

Досліджено процес одержання оксометансульфоната цирконію (IV) шляхом взаємодії метансульфонової кислоти ($\text{CH}_3\text{SO}_3\text{H}$) (МСК) з цирконій(IV) оксокарбонатом ($\text{ZrOCO}_3 \cdot n\text{H}_2\text{O}$), вивчені його основні фізико-хімічні та технологічні властивості. Проведення досліджень було обумовлено відсутністю даних по хімії цього класу органічних сполук цирконій(IV) та їх можливого застосування в сучасному матеріалознавстві.

Методами елементного, рентгенофазового, термічного та ІЧ-спектроскопічного аналізу підтверджено, що продуктом взаємодії цирконію(IV) оксокарбонату ($\text{ZrOCO}_3 \cdot n\text{H}_2\text{O}$) з метансульфоновою кислотою є цирконію(IV) оксометансульфонат складу $\text{ZrO}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$.

Встановлено, що синтезований оксометансульфонат цирконію(IV) представляє собою білий кристалічний порошок, добре розчинний у воді і слоборозчинний в етанолі та ізопропиловому спирті. На повітрі поглинає вологу. Термічно розкладається в інтервалі температур 390–410 °С з утворенням низькотемпературної кубічної модифікації діоксиду цирконію, яка при температурі вище 750 °С послідовно переходить в моноклінну структуру діоксиду цирконію. При термолізі оксометансульфонату Цирконію(IV) формуються нанодисперсні порошки діоксиду цирконію з розміром первинних часток 20–50 нм, які під дією дисперсійних сил агрегуються в агрегати 200–400 нм. Питома поверхня порошків визначена за методикою BET становить 32 м²/г. Показано, що водно-спиртові розчини $\text{ZrO}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ активно взаємодіють з твердими поверхнями, утворюючи надтонкі приповерхневі полімеризовані плівки, з яких при термічній обробці формуються поверхневі покриття з діоксиду цирконію. Таким чином, отримані нові дані щодо хімії комплексних сполук цирконію(IV). Показана перспективність застосування оксометансульфоната цирконію(IV) для потреб сучасного матеріалознавства

Ключові слова: метансульфонова кислота, метансульфонат, оксиметансульфонат цирконію(IV), комплексна сполука, нанокристалічні порошки, оксид цирконію, поверхневі плівки

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OBTAINING, STUDYING THE PROPERTIES, AND APPLICATION OF ZIRCONIUM(IV) OXYMETHANE- SULFONATE

V. Vereshchak

Doctor of Technical Sciences,
ProfessorDepartment of Technology of
Inorganic Substances and Ecology
Ukrainian State University of
Chemical Technology
Gagarina ave., 8, Dnipro,
Ukraine, 49005

E-mail: Vereschak@bigmir.net

1. Introduction

Obtaining new organic compounds of zirconium (IV) oxymethanesulfonate and their application to solve modern tasks of materials science is a promising field in the chemistry and technology of materials based on it [1]. This primarily relates to obtaining the nanodispersed oxide zirconium-containing powdered materials and ultra-thin film coatings for advanced equipment [2].

Currently available scientific developments are based on the application of complex organic compounds of zirconium [3].

The most common organic compounds of zirconium that are used to obtain the nanodispersed powders of zirconium dioxide, as well as film coatings, are alcoholates (ethoxide and propoxides), zirconium(IV) glycerates and acetylacetonates [4, 5].

The main disadvantage of these compounds as the precursors for obtaining nanodispersed powders and film coating is the awkwardness of organic ligands, which, at thermohydrolysis and thermal decomposition, leave carbon, etc., as well the complexity of technology for obtaining them and high production costs.

Thus, the synthesis of new organic compounds of zirconium(IV), which would be devoid, at least partially, of these problems, and could become promising precursors for obtaining the nanodispersed powders of zirconium dioxide, is a relevant task for modern materials science.

The alternative is the simple metallic-organic salts and complexes of methane sulfonic acid and other metals that are the products of the so-called “green chemistry” [6]. Methane sulfonates are characterized by great solubility in water and alcohols, relatively low cost, the possibility to form hetero-metallic complex compounds, low temperature of decomposition and high film-forming properties. These properties give reason to argue about the prospect of applying methane sulfonates to obtain ... in order to solve tasks in modern materials science.

2. Literature review and problem statement

The salts of methane sulfonic acid attracted attention of chemists after industrial implementation of the technology for obtaining methane sulfonic acid. In 1960s-70s, methane sulfonates for most elements were received; their primary

physical-chemical properties and possible scope of application were explored.

Papers [7] addressed all aspects of the application of methane sulfonates in applied electrochemistry. They showed high efficiency of employing methane sulfonates in electroplating, the cathode sedimentation of metals, and the anode obtaining of oxide film coatings.

Low temperatures of methane sulfonates decomposition, their affordability for industrial utilization make them the promising precursors to obtain the nanosized powdered oxides. Of particular interest is their application for obtaining the nanodispersed oxide powders of zirconium and its compounds.

Thus, paper [8] considered the chemical aspects related to obtaining the methane sulfonates of arsenic(III), antimony(III), and bismuth(III). Their chemical composition was established, as well as the thermochemical properties, and a possibility to form the hetero-metallic complexes of type $\text{Me}^1(\text{Me}^2\text{CH}_3\text{SO}_3)_3$ ($\text{Me}^1\text{-Cs}$; $\text{Me}^2\text{-As}$, Sb , Bi). However, the work did not provide data on obtaining the compounds of zirconium.

Articles [9, 10] addressed the obtaining of hexaaca aluminum methane sulfonate. Its structure was studied, as well as the chemical properties. The articles did not report the result of the further use of the obtained compounds.

Paper [11] examined obtaining germanium methane sulfonate ($\text{Ge}(\text{CH}_3\text{SO}_3)_2$). Its crystalline-chemical structure was explored; parameters of the lattice were given. However, the paper did not report the results for practical application of the synthesized compound.

Thus, there have been no data in the scientific literature on direct application of the methane sulfonate complexes as precursors for obtaining functional materials and film coatings.

No systematic research has been undertaken into obtaining, studying the physical-chemical properties and practical application of simple methane sulfonates of elements from group IV in the periodic system, specifically zirconium, titanium, and hafnium.

The prospects for obtaining and utilization of methane sulfonate complexes of zirconium(IV) as the starting precursors for receiving the nanosized powders of zirconium oxides were first outlined and demonstrated in papers [12–14].

Thus, the lack of systematic data on obtaining the methane sulfonate complexes and the practical application of methane sulfonates of elements from group IV in the periodic system, primarily zirconium(IV), allows me to argue about the relevance of research in this field.

3. The aim and objectives of the study

The study conducted set the aim to synthesize zirconium(IV) oxymethanesulfonate, to establish its physical-chemical characteristics, in order to use it as a precursor for obtaining the nanodispersed powders of zirconium dioxide, as well as zirconium-containing oxide coatings.

To accomplish the aim, the following tasks have been set:

- to choose a procedure for synthesis and to obtain the samples of zirconium(IV) oxymethanesulfonate;
- to identify its element, chemical, and phase composition;
- to obtain the nanodispersed powders of zirconium dioxide via the spraying thermolysis of aqueous solutions of zirconium(IV) oxymethanesulfonate;

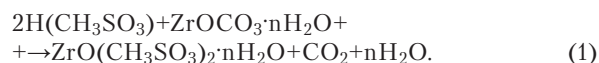
- to obtain the nanocrystalline zirconium-containing oxide coatings on aluminosilicate microspheres.

4. Materials and research methods applied in the experiments on obtaining, studying the properties, and using zirconium (IV) oxymethanesulfonate

4.1. Materials used in experiments

The starting materials used: methane sulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$), manufactured by BASF; zirconium (IV) oxocarbonate ($\text{ZrO}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$) (TU 6-09-3677-74), produced at Vilnohirsk GMK; distilled water; yttrium oxide (Y_2O_3).

The starting samples were obtained from the interaction between zirconium (IV) oxocarbonate and methane sulfonic acid:



Zirconium (IV) oxocarbonate was slowly added, at constant agitation, to the solution of methane sulfonic acid heated to 30–60 °C. The process was carried out until the complete dissolution of the calculated batch; the cooled solutions were filtered. Solid salt of methane sulfonate complex of zirconium(IV) was obtained through the crystallization until the complete removal of the solvent by vacuum evaporation.

The sequence of coating application included four stages:

- obtaining the methane sulfonate complexes of zirconium(IV);
- preparation of aqueous or aqueous-alcoholic solutions of zirconium methane sulfonate $\text{ZrO}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$;
- impregnation of aluminosilicate microspheres with solutions of salts of zirconium(IV) methane sulfonate;
- drying at a temperature of 100 °C;
- calcination at a temperature of 550–600 °C.

4.2. Research methods and equipment to obtain, study the properties and application of zirconium (IV) oxymethanesulfonate

Determining the composition and studying the properties of zirconium salt, formed in the interaction between methane sulfonic acid and zirconium carbonate, were carried out using the methods of physical-chemical analysis. The amount of carbon, hydrogen and sulfur was determined by an element analysis using the automated microanalyzer CHN; PE 2400 (Perkin Elmer, United States). The amount of metal was determined by a weight method in the form of ZrO_2 . The content of oxygen was calculated based on the difference. In addition, when determining the composition of zirconium(IV) oxymethanesulfonate, the data from thermal analysis and IR-spectroscopy were taken into consideration. The structure of products of synthesis was determined using the X-ray diffractometer DRON-2 (monochromatized $\text{Co-K}\alpha$ radiation); studying the process of thermal decomposition of the obtained synthesized compounds was carried out at the derivatograph Q-1500D (at a heating rate of 5 °/min) based on the system by F. Paulik, J. Paulik and L. Erdey, as well as by the method of differential scanning calorimetry (DSC) (NETSTAZSCH STA, 449F1, atmosphere: air/argon, a heating rate of 1 °/min). The structure and particle size of the obtained powders were explored using the methods of translucent electron microscopy (TEM) at the electron microscope JEM-2800 made by JOEL, Japan. The magnitude of specific surface was determined by a BET

method (Quantachrome 4200e) based on the low-temperature of nitrogen adsorption.

5. Results of research into obtaining, studying the properties and application of zirconium(IV) oxymethanesulfonate

Results of the physical-chemical analysis are given in Table 1.

Table 1

Results of the elemental analysis of zirconium(IV) oxymethanesulfonate

	Zr	C	H	S	O
Experimental data on zirconium(IV) oxymethanesulfonate, % by weight	24.69	6.49	3.79	17.34	47.65

Based on the elemental analysis, a chemical formula for the derived compound can be represented as zirconium(IV) tetra hydro oxymethanesulfonate – $ZrO(CH_3SO_3)_2 \cdot 4H_2O$.

The synthesized zirconium(IV) tetra hydro oxymethanesulfonate is a white, relatively hygroscopic finely-crystalline substance with specific weight, which, based on data from the pycnometric study, is equal to 2 g/cm^3 . The compound is relatively well dissolved in water, partially – in ethanol and isopropyl alcohols. At evaporation, a solution of methane sulfonate is exposed to the polymerization processes (similar to zirconium nitrate), forming viscous consistencies that are easily applied and which demonstrate good adhesiveness to a metallic and dielectric (oxide ceramic) surface. In accordance with data from the elemental analysis, a chemical formula for the obtained zirconium(IV) oxymethanesulfonate can be recorded as $ZrO(CH_3SO_3)_2 \cdot 4H_2O$.

In order to confirm the chemical composition of the derived compound of zirconium(IV) oxymethanesulfonate, and to establish its basic physical-chemical characteristics, the obtained samples were examined using the X-ray structural, thermal analyses, as well as IR-spectroscopy.

Fig. 1 shows a diffractogram of the product from the interaction between MSA and zirconium oxycarbonate.

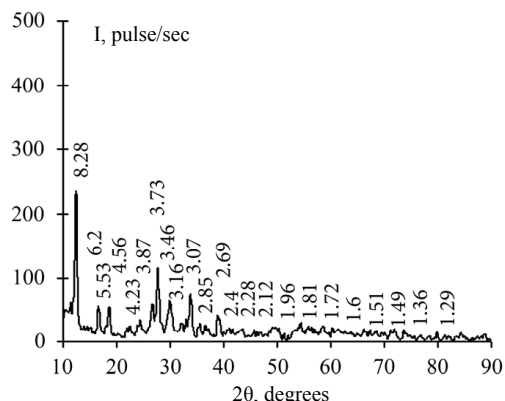


Fig. 1. Diffractogram of the product from the interaction between MSA and zirconium(IV) oxocarbonate (Cu- K_{α} -radiation)

Fig. 2 shows the observation IR-spectrum of samples of the product from the interaction between MSA and zirconium(IV) oxocarbonate.

The wave numbers for the maxima in absorption bands of HCH_3SO_3 , $Sb(CH_3SO_3)_3$, and $ZrO(CH_3SO_3)_2 \cdot 4H_2O$ are given in Table 2.

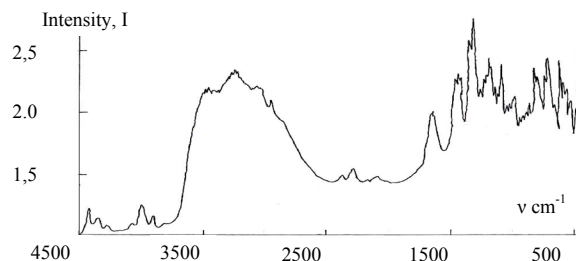


Fig. 2. Observation IR-spectrum of zirconium (IV) oxymethanesulfonate

Table 2

Wave numbers for the maxima of absorption bands CH_3SO_3H [14], $Sb(CH_3SO_3)_3$ [8], $ZrO(CH_3SO_3)_2 \cdot 4H_2O$

No.	Assignments	Chemical compound		
		CH_3SO_3H [14]	$Sb(CH_3SO_3)_3$ [8]	$ZrO(CH_3SO_3)_2 \cdot 4H_2O$
1	OH stretch	3,582.3 (sh) ^d ; 3,579.4	–	3,510; 3,448.18
2	CH_3 anti-symmetric stretch	3,204.5	–	3,232.39
3	CH_3 anti-symmetric stretch	3,1885	–	3,185.88
4	CH_3 symmetric stretch	3,047.0	–	3,036
5	CH_3 anti-symmetric deformation	1,434.0	–	1,441
6	CH_3 anti-symmetric deformation	1,422.1	–	1,417.5
7	SO_2 anti-symmetric stretch	1,397 (sh) ^d ; 1,393.4; 1,377.4 ⁶	1,260 m; 1,200 s. br	1,340; 1,295
8	CH_3 symmetric deform.	1,332.8	–	–
9	SO_2 symmetric stretch	1,199(sh) ^d ; 1,193.6	1,065 m; 1,055 m	1,181
10	S–OH bend	1,118.3	–	1,115.59
11	CH_3 rock	975.3	–	992.73
12	CH_3 rock	967.0	–	965.54
13	S–O stretch	835.5 (sh) ^d ; 832.5; 822.4 ^C	–	845.34; 817.45
14	C–S stretch (S– CH_3)	746.5; 741 T	795 m	798.4; 781.07; 772.81; 743.19
15	SO_2 deformation	526.9	560 m; 540 m; 515 m	542.94; 520.79
16	SO_2 wag	496.8	–	481.06
17	SO_2 rock	454.4	350 m; 330 m	466.19
18	V (Me-O)	–	–	594.37; 580.07; 542.94; 520.79; 481.06. 466.19

Since the formed salt of zirconium(IV) oxymethanesulfonate is thermally unstable, the analysis of the processes that proceed during thermal decomposition of this salt involved the method of differential scanning calorimetry. Thermal decomposition of the resulting sample, as demonstrated by the DSC-gram (Fig. 3), proceeds in several stages, which is registered by the DTG and DSC curves. An analysis of the totality of curves made it possible to reveal the complex character of this process.

Separate stages in the process of thermal decomposition of zirconium oxymethanesulfonate, as well as their thermal characteristics, are given in Table 3.

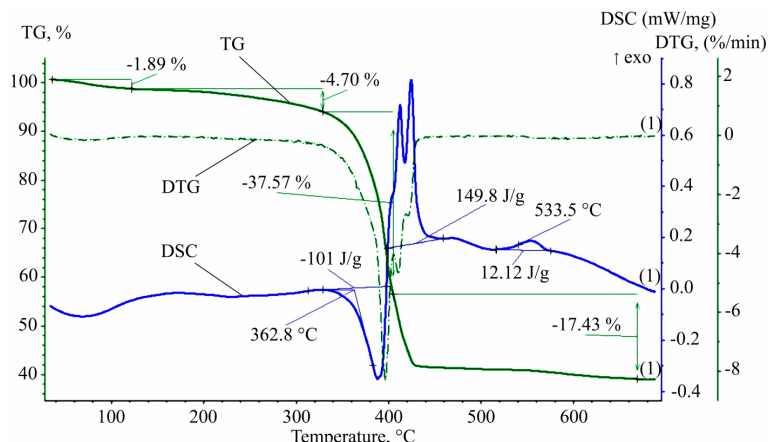


Fig. 3. TG, DTG, DSC – curves of thermal decomposition of $ZrO(CH_3SO_3)_2 \cdot 4H_2O$

Table 3

Temperature intervals and values for thermal effects at the stage of decomposition of $ZrO(CH_3SO_3)_2 \cdot 4H_2O$ in the environment of air

No.	Mass loss Δm , %	Temperature interval, °C	Thermal effect, ΔH (J/g)	Probable chemical process
1	1.89	50–150 °C	–	–0.5 H_2O
2	4.7	150–300 °C	–	–1.5 H_2O
3	37.57	362.8 °C	–101 J/g	–1.5 (CH_3SO_3H) – –2 H_2O [$SO_2 + CO_2$]
4	17.43	405–440 °C	149.8 J/g	–0.5 (CH_3SO_3H) [$SO_3 + H_2O + CO_2$]
5	–	535.5 °C	12.12 J/g	am- $ZrO_2 \rightarrow k-ZrO_2$

The obtained compounds of zirconium methane sulfonate were used as a precursor for receiving the nanopowders of zirconium dioxide and the ultra-thin oxide films of zirconium on aluminosilicate microspheres.

In order to obtain the powders, a method of sprayed thermolysis of water solutions was applied followed by the disaggregation of the derived products of pyrolysis in a bead-mill. TEM images of the obtained powders are shown in Fig. 4.

Deposition of films was performed using a method of impregnating the aluminosilicate microspheres with water or water-alcohol solutions of $ZrO(CH_3SO_3)_2 \cdot 4H_2O$ followed by drying and calcination at a temperatures above 500 °C.

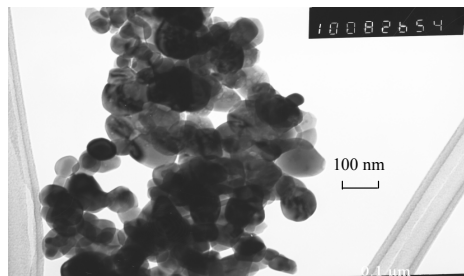


Fig. 4. TEM images of the zirconium dioxide powders obtained from an aqueous solution of $ZrO(CH_3SO_3)_2 \cdot 4H_2O$ using a spray thermolysis method

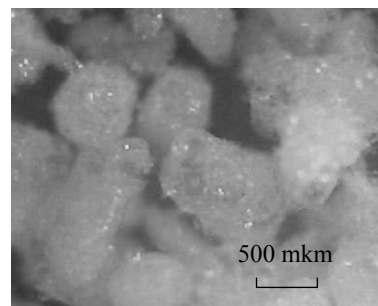


Fig. 5. Structure of the aluminosilicate microspheres impregnated with a solution of $ZrO(CH_3SO_3)_2 \cdot 4H_2O$ after the stage of calcination

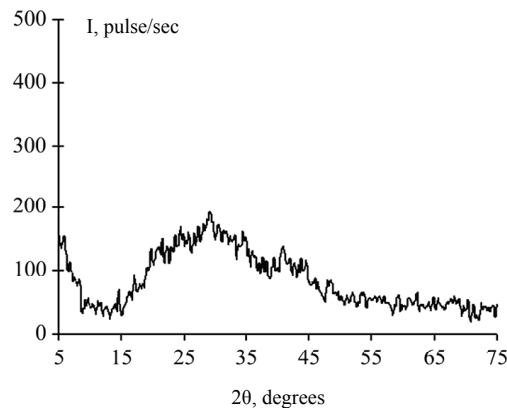


Fig. 6. X-ray diffractogram of the starting aluminosilicate microspheres

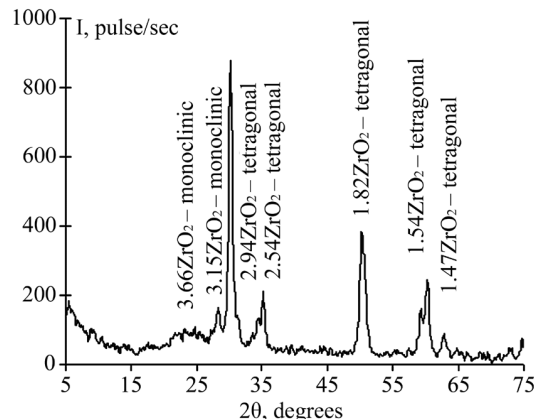


Fig. 7. X-ray diffractogram of aluminum silicate spheres, impregnated with a solution of $ZrO(CH_3SO_3)_2 \cdot 4H_2O$ after the stage of calcination

6. Discussion of results of research into obtaining, studying the properties and application of zirconium (IV) oxymethanesulfonate

The diffractogram in Fig. 1 shows that the product from the interaction between MSA and zirconium (IV) oxymethanesulfonate is a weak crystallized structure with the magnitudes of interplane distances typical for such salts of zirconium as its oxychloride or basic sulfate. The presence of the amorphized component in the diffractogram indicates the existence in the composition of the obtained compound of the crystalline and free water. This is confirmed by data from IR spectroscopy, which are given in Fig. 2.

Comparison of the infrared spectra of MSA IR-spectra from the obtained salt and antimony (III) methane sulfonate (Table 2) reveals that the resulting compound has the bands of fluctuations characteristic of MSA and, accordingly, $\text{Sb}(\text{CH}_3\text{SO}_3)_3$. Based on data on the infrared spectrum of $\text{ZrO}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, the most intense are the bands of 3,500–3,400 cm^{-1} , which probably belong to the fluctuations of water molecules, while the intense band of 3,530 cm^{-1} is probably related to fluctuations of the bound hydroxyl groups. There is also a band of deformation water fluctuations with a frequency of 1,620 cm^{-1} . Along with the frequencies of water fluctuations, the IR spectra of the synthesized product revealed, in the region of 1,300–900 cm^{-1} , the bands with frequencies of 990; 1,010; 810; and 780 cm^{-1} . Absorption in the region of 1,000–1,100 cm^{-1} could be interpreted as the deformation fluctuations of hydroxyl groups $\text{Me}-\text{OH}$, which form the bridge bonds between the two atoms of metal $\text{Me}-\text{O} \dots \text{Me}$. Bands in the low-frequency region of 594.37; 580.07; 542.94; 520.79; 481.06, 466.19 cm^{-1} are typically characteristic of the bond $\text{Me}-\text{O}$. The crystalline structure of zirconium(IV) oxymethanesulfonate probably represents the endless chain structures, in which the atoms of zirconium are interconnected by the bridge OH-groups, while the methane sulfonate ligand is coordinated by the positively charged hydroxocomplex of zirconium.

Thermal decomposition of zirconium(IV) oxymethanesulfonate proceeds in several stages (Fig. 3, Table 3), which is registered along the curves of TG, DTG, DSC. An analysis of the totality of curves (Fig. 3) has made it possible to reveal the complex character of thermal decomposition of zirconium(IV) oxymethanesulfonate.

In the temperature range of 50–200 °C, as demonstrated by the curve of DSC, $\text{ZrO}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ loses 0.5 molecules of water. An increase in temperature to 300 °C leads to the loss of 1.5 molecules of H_2O . The loss of mass with further heating (endothermic peak at 378 °C and two exothermic peaks at 380 °C and 390 °C), are predetermined by the release of water from inside the sphere, methane sulfonic acid and its thermal decomposition to oxides of carbon and sulfur anhydride.

The product of thermolysis of zirconium(IV) oxymethanesulfonate is amorphous zirconium dioxide, which, at temperatures above 500 °C, crystallizes in a cubic structure, followed by the further polymorphic transition at temperatures above 800 °C to a monoclinic modification.

Low temperatures of decomposition of zirconium(IV) oxymethanesulfonate make it an attractive precursor for obtaining the nanosized powders of zirconium dioxide.

Study into the process of obtaining the nanosized powders of zirconium dioxide was based on the method of spray thermolysis. It was shown (Fig. 4) that at the thermolysis of zirconium(IV) oxymethanesulfonate there form the nanodispersed powders of zirconium dioxide whose size of primary particles is 20–50 nm, which, under the influence of dispersion forces, agglomerate into aggregates of 200–600 nm. The specific surface of powders, determined based on a BET procedure, is 32 m^2/g .

It was established in the course of the study that water and water-alcohol solutions of zirconium(IV) oxymethanesulfonate demonstrate good film-forming and adhesive properties to both metallic and dielectric (ceramic) substrates, which made it possible to obtain various protective and functional coatings based on them.

The deposition of films was carried out by applying a method for impregnating aluminosilicate microspheres with water or water-alcohol solutions of zirconium(IV) oxymethanesulfonate followed by drying and calcination at a temperature above 500 °C.

As shown by the results of X-ray structural analysis, the starting aluminosilicate microspheres are the amorphized structures (Fig. 6). At appropriate treatment of their surfaces with solutions of zirconium(IV) oxymethanesulfonate, and at conducting heat treatment, a thin layer of crystalline zirconium dioxide forms at the surface of aluminosilicate spheres (Fig. 7). The size of crystals in the surface layer of zirconium dioxide, calculated based on data from an X-ray analysis, is 10–20 nm. The formation of such structures on porous carriers is of practical importance in terms of developing effective and cheap catalysts and adsorbents.

Thus, the result of this study is the new data acquired on the organic compounds of zirconium(IV). The synthesized zirconium(IV) tetra hydro oxymethanesulfonate due to its physical-chemical properties is a promising precursor for obtaining the nanodispersed oxides of zirconium, as well as surface film coatings, which is extremely important for modern materials science. In order to extend the scope of application of zirconium (IV) oxymethanesulfonate, it is necessary to conduct studies into its use for obtaining the zirconium-containing functional and structural ceramics.

It is known that the conditions of synthesis significantly affect characteristics of both the starting compounds and the products of thermolysis. Therefore, further research might include examining the effect of original raw materials, conditions of synthesis, as well as conditions for thermal decomposition, on the properties of the obtained zirconium oxides.

One of the shortcomings of this study is the absence of data on parameters for the crystal lattice of the synthesized compound, kinetic data and the mechanism of thermal decomposition of zirconium(IV) oxymethanesulfonate. The further development of a given research could aim at solving these issues and to synthesize methane sulfonates of elements from group IV in the periodic system, to study their physical-chemical properties and practical application.

7. Conclusions

1. Based on the elemental analysis, it was established that the interaction between zirconium(IV) oxocarbonate

($ZrOCO_3 \cdot nH_2O$) and methane sulfonic acid yields zirconium (IV) tetra hydro oxymethanesulfonate with composition $ZrO(CH_3SO_3)_2 \cdot 4H_2O$.

2. It was established that the thermolysis of $ZrO(CH_3SO_3)_2 \cdot 4H_2O$ proceeds in line with a complex chemical mechanism and terminates at temperatures of 540–550 °C with the formation of the nanocrystalline powders of zirconium dioxide with a tetragonal or cubic structure whose size of primary particles

is 20–30 nm, the size of aggregates is 50–200 nm, and specific surface of 32 m²/g.

3. It was shown that the water and water-alcohol solutions of zirconium(IV) oxymethanesulfonate demonstrate good film-forming and adhesive properties both to the metallic and dielectric materials, which makes it possible to obtain the nanocrystalline zirconium-containing oxide coatings based on them.

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