180 minutes.

The second method is aimed at the decomposition of an excess of oxalate ions at a set temperature of 453...473 K for 50...70 minutes in vacuum conditions. Due to the peculiarities of the rotational evaporator, a simultaneous separation of the sediment occurs due to distillation of the filtrate and its drying, which greatly reduces the synthesis time of $(NH_4)_2V_4O_9$.

As seen from X-ray diffraction (Figure 2), dried ammonium powders of tetravanadate, obtained by two methods, have a pronounced crystalline structure with diffraction peaks, which are inherent to the phases $(NH_4)_2V_4O_9$ and $(NH_4)_4V_6O_{16}$.

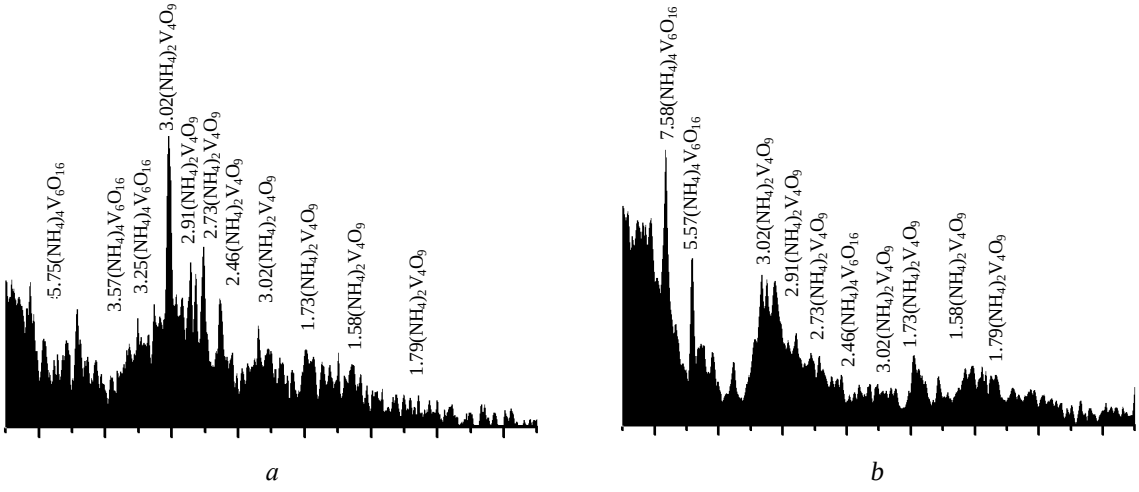

Fig. 2. X-ray diffraction pattern of ammonium powder of tetravanadate, obtained by the following method: centrifugation (a); sublimation drying (b)

When thermally treated, structural compounds $(NH_4)_2V_4O_9$, $(NH_4)_4V_6O_{16}$ exposed decomposition processes and do not affect the composition of vanadium oxides, which is confirmed by qualitative identification using the method of X-ray diffraction analysis.

For final products nanodispersed vanadium oxide powders the ammonium tetravanadate, obtained by both methods, was heat treated in two steps: at a temperature of 873...923 K for 50...60

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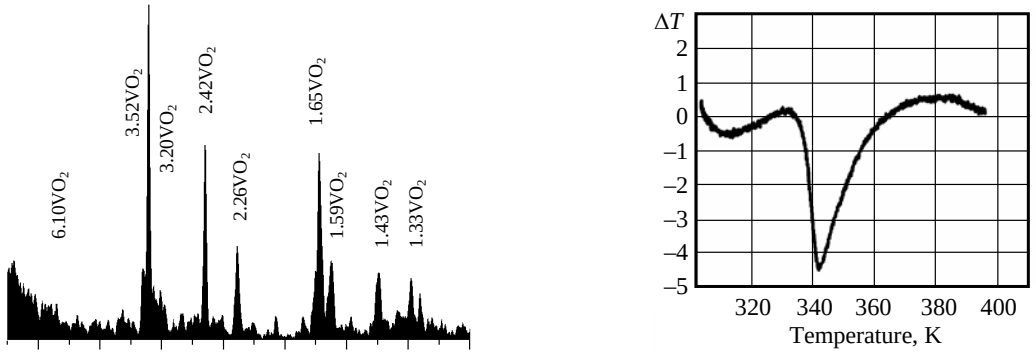
minutes with subsequent exposure at a temperature of 1123...1173 K for 10...15 min. in an atmosphere of argon.

The result of such a heat treatment of ammonium precursor, synthesized by centrifugation, is a chemically pure crystalline powder of vanadium dioxin. This is evidenced by the diffractogram (Fig. 3, *a*) and the expressive endothermic peak on the curve obtained by differential thermal analysis (DTA) at a temperature of 341 K (Fig. 3, *b*), corresponding to the characteristic of vanadium dioxide semiconductor-metal transition.



a *b*

Fig. 3. Diffraction diagram of vanadium dioxide powder obtained by thermal decomposition of tetravanadate of ammonium, synthesized using a centrifugation method at a temperature of 873 K - 60 min and with subsequent exposition 1173 K - 10 min in the atmosphere of argon (a) and the DTA VO2 curve obtained from (NH4) 2V4O9 (b)

Identical heat treatment of the powder $(NH_4)_2V_4O_9$, obtained by sublimation drying results in the production of V_2O_3 (Fig. 4).

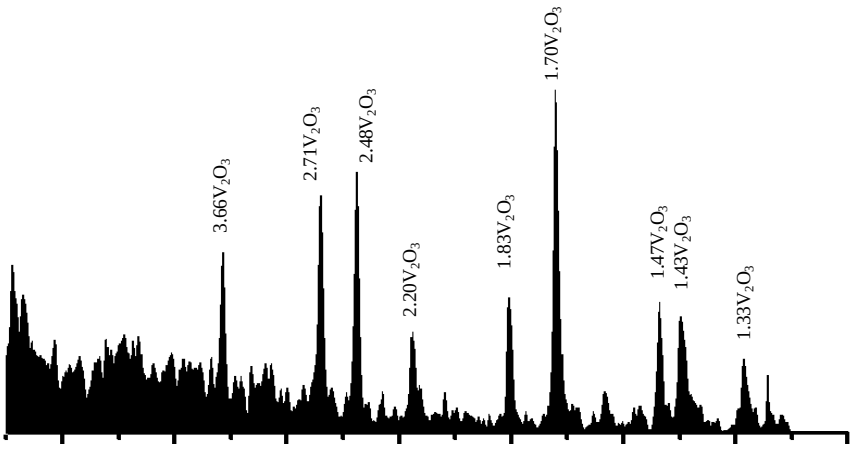


Fig. 4. Diffraction diagram of vanadium dioxide powder obtained by thermal decomposition of tetravanadate ammonium, synthesized using sublimation drying at a temperature of 873 K for 60 min. and heat treatment at a temperature of 1173 K for 10 minutes. in an atmosphere of argon

This is explained by the fact that an excess of oxalic acid, present in the precipitate is not removed and helps restore V^{+5} до V^{+3}.

To obtain nanocrystalline pentaoxide vanadium (Fig. 5), precursors synthesized by both methods were thermally treated at a temperature of 643...663 K for 50...60 minutes in the atmosphere of air.

It has been shown that nanosized crystals of vanadium pentoxide have improved electrochemical properties, which makes it possible to use them as a cathode material for lithium batteries [2].

Conclusion. Thus, the influence of the conditions of obtaining and thermo-destruction of tetravanadate ammonium on the composition of vanadium oxides (V_2O_3, VO_2, V_2O_5) is investigated. The synthesis process of $(NH_4)_2V_4O_9$ involves three basic steps: obtaining an aqueous solution of oxovanadium (IV), precipitating the product with a solution of ammonia, and separating the salt precipitate. The corresponding vanadium oxides are formed at the fourth stage of the thermal decomposition of the resulting precipitate.

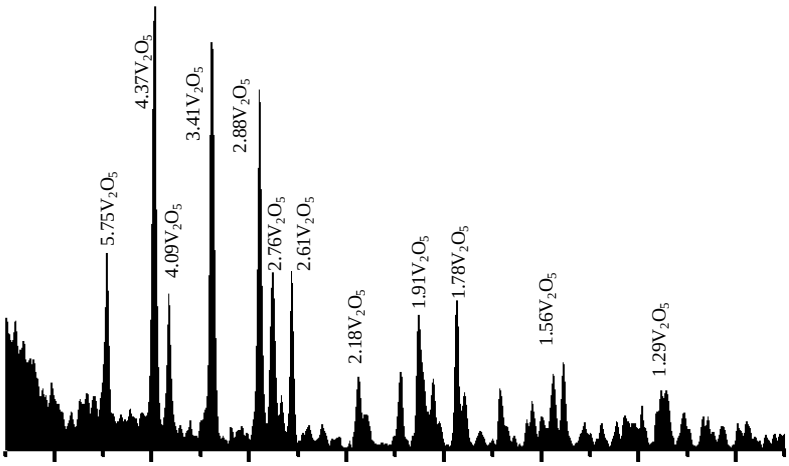


Fig. 5. Diffractogram of powder of vanadium pentoxide obtained by thermal decomposition of tetravanadate ammonium at a temperature of 653 K for 50 min. in the atmosphere of air

The possibility of separating the sediment by methods of centrifugation and sublimation drying was investigated taking into account the physical and chemical properties of the precursor (high solubility and high oxygen oxidation rate),

It is shown that VO_2 is formed as a result of thermal decomposition in an inert atmosphere of a precipitate obtained by centrifugation at the third stage of the technological process. At the same time, it is possible to obtain only V_2O_3 as a result of thermal degradation in an inert atmosphere from a precipitate containing the salt of tetravanodate of ammonium separated from the solution by sublimation drying.

Separation of a precipitate by heat treatment in an oxidized atmosphere, regardless of the method, allows for the production of highly dispersed V_2O_5.

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