SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF AMMONIUM TETRAVANADATE FOR OBTAINING VO$_2$

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Abstract. In order to develop a technological process for obtaining vanadium dioxide by the thermal decomposition, we developed the method of synthesis of highly dispersed vanadium(IV) salt as a precursor. It comprises vanadium pentoxide interaction with the oxalic acid in the solution, which gives intermediate oxovanadium solution, following precipitation of the product (ammonium tetravanadate) by adding ammonium hydroxide to oxovanadium, rinsing and drying the product. With the use of photocolorimetry and potentiometric titration the intermediate product was identified as $H_2[VO(C_2O_4)_2]$ and the final product as $(NH_4)_2V_4O_9$. Kinetic constants and activation energy of limiting reaction (E_a = 73.0 kJ/mol) were found, as well as the standard heat of the product formation (ΔH^0_f = –3494.5 kJ/mol), its solubility and density. It is shown that after high temperature treatment the substance transforms into vanadium dioxide of high quality with a typical semiconductor-metal transition.

Keywords: vanadium dioxide, ammonium tetravanadate, synthesis, kinetics, physicochemical properties.

1. Introduction

Vanadium(IV) oxide has the unique semiconductor-metal phase transition (SMPT) at the temperature of 340 K which is accompanied by a fivefold change of the electrical conductivity. The parameters of the transition depend on various factors such as stoichiometry, the presence of impurities and defects. Furthermore, the phenomenon of electrical switching in a vanadium dioxide related to SMPT is observed – considerable sharp reversible change of the system conductivity under the influence of applied electric field [1].

SMPT and electrical switching determine the use of vanadium dioxide in temperature sensors, optical switches, memory elements, energy-saving coatings for glass, optical information carriers, and thermochromic indicators [2-5].

The shortcoming of electronic devices based on vanadium dioxide is currently their low stability due to the destruction of the microcrystals during the cyclic phase transition, resulting in a drop of conductivity. Preliminary studies have shown that reduction of crystals size to nanoscale allows to obtain materials based on vanadium dioxide with stable characteristics during thermo-cycling [6].

Among widespread methods of obtaining vanadium dioxide nanocrystals are hydrothermal method [7], atomic layer deposition [8] and sol-gel method [9].

One of the promising methods for producing vanadium dioxide fine-grained particles is high-temperature decomposition of precursors – vanadate(IV) salts. Nanoscale particles of the precursor can be obtained by precipitation from solutions. The main advantage of this method is the capability to obtain highly dispersed powders with a high degree of chemical purity. This method allows to carry out the synthesis under optimal conditions in terms of management efficiency of the final product properties, energy consumption and performance [10].

The aim of this work is to develop the method of preparation the highly dispersed vanadium(IV) salt (vanadium dioxide precursor). The method consists in precipitating vanadium(IV) salt from the oxovanadium solution with ammonia. It is important to study the composition, kinetics, the standard heat of formation and properties of the substance to create the basis of a technological process for obtaining vanadium dioxide which properties can be easily modified through modification of its precursor properties.

2. Experimental

Oxovanadium(IV) solutions were prepared by dissolving of 2.4–3 g of V$_2$O$_5$ (reagent grade) and 8.32 g of H$_2$C$_2$O$_4 \cdot$2H$_2$O (reagent grade) (which corresponds to a molar ratio of V$_2$O$_5$:H$_2$C$_2$O$_4$ from 1:4 to 1:5) in 100 ml of water when heating to 353 K.

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Ammonium(IV) tetravanadate was precipitated from oxovanadium(IV) solution by adding concentrated ammonia (30% solution) to pH about 10.2. The precipitate was separated in a centrifuge with adjustable speed of 2000 rpm for 10 min.

Kinetic measurements were made in a thermostatic glass. Temperature was maintained by ultrathermostate U-4 within ± 1 K.

The quantity of vanadium(V) was determined by the standard method [11] where an aliquot was titrated with standard mohr's salt solution. Total vanadium was found by titration of an aliquot pre-oxidized with potassium permanganate according to [11]. The content of vanadium(IV) was calculated as the difference between the total vanadium and vanadium(V).

pH metric titration was performed using a standard pH meter 150MI. Photometric measurements were carried out with the use of CF-2000. X-ray diffraction analysis performed on DRON-3 in a monochromatic copper radiation (Cukα). Differential thermal analysis (DTA) was carried out on Q-150 derivatograph. The endothermic peak at the temperature of ~341 K was used for the determination of VO_2 by the method described in [12].

3. Results and Discussion

The preparation of vanadium(IV) salt involves three basic steps: preparing an aqueous solution of oxovanadium, precipitation of the product with aqueous ammonia, washing and separating the precipitate.

VO^{2+} solution can be obtained by the action of various reducers on vanadium pentoxide or vanadium(V) salts, for example by dissolving them in organic acids such as oxalic, tartaric and salicylic or malonic [13-15].

In this work oxalic acid was used because of its sufficiently high reduction potential and, which is especially important in view of the production of the final product without impurities, oxalate-ion can be completely removed by heating to a temperature of 373–403 K.

A number of papers [13, 14, 16, 17] concerns the study of oxovanadium(IV) compounds in organic acids, in particular $H_2C_2O_4$. It follows from these works that VO^{2+} forms rather stable complexes (pK ~ 9–10) which composition depends on the ratio of the complexing agent to a ligand in a solution: VOC_2O_4, $[VO(C_2O_4)_2]^{2-}$, $[(VO)_2(C_2O_4)_3]^{2-}$, $[VO(C_3H_2O_4)_2]^{2-}$. Depending on the composition of the oxalate complex, in particular, the color of the solution ranges from dark blue to bright blue.

In this paper, the molar ratio of reactants $V_2O_5:H_2C_2O_4$ was selected as 1:4 and 1:5. High concentrations of acid are caused by the need to maintain sufficiently low pH (1–2) to dissolve vanadium pentoxide and prevent the transition of oxovanadium(IV) cation into the anionic form [18].

3.1. Compositional Analysis of Oxovanadium Complex

For the following investigations of kinetics and thermodynamics of the process, it is necessary to identify the composition of the substance which is generated during the first stage – oxalate complex of oxovanadium(IV).

The composition of VO^{2+} complex compound with oxalate-ion at a given ratio of V_2O_5 to $H_2C_2O_4$ was determined by the saturation method. The initial solution of VO_2^+ was prepared by dissolution of V_2O_5 in concentrated (about 10 M or more) H_2SO_4 and further dilution with water to the concentration $C(VO_2^+) = 0.2$ mol/l (VO_2^+ concentration was determined by the method [11]). The initial $H_2C_2O_4$ solution with normality $C(\frac{1}{2}H_2C_2O_4) = 0.2$ mol/l was obtained by dissolution of the appropriate mass. The initial solutions of VO_2^+ and $H_2C_2O_4$ were placed in 25 ml flasks with the volume ratio of 1:1, 1:3, 1:4, 1:5, 1:7, 1:9, 1:10, 1:11 and adjusted to the flask's mark with water. After reduction of VO_2^+ to VO^{2+} the ratio of VO^{2+} to $C_2O_4^{2-}$ in the complex which forms was determined as the ratio $[C(VO_2^+) \cdot V(VO_2^+)]$:$[(C(\frac{1}{2}H_2C_2O_4) \cdot V(H_2C_2O_4) - C(VO_2^+) \cdot V(VO_2^+))/2]$. That is for the initial solutions of VO_2^+ and $H_2C_2O_4$ with the volume ratio of 1:1 the product is $VOSO_4$, for 1:3 product is VOC_2O_4, and for 1:5 – $H_2[VO(C_2O_4)_2]$. The ratio of normalities $C(VO_2^+):C(\frac{1}{2}H_2C_2O_4)$ coincides with the ratio of molarities $C(V_2O_5):C(H_2C_2O_4)$.

Analysis was carried out with the use of photometric method (Fig. 1) since vanadium solutions are colored: dark yellow VO_2^+ (λ_{max}=300 nm) (1); dark blue VO^{2+} (λ_{max}=300 and 780 nm) (2) and intense blue solution of VO^{2+} complex compound with an excess of $C_2O_4^{2-}$ (λ_{max}=300 and 780 nm) (3). The saturation curve is shown in Fig. 2.

It can be concluded that the complex with maximum ligands forms when the normalitis ratio of V_2O_5 to $H_2C_2O_4$ in the reaction mixture is 1 to 9 (or $C(VO_2^+)$: ($\frac{1}{2}H_2C_2O_4$)=1:9. Since one mole of $C_2O_4^{2-}$ is spent on the reduction of one mole of V_2O_5, after the reaction ends the ratio of ions VO^{2+}: $C_2O_4^{2-}$ in the solution is 2:8 (1:4) which can correspond to the compound of $[VO(C_2O_4)_4]^{6-}$. According to [19] the coordination number of VO^{2+} ion can be more than 3. It is obvious that at lower ratios of the reactants V_2O_5 : $H_2C_2O_4$ all unoxidized oxalate ions enter the complex compound VO^{2+}.

Three inflections of the curve correspond to the ratio of VO_2^+: $H_2C_2O_4$ as 1:3, 1:5 and 1:9 which are appropriate for VOC_2O_4, $[VO(C_2O_4)_2]^{2-}$ and most probably $[VO(C_2O_4)_4]^{6-}$. When initial ratio $C(V_2O_5):C(H_2C_2O_4)$ is 1:4, a mixture of the above compounds or $[(VO)_2(C_2O_4)_3]^{2-}$ forms. Existence of $H_2[(VO)_2(C_2O_4)_3]$ is mentioned in [17, 19]. However, due to the lack of inflection on the saturation curve at this point it was accepted that a mixture of $H_2[VO(C_2O_4)_2]$ and VOC_2O_4 forms. When the initial ratio of $C(V_2O_5):C(H_2C_2O_4)$=1:5 the overall reaction can be written as:

$$V_2O_5 + 5H_2C_2O_4 = 2H_2[VO(C_2O_4)_2] + 3H_2O + 2CO_2 \quad (1)$$
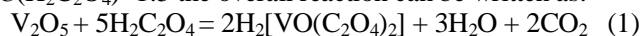
Fig. 1. Absorption spectra of aqueous solutions: VO$_2^+$ (1); VO^{2+} without oxalate-ions excess in H$_2$SO$_4$ (2) and oxovanadium(IV) complex (3). Vanadium concentration $C_V = 0.011$ mol/l; pH = 1.5; 293 K
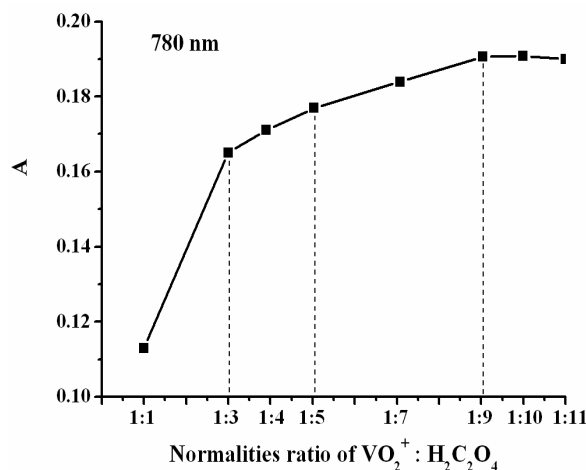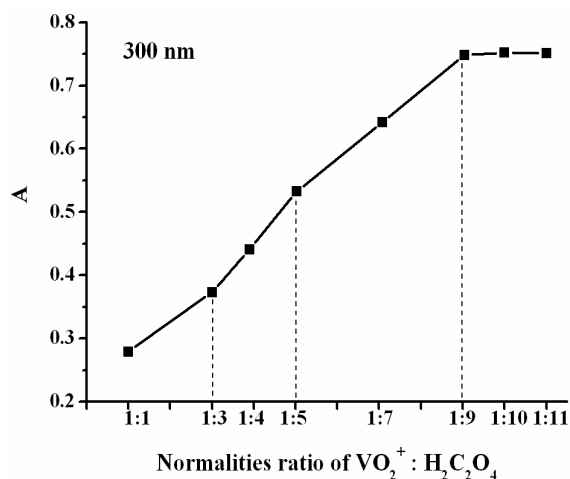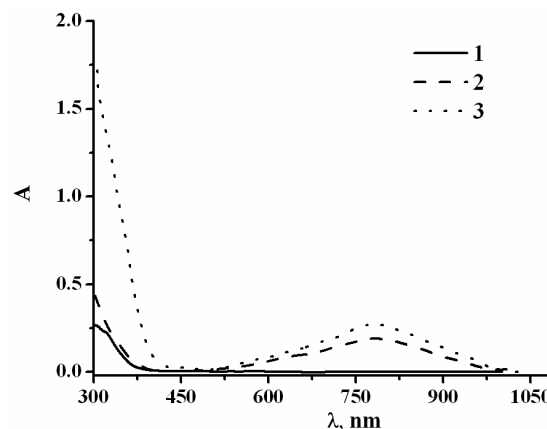

Fig. 2. Saturation curve: dependence of optical density of complex compound solutions (VO^{2+} +C$_2$O$_4^{2-}$) on the reagents ratio (VO$_2^+$: H$_2$C$_2$O$_4$); 293 K; pH = 1; vanadium concentration $C_V = 7.83 \cdot 10^{-3}$ mol/l

3.2. Kinetic Measurements

The reaction of oxovanadium(IV) complex formation is rather slow and its speed increases considerably with increasing temperature. This reaction obviously goes through three stages which are indicated by the formation of different coloured intermediates during the reaction progress: 1) dissolution of V$_2$O$_5$ and formation of VO$_2^+$ cation (dark yellow solution); 2) redox interaction with oxalate ion to form VO^{2+} (the accumulation of VO^{2+} in the solution leads to a colour change from light green to turquoise and blue); 3) complexation with C$_2$O$_4^{2-}$ excess. The reaction end was judged by the achievement of the constant value of optical density at 780 nm.

Spectral studies of the kinetics of this process show that the second stage (vanadium reduction) is apparently limiting: for the first 15 min after the start of the reaction (1) the solution remains yellow, the optical density at 300 nm increases (*i.e.* VO$_2^+$ concentration increases) while at 780 nm it remains zero.

To determine the constants and activation energy of the reduction reaction, the solution was prepared just as for the compositional analysis of oxovanadium(IV) with the normalitis ratio of VO$_2^+$ to H$_2$C$_2$O$_4$ as 1:10. The change of optical density with time caused by the increasing concentration of the product oxovanadium(IV) $D = f(\tau)$ was recorded. The measurements were carried out at 670 nm to avoid going beyond the upper limit of the spectrophotometer measuring range with an increasing concentration of the product, which is possible at $\lambda_{max} = 780$ nm.

On the basis of the compositional analysis it was assumed that at the given molar ratio one of the reactants is always in a considerable excess and the product is the complex of the fixed composition, that is the molar extinction coefficient is constant during the measurements. Having found the molar extinction coefficient of the complex, time dependences of concentration $C = f(\tau)$ were calculated from $D = f(\tau)$ dependences at different temperatures. Analysis of the kinetic curves showed that the reaction rate is described by the first order equations. Effective rate constants and activation energy ($E_a = 73.3$ kJ/mol) of the reaction were found (Fig. 3).

3.3. Compositional Analysis
of Ammonium(IV) Vanadate

The next stage is deposition of vanadium(IV) compound with a concentrated ammonia solution.

Fig. 4 shows the titration curves of 0.20 M oxovanadium(IV) solution $H_2[VO(C_2O_4)_2]$ with 0.46 M solutions of NaOH and NH_4OH (standardized by $H_2C_2O_4$), which allow to suggest what processes occur in the solution.

There are two inflection points on the acid-base titration curve of oxovanadium(IV) aqueous solution with the base titrants. In the first equivalence point pH ~ 4.9 a strong acid is apparently titrated $n(H^+) = 2 \cdot 0.20 \cdot 5 \cdot 10^{-3} = 2 \cdot 10^{-3}$ mol. Next a turbidity of the solution and precipitation are observed. At pH > 9 there is a second end point and after a while the product completely precipitates. The amount of OH-ion which is spent on the deposition of $1 \cdot 10^{-3}$ mol of VO^{2+} at the second equivalence point is $(2.50–2.65) \cdot 10^{-3}$ mol, corresponding to Eq. (2), *i.e.* the ratio of VO^{2+} to OH^- is 1:2.5 = 4:10.

$$4VO^{2+} + 10OH^- = V_4O_9^{2-} + 5H_2O \qquad (2)$$
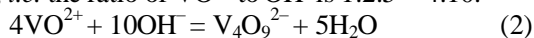
In the case of formation of $V_2O_5^{2-}$, for example, the stoichiometric ratio VO^{2+} to OH^- must be 1:3 (2:6). The results of the titration are reproduced quite well, do not depend on the concentration of the reagents and are in the range of (2:5)–(2:5.3).

Titration curves with ammonium hydroxide and strong bases as a titrant are very similar. However, in case of NH_4OH titrant, pH after the second equivalence point is slightly lower because NH_4OH is a weak base.

Thus the product was identified as $(NH_4)_2V_4O_9$ (or $Na_2V_4O_9$ in the case of deposition with sodium hydroxide).

One of the first works on the properties and structure of vanadium(IV) compounds with soluble bases was published in 1876 [20]. By means of the method of quantitative elemental analysis it was showed that the interaction between VO_2 and bases in highly alkaline medium gives $K_2V_4O_9$, $Na_2V_4O_9$, $(NH_4)_2V_4O_9$, BaV_4O_9, $Ag_2V_4O_9$. In alkaline solutions these compounds are not soluble and have a dark brown colour. Aqueous solutions of these substances with pH close to neutral are green. $(NH_4)_2V_4O_9$ has the high solubility and the largest oxidation rate to vanadium(V) of all listed above compounds. In all following publications [21-26] the formation of $M^I_2V_4O_9$ compounds in alkaline medium is mentioned, however, without any references to works and methods of identification of these substances.

Our product which was precipitated in the NH_4OH medium at pH > 9 is apparently $(NH_4)_2V_4O_9$, also has the dark brown colour, and its solubility is getting higher as pH decreases which makes it extremely difficult to rinse, forms dark green solutions and has the high oxidation rate.

However, this process takes place mainly in the surface layer and depends on the rate of oxygen dissolution and its diffusion, and the rate of this process decreases with pH decrease. Thus the effective rate constant of this reaction in three millimeter layer of $(NH_4)_2V_4O_9$ slurry at 298 K and pH 10.2 is about $1 \cdot 10^{-4}$ s^{-1}.

The overall reaction of ammonium vanadate(IV) formation can be written as:

$$4H_2[VO(C_2O_4)_2] + 18NH_4OH = (NH_4)_2V_4O_9 + $$
$$+ 8(NH_4)_2C_2O_4 + 13H_2O \qquad (3)$$
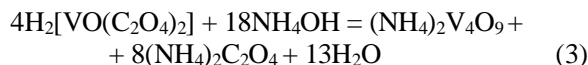
where the composition of oxovanadium(IV) depends on the initial amount of oxalic acid.

3.4. Thermodynamic Measurements

The reaction of ammonium(IV) vanadate preparation according to the proposed method is performed in an aqueous medium by adding a concentrated ammonium hydroxide to the solution of oxovanadium(IV). This reaction is exothermic with a significant thermal effect. It can be written as an ionic reaction:

$$4VO^{2+} + 2NH_4^+ + 10OH^- \rightarrow (NH_4)_2V_4O_9\downarrow + 5H_2O \quad (4)$$
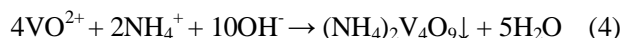
The total thermal effect of the reaction $\Delta H_{exp} = -459.2$ kJ/mol (for 1 mol of the product) was found experimentally by calorimetric method. This value includes the heat of the reaction (4) ΔH_r and the heat of neutralization of oxalic acid excess by ammonium hydroxide, which was found $\Delta H_{neutr} = -47$ kJ for the excess of oxalic acid in the bulk solution taken for obtaining 1 mol $(NH_4)_2V_4O_9$. Hereby, $\Delta H_r = \Delta H_{exp} - \Delta H_{neutr} = -412.2$ kJ. From the Hess's law for the reaction (4) with the use of formation enthalpy of ions VO^{2+}, NH_4^+, OH^- and H_2O molecule [27, 28] the standard formation enthalpy of ammonium tetravanadate was calculated $\Delta H^0_f(NH_4)_2V_4O_9 = -3494.5$ kJ/mol.

3.5. Physicochemical Properties
of the Product

For the production of the best quality end product – vanadium dioxide, the precursor must contain the minimum amount of vanadium(V) compounds and oxalate ions. It was shown that at high-temperature processing of the ammonium tetravanadate salt the presence of impurities of oxalate ions can lead to the formation of V_2O_3. It means that an important stage of precursor production is its rinsing.

To separate the precipitate from the solution the use of a centrifuge was accepted. After removing a centrifugate the three-fold volume excess of rinsing water to the sediment volume is added to the precursor and it is centrifuged again. To remove the excess of oxalate ions three or four rinsing operations are enough.
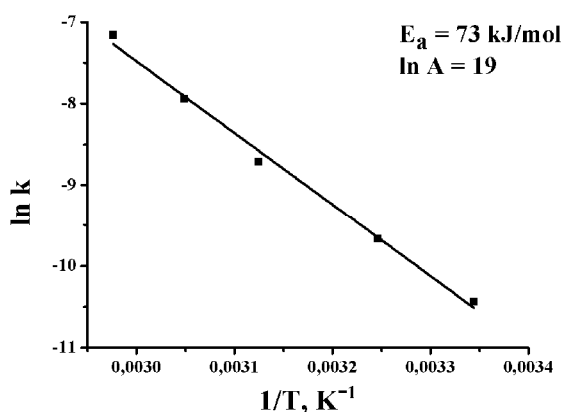
Fig. 3. Determination of an activation energy of the reaction of oxalate oxovanadium (IV) formation when VO_2^+ is reduced in an oxalate ions excess. Initial normalities: $C^0(VO_2^+) = 0.0384$ mol/l, $C^0(\frac{1}{2}H_2C_2O_4) = 0.3840$ mol/l

Fig. 4. Potentiometric titration curve of $5 \cdot 10^{-3}$ l $H_2[VO(C_2O_4)_2]$ solution (0.20 mol/l) with NH_4OH and $NaOH$ titrants (0.46 mol/l); 293 K

Fig. 5. Solubility curve of $(NH_4)_2V_4O_9$ in water depending on pH at 293 K
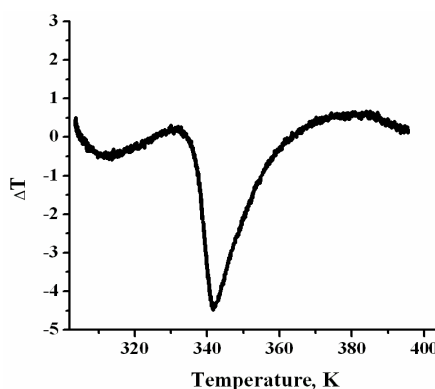
Fig. 6. Thermogravimetric differential thermal analysis of VO_2 obtained from the prepared $(NH_4)_2V_4O_9$

An important characteristic of the product is its solubility. Solubility of $(NH_4)_2V_4O_9$ in water considerably depends on pH (Fig. 5). For the fresh precipitate it was found 0.0176 mol/l at pH ≥ 8.8. After drying in argon atmosphere at $T = 383$ K its solubility in a distilled water significantly reduces to $5 \cdot 10^{-4}$ mol/l giving pH 6.3. $(NH_4)_2V_4O_9$ does not dissolve in 95.6% ethanol.

It should be noted that the product is X-ray amorphous regardless of the drying conditions in the temperature range from 323 to 383 K in an inert atmosphere during 2 h.

The density of the product dried at 383 K is (2.1 ± 0.1) g/cm³. Apparent density is 1.1 g/cm³.

After the heat treatment of $(NH_4)_2V_4O_9$ by the technique described in [29] pure vanadium(IV) oxide is obtained that is confirmed by the distinct endothermic peak on its DTA at the temperature of 341 K which corresponds to the typical vanadium dioxide semiconductor-metal transition.
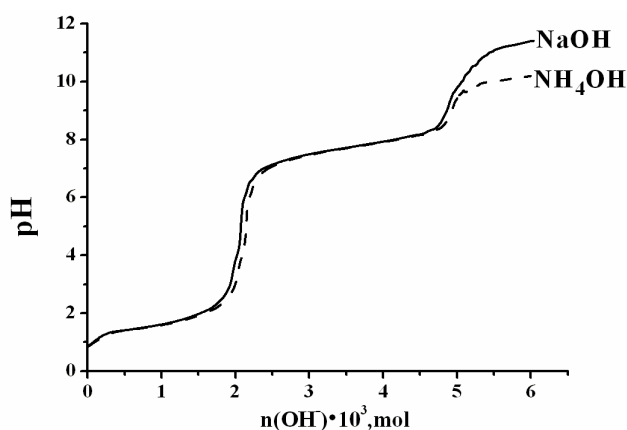
4. Conclusions

As a result of the work the four-stage method of production of the chemically pure precursor of vanadium dioxide was proposed. The first stage is V_2O_5 reduction with $H_2C_2O_4$ in aqueous medium which gives oxovanadium(IV) solution $H_2[VO(C_2O_4)_2]$. Activation energy of this reaction $Ea = 73.0$ kJ/mol and logarithm of pre-exponential factor of the Arrhenius equation $\ln A = 19.0$ were found. The second stage is the product deposition, identified as $(NH_4)_2V_4O_9$, by adding concentrated 30% solution of ammonia to oxovanadium(IV). Then the precipitate should be rinsed and separated from the solution by centrifugation. Drying in an inert atmosphere at 383 K is obligatory for storing the salt since the presence of water promotes rapid oxidation of vanadium to the pentavalent state. Enthalpy of formation $\Delta H^0_f(NH_4)_2V_4O_9 = -3494.5$ kJ/mol was found experimentally. Solubility of the fresh precipitate at

pH > 8.8 is 0.0176 mol/l and it increases significantly with pH decrease. Solubility of dried $(NH_4)_2V_4O_9$ at 383 K is $5 \cdot 10^{-4}$ mol/, giving pH 6.3. The density of the product dried at 383 K is (2.1 ± 0.1) g/cm^3, apparent density is 1.1 g/cm^3. It is shown that the product is X-ray amorphous. After the heat treatment at temperatures above 1073 K $(NH_4)_2V_4O_9$ decomposes to vanadium(IV) oxide, which has a typical semiconductor-metal transition at the temperature of 341 K.

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СИНТЕЗ ТА ФІЗИКО-ХІМІЧНІ ВЛАСТИВОСТІ ТЕТРАВАНАДАТУ АМОНІЮ ДЛЯ ОТРИМАННЯ VO₂

Анотація. *Для створення технологічного процесу одержання діоксиду ванадію внаслідок термічного розкладання розроблено спосіб синтезу солі високодисперсного ванадію(IV) як прекурсору. Спосіб включає в собі взаємодію п'ятиоксиду ванадію з щавлевою кислотою в розчині, який дає проміжний розчин оксованадію, подальше осадження продукту (амонію тетраванадату) при додаванні гідроксиду амонію до оксованадію, промивання та висушування продукту. З використанням фотометрії і потенціометричного титрування проміжний продукт був ідентифікований як $H_2[VO(C_2O_4)_2]$, а кінцевий продукт як $(NH_4)_2V_4O_9$. Знайдено кінетичні константи та енергію активації лімітуючої реакції ($E_a = 73.0$ кДж/моль), а також стандартну теплоту утворення продукту ($\Delta H^0_f = -3494.5$ кДж/моль), його розчинність і щільність. Показано, що після високотемпературного оброблення речовина перетворюється в діоксид ванадію високої якості з типовим переходом напівпровідник-метал.*

Ключові слова: *діоксид ванадію, тетраванадат амонію, синтез, кінетика, фізико-хімічні властивості.*