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OBTAINING OF ZIRCONIUM SILICATE MATERIALS OF AEROGEL TYPE FROM AQUEOUS SOLUTIONS OF Na_2SiO_3 AND ZrOCl_2 SALTS

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Aerogels are gels in which the liquid phase is completely replaced by a gaseous one. They form a new class of solids with a very low density, a large specific surface area and high porosity, which opens up wide possibilities for their practical application. $\text{ZrO}_2\text{-SiO}_2$ aerogels, due to the strong binding energy of Zr-O-Si, very low thermal conductivity, and the presence of acid and basic centers, exhibit excellent properties like aerospace heat insulators, selective sorbents, catalysts, and catalyst supports for high-temperature reactions. The traditional way of obtaining aerogels is formation of a branched, three-dimensional, irregular network of wet gels by sol-gel synthesis from alkoxides of elements, aging of gels, replacement of intermicellar water by organic liquids with low surface tension and careful removal of the solvent by drying under supercritical conditions or under ambient pressure. But alkoxides of the elements are expensive and toxic, drying at elevated pressures requires special equipment and is also expensive and energy-intensive, and drying at atmospheric pressure requires complicated and lengthy gel modifications. In this work, the task was posed, on the basis of the direct method of large-scale sol-gel synthesis of highly porous, nanostructured, spherically granulated zirconium silicates from aqueous solutions of cheap, accessible salts, to obtain materials of aerogel type, without resorting to lengthy equipment and chemically complex methods of processing the resulting hydrogels. The gels were prepared by forming a zirconium carbonate complex from aqueous solutions of ZrOCl_2 and K_2CO_3 and its subsequent interaction with a Na_2SiO_3 solution by their coagulation in a drop. The obtained strong spherical granules of $\text{ZrO}_2 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ hydrogel were thoroughly washed from impurities with distilled water and subjected to hydrothermal treatment for various times, followed by decantation with ethanol mixed with benzene or alkohermal treatment in this mixture in tightly closed containers at supercritical temperature for ethanol. The heat resistance of the samples was determined by calcining them in air at high temperature. Using SEM, XRD, and N_2 adsorption / desorption methods, it has been found that the amorphous Zr-Si materials obtained containing 45 wt. % ZrO_2 have a specific surface area of more than $500 \text{ m}^2/\text{g}$, pore volume $> 2 \text{ cm}^3/\text{g}$, average pore diameter of $\sim 18 \text{ nm}$, wide mesopores with a diameter of $\sim 28 \text{ nm}$, bulk density less than $0.3 \text{ g}/\text{cm}^3$, which typical for aerogels based on oxides of metal and silicon, and exhibit high thermal stability.

Keywords: $\text{ZrO}_2\text{-SiO}_2$ aerogels, sol-gel synthesis, supercritical drying, alkohermal treatment, mesoporous materials

INTRODUCTION

The aerogels are gels in which the liquid phase is completely replaced by a gaseous one. They form a new class of solids having a very low density, from 0.004 to $0.5 \text{ g}/\text{cm}^3$, large specific surface area and high porosity, with cavities, occupying more than 50 % of the bulk. In addition, their state is thermodynamically metastable. These unique properties of aerogels open up wide possibilities for their practical applications as heat and sound insulators, heat and energy accumulators, cosmic dust absorbers and radioactive particles, components of electrochemical systems, glasses, sorbents, ion exchangers, heterogeneous catalysts, photocatalysts, etc. [1–6].

By their chemical nature, aerogels are classified as organic, inorganic and hybrid. Among them, ZrO_2 aerogel is one of the most important materials, due to its very high melting point, the lowest thermal conductivity among metal oxides, and the presence of both acidic and basic active centers [7]. But heating of a pure single-component ZrO_2 aerogel leads to the degradation of its nanopores and a significant decrease in surface area due to the ongoing phase modification of ZrO_2 , from amorphous to tetragonal and monoclinic [8]. The stabilization of the structure of the ZrO_2 aerogel by introducing silicon dioxide into its composition allows us to create $\text{ZrO}_2\text{-SiO}_2$ materials showing excellent properties as aerospace heat insulators

[9] and carriers for high temperature reaction catalysts [10].

The first and key step in the preparation of aerogels is the formation of a three-dimensional, highly porous, irregular, branched network of wet gels, which usually forms during the condensation of colloidal particles. Most aerogel syntheses follow this sol-gel route, with two options: a) hydrolysis and condensation reactions are initiated in aqueous solutions of ionic precursors; b) precursor molecules in an organic solvent are transformed into species capable of undergoing condensation [1]. The first silicate aerogels were obtained on the basis of an aqueous solution of water-glass - Na_2SiO_3 , by its interaction with hydrochloric acid to form a gel of silicic acid, followed by the replacement of water with ethanol and drying at supercritical temperature [11]. However, this method was lengthy and also required thorough washing of the gels from foreign ions of the resulting NaCl salt. Hydrolysis and condensation of alkoxides of elements in alcohol-water solutions turned out to be relatively simple and controlled processes with the rapid formation of gels without the need for extraction, filtration and water replacement [12], which made it possible to reduce the time of production and processing of aerogels from week to day. Therefore, this method of producing oxide nanocomposites is widely distributed and is most often used [2]. Since the reactivity in the hydrolysis reactions of metal alkoxides is much higher than that of alkoxysilanes, the processes of their joint gel formation must be carefully monitored. This is achieved by the use of modifying or ligand-forming agents and acidic and / or basic catalysts [1–5]. Under their action, gels with a uniform distribution of components, a large specific surface area and an adjustable pore size distribution are formed. At this stage, there the basic properties of the final material.

But metal alkoxides, and in particular zirconium, are usually expensive and toxic. Therefore, their replacement with aqueous-alcoholic solutions of inorganic salts – $\text{ZrO}(\text{NO}_3)_2$ [13, 14], ZrOCl_2 and ZrCl_4 [15, 16], in the process of sol-gel synthesis together with silicon alkoxides, is considered a progressive method for producing ZrO_2 - SiO_2 aerogels. This method allows for inexpensive, easy to handle procedures with a short gelation

time and to obtain products with a high surface area.

The second stage of preparation of aerogels is the aging of the obtained wet gels in the mother liquor while controlling the pH, temperature and time [17–19]. During this lengthy process, the unreacted small oxide groups dissolve and precipitate between the larger particles of the polymer chain. This strengthens the structure of the gel and prepares it for the next critical stage of obtaining aerogel – the drying process [3].

The capillary compressive forces of the gel during drying are determined by the bond strength of the particles in the gel framework and the surface tension of the pore fluid, which shows the highest values for water. Therefore, the pore water of the gel should be completely replaced with an organic liquid with a low surface tension. This is followed by the stage of high-temperature or low-temperature supercritical drying [3, 5, 20, 21]. In the first case, the gel with the solvent is placed in the autoclave and the temperature and pressure in it are increased above the critical point of the solvent, while the liquid passes into a gaseous state and then is discharged from the autoclave without violating the integrity of the gel structure. In the second case, the liquid is displaced from the pore space by means of CO_2 , the compressed to its critical liquid state. However, these drying methods are energy-intensive and expensive due to the need to use high pressure and related equipment.

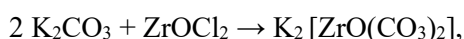
Therefore, in recent years, the method of producing aerogels using drying at atmospheric pressure has been intensively developed. This method consists in the phased replacement of the gel pore liquid by a liquid with an ever lower surface tension and drying at their subcritical temperature and ambient pressure. Especially often, this treatment is used in the development of more advanced methods for producing aerogels from cheap and affordable sodium silicate instead of expensive, toxic and flammable alkoxysilanes, which cannot be used in mass commercial production. However, the necessity of using cation exchange, co-precursors from organo-silanes and additional silylation of the gel makes these methods quite expensive and complicated [22–24].

In this work, the task was posed, on the basis of the previously developed method of direct

large-scale sol-gel synthesis of highly porous, nanostructured, spherically granulated zirconium silicates from aqueous solutions of cheap, available salts - sodium silicate and zirconium oxychloride [25], to try to obtain materials such as aerogels without resorting to lengthy apparatus and chemically complex processing methods for the resulting hydrogels.

EXPERIMENTAL PART

The method used to obtain the mixed oxide $\text{ZrO}_2\text{-SiO}_2$, according to the patent [25], is based on conducting of the following reactions:



It is known [26] that, in aqueous solutions, the addition of Zr(IV) salts to an excess of alkali metal or ammonium carbonates leads to the formation of metastable anionic carbonate complexes of Zr(IV), which can serve as precursors for the synthesis of new zirconium based materials. Treatment of such complexes with an aqueous solution of sodium metasilicate causes gel formation [27].

An additional application of droplet coagulation technology [28] ensured the production of spherically granulated $\text{ZrO}_2\text{-SiO}_2$ hydrogel [25]. The process was carried out as follows.

Under stirring, a 2M ZrOCl_2 solution was gradually added to a 5M K_2CO_3 solution with the formation of a zirconium carbonate complex. Its solution at a rate of 164 ml/min. and a sodium metasilicate solution, with a concentration necessary to obtain a Zr/Si ratio of 0.6, was fed at a rate of 100 ml/min into a flow reactor in which the solutions were mixed to form a mixed sol of zirconium oxyhydrate and silicic acid. A jet of sol was directed into a column filled with two layers of liquids. The top layer is undecane, and the bottom is running tap water. During the passage of the undecane layer (1.0–1.5 m), the sol stream was broken into separate drops, which in 3–5 s turned into durable spherical granules of Zr-Si hydrogel. They were transferred with water and first fell on a sieve, and then into a container, where they were washed with distilled water from alkalis, salts and traces of undecane, treated with a solution of NH_4OH and washed again with water until neutral.

External moisture was removed from a part of the obtained hydrogel spheres and dried at 130 °C for further structural and elemental analysis of initial sample N 1 (Table 1). The other four parts of the spherical hydrogel were placed in four tightly closed massive cylindrical forms with a volume of 40 cm³ made of stainless steel, filling their volume almost completely. Then forms were heated in a muffle furnace in different liquid media at a gradual increase of its temperature during various period of time (samples 2–5, Table 2).

Sample N 2 was subjected to hydrothermal treatment (HTT) for 5 h at 270 °C. It was shown [29] that the continuous dissolution and reprecipitation of hydroxides during HTT leads to the production of materials with a more defect-free structure, which can withstand the loss of surface area upon exposure to high temperatures. Therefore, this treatment can replace the long stage of aging of the hydrogel.

Samples N 3 and N 4 were acted upon by the HTT for a shorter time – 2 h. After that, the samples were removed from the molds and washed thoroughly – first with ethanol and then with anhydrous ethanol (N 3) and its mixture with 2 % benzene (N 4) and left in these liquids for 6 h. Hydrogel N 5 was not subjected to HTT, and after washing it in a similar way, it was left in ethanol-benzene medium for 12 h and then placed in a closed form and subjected to alkothermal treatment (ATT) in this mixture at 270 °C for 5 h. After the described treatment, all the samples were dried at 130 °C, their bulk density was measured by weighing and then they were calcined in air at 600 °C. The texture of the samples was determined before and after calcination.

The isotherms of adsorption / desorption of N_2 for the traditional analysis of the texture of the samples were obtained according to the standard procedure after vacuum treatment at 150 °C on an ASAP 2405N Micromeritics instrument. Pore size distribution was calculated using the density functional theory (DFT).

An analysis of the microstructure and elemental composition of the sample N 1 was determined by scanning electron microscopy (SEM) using a JEOL JSM 7001F scanning electron microscope with an microanalyzer system.

X-ray diffraction patterns of the studied samples were recorded on a DRON-4-07

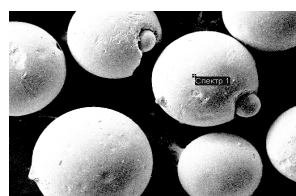
diffractometer in the $\text{CuK}\alpha$ radiation of the anode line with a Ni filter in the reflected beam with Bragg – Brentano geometry.

RESULTS AND DISCUSSION

From the data given in Table 1 it is seen that the amount of zirconium dioxide included in the

structure of the obtained gel is lower than it was in the synthesis ash and the real Zr/Si ratio in it is ~ 0.45 . Spherical granules are well defined and have a size of 200–700 μm .

Table 1. Surface topography and distribution of elements for a sample of Zr-Si



SEM image Zr-Si hydrogel

Element	Weight %	Atomic %	Compounds, %	Formula	Ratio of elements
Si K	24.41	23.09	52.21	SiO_2	Zr/Si = 0.45
Zr L	35.39	10.29	47.78	ZrO_2	Si/Zr = 2.24
O	40.2	66.66			

Table 2. The texture parameters of granulated Zr-Si gels after various treatment

N	Preliminary processing	* S_{BET} , m^2/g	V_{nop} , cm^3/g	D_{pores} DFT, nm	D_{pores} average, nm	ρ , g/cm^3	S_{BET} , % losses
1	Drying at 130 °C (D)	389.3	0.25	2.504	2.62	1.33	
	Calcination at 600 °C (C)	219.9	0.16	4.88	2.88		43.51
2	**HTT - 5 h. (D)	517.5	0.60	5.68	4.61	1.05	
	HTT - 5 h. (D, C)	414.7	0.49	7.03	6.34		19.86
3	HTT - 2 h. Ethanol. (D)	540.8	1.15	9.42	8.54	0.40	
	HTT - 2 h. Ethanol. (D, C)	450.3	0.83	9.42	9.11		16.59
4	HTT - 2 h. Ethanol + benzine. (D)	549.1	1.98	25.24	14.39	0.26	
	HTT - 2 h. Ethanol + benzine. (D, C)	485.8	1.81	27.38	14.88		11.53
5	***ATT in ethanol with benzine - 5 h. (D)	511.0	2.26	27.38	17.68	0.22	
	ATT in ethanol with benzine - 5 h. (D, C)	494.3	2.14	27.38	18.30		3.27

* S , V , D , ρ – surface area, volume, diameter, bulk density,

** – hydrothermal treatment at 270 °C;

*** – alkothermal treatment at 270 °C.

Hydrothermal treatment and replacement of water in the pore space of a zirconium silicate hydrogel with “organic fluids” leads to a change in the form of adsorption isotherms of N_2 desorption (Fig. 1 *a*) and to the corresponding character of pore distribution (Fig. 1 *b*). The isotherm of the initial hydrogel, type IV, has an H2-type hysteresis loop [30] with a long horizontal section on the desorption branch characteristic of corpuscular systems of an indeterminate nature with narrow “throats” and various wider cavities. This structure is also confirmed by the calculation of the pore size distribution of the sample, showing the presence

of pores with diameters of ~ 1.4 , 2.7 and 4.8 nm, which is typical for micro/mesoporous systems. The HTT of the Zr-Si hydrogel within 5 h changes the shape of the hysteresis loop on its isotherm – the horizontal section on the desorption branch becomes shorter, which indicates a decrease in the difference between the diameters of the “throat” and “cavity” in the pore structure of the sample. In this case, the type of hysteresis loop H2 transforms into H1, which is typical for systems with a uniformly developed mesoporous structure. The calculation of the pore size distribution shows the presence of mesopores with a diameter of mainly 5.7 nm.

After 2 h HTT, replacing intermicellar water in Zr-Si hydrogels with dehydrated ethanol or its mixture with benzene leads to a narrowing of the hysteresis loops on the isotherms of the samples, indicating an additional equalization of pore sizes, their diameter increases, remaining within the mesopore range, and volume significantly

increased. Such structural changes reach the greatest degree after the ATT of gel (Table 2). At the same time, each successive stage of sample processing leads to a gradual decrease in the bulk density of the resulting material from 1.33 to 0.22 g/cm^3 .

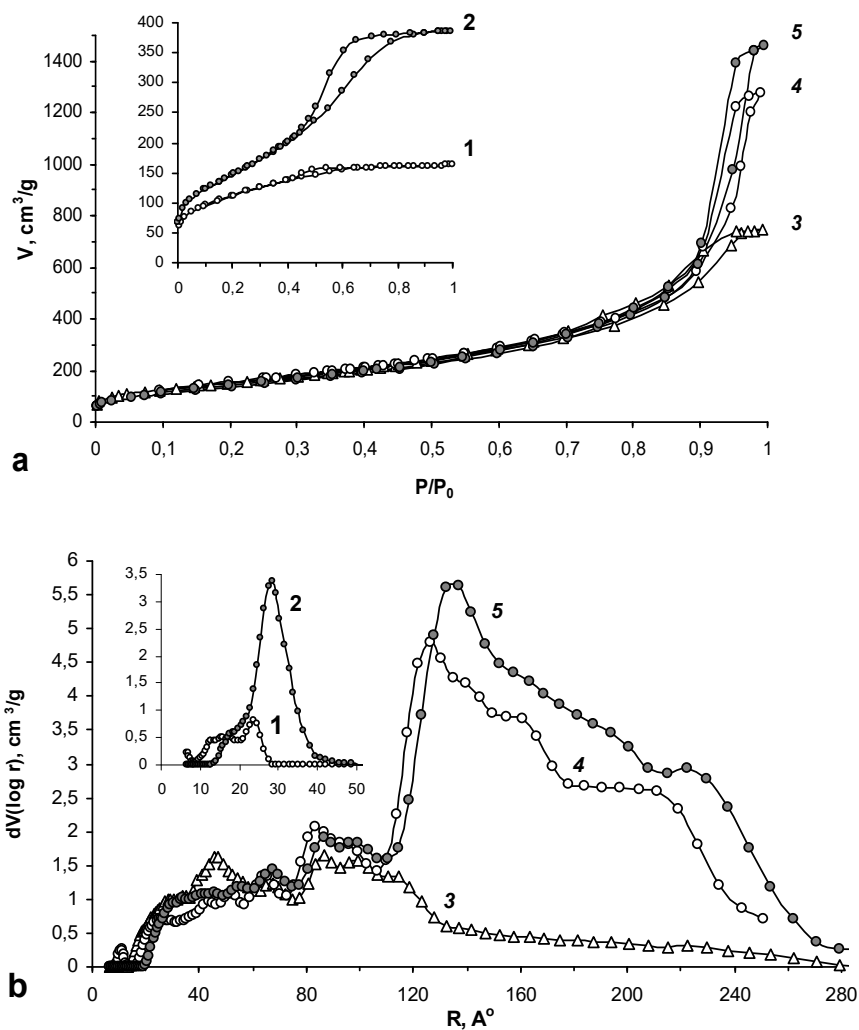


Fig. 1. Isotherms of N_2 adsorption-desorption (a) and the character of the DFT distribution pore by size radius (b) for Zr-Si samples: 1 – initial dried hydrogel, 2 – after HTT for 5 h at 270°C ; 3 – 2 h HTT and decantation with ethanol; 4 – 2 h HTT and decantation with ethanol with 2 % benzene; 5 – 5 h ATT in ethanol with 2 % benzene at 270°C

Comparison with the data of the scientific literature shows that, in the form of nitrogen adsorption/desorption isotherms, pore distribution, and texture parameters, the materials obtained are close to the published characteristics of aerogels. For example, in [13] $\text{ZrO}_2\text{-SiO}_2$ aerogels with a zirconia content of 50 wt. % were prepared from tetraethoxysilane (TEOS) and zirconyl nitrate dihydrate salt by

supercritical drying in ethanol. The values of texture parameters S_{BET} , V_{pores} and average D_{pores} , given after calcination of the sample at 500°C , are $547.9 \text{ m}^2/\text{g}$, $1.67 \text{ cm}^3/\text{g}$ and 6.3 nm , respectively. The authors of [13] carried out drying of the gel in an autoclave as described in detail in [2]. A wet gel coated with an ethanol layer in a stainless steel liner was placed in a volume autoclave with additional ethanol outside

the liner to create a critical volume of the mixture, and the autoclave was kept under supercritical conditions for ethanol – 270 °C and a pressure of 8.0 MPa.

In our work, when the ATT gel was in an ethanol-gasoline mixture, the liquid layer above the wet gel, which almost completely filled the volume of the metal form, did not exceed 0.5–1.0 cm, therefore the volume of the mixture could be insufficient for achieve the critical pressure of the mixture. But it was shown in [31] that SiO₂ aerogels with minimal shrinkage can be obtained under the pressures significantly lower than the critical pressure of the organic solvents used as pore liquids. The aerogel drying pressure can be reduced by increasing the initial gel strength. Heating silicate gels in organic solvents to their supercritical temperatures causes the gel network to rearrange, the surface of the aerogels is transesterified, becoming hydrophobic, more rigid and stable. In addition, the full filling of the drying container with wet gel [32] ensured a relatively fast ventilation of the supercritical fluid, preventing swelling and destruction of the gel monolith.

In [33], an aerogel was obtained from TEOS by a two-stage catalytic process during drying under ambient pressure by long periods of aging of the gel in ethanol, washing with *n*-hexane, modification with trimethylchlorosilane, again washing with *n*-hexane and drying at 50 °C. Calculating the texture parameters of the obtained material from an isotherm similar to those shown in Fig. 1 *a* (curves 4 and 5), the authors give the following values of S_{BET} , V_{pores} and average D_{pores} – 434 m²/g, 1.96 cm³/g and 18 nm, very close to the data us obtained, but the bulk density of the obtained silicate aerogel – 0.418 g/cm³ – turned out to be higher.

The thermal stability of the samples obtained in this work was evaluated by changing their texture after calcining in air to 600 °C, the shape of their isotherms and the nature of the distribution of pores changed little, the calculated quantitative texture parameters are given in Table 2. As can be seen, calcination reduces the specific surface area of the dried Zr-Si gel by almost 45 %. A preliminary HTT within 5 h strengthens the gel structure and more than doubles its thermal stability – the S_{BET} value decreases only by ~ 20 %. Additional gel decantation with ethanol, even with a shorter duration of the HTT action, within 2 h, leads to a

significant increase in pore volume and at the same time increases the thermal stability of the sample. The addition of 2 % benzene to the decantation mixture improves these parameters and leads to a significant expansion of mesopores. The alkothermal treatment of the gel in a mixture of ethanol and benzene for 5 h at 270 °C makes it possible to obtain the most thermostable sample with the largest volume and pore diameter.

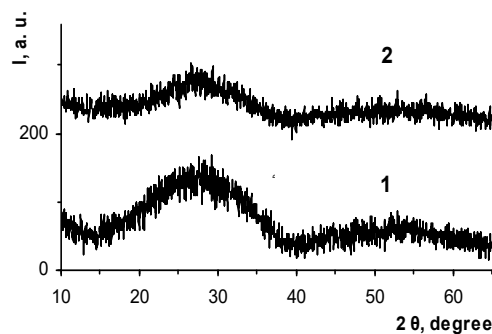


Fig. 2. X-ray diffraction patterns of ZrO₂-SiO₂ gels calcined at 600 °C in air: 1 – initial gel, 2 – gel subjected to preliminary ATT

The X-ray diffraction patterns of the initial sample and the final one subjected to ATT before calcining at 600 °C show only an amorphous halo (Fig. 2), which is typical for aerogels [2], which are usually amorphous. The absence of reflections of tetragonal zirconia t-ZrO₂ in our case is also consistent with the data of [34], which showed that the amorphous SiO₂ matrix, with its content of ≥ 50 % in the binary oxide ZrO₂-SiO₂, contributes to the preservation of the amorphous state of ZrO₂ to the calcination temperature mixed oxide up to 800 °C.

Thus, the study shows that by combining the HTT, ATT and decantation with organic liquids, it is possible to obtain materials with a structure similar to aerogels without using expensive hardware and chemically complex long-term methods for processing synthesized hydrogels of metallosilicates.

CONCLUSIONS

It has been shown that the use of the direct one-step sol-gel synthesis method from aqueous solutions of cheap and affordable salts – sodium metasilicate, zirconium oxychloride and potassium carbonate, supplemented by drop coagulation technology, allows for a short time to obtain strong spherically granular zirconium

silicates hydrogels that can serve as the basis for further preparation of aerogels. It has been found that strengthening the hydrogel structure by hydrothermal treatment promotes an increase in its surface area, pore volume and width, and more than doubles the thermostability of the sample upon calcination. Additional decantation with ethanol and, even more anhydrous ethanol with an admixture of gasoline, improves these parameters and also reduces the density of the

samples obtained, even with a shorter duration of their preliminary hydrothermal treatment. Alkothermal treatment of the sample in ethanol-benzene mixture leads to the production of the most thermostable amorphous zirconium silicate material with a density of $< 0.3 \text{ g/cm}^3$, having a specific surface area of more than $500 \text{ m}^2/\text{g}$, pore volume $> 2 \text{ cm}^3/\text{g}$, average pore diameter of $\sim 18 \text{ nm}$, and mesopores diameters $> 27 \text{ nm}$, characteristic of metal oxide silicate aerogels.

Одержання цирконійсилікатних матеріалів типу аерогелів з водних розчинів солей Na_2SiO_3 та ZrOCl_2

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Аерогелі – це гелі, в яких рідка фаза повністю замінена на газоподібну. Вони утворюють новий клас твердих речовин з дуже низькою густиною, великою питомою поверхнею та високою пористістю, що відкриває широкі можливості для їх практичного застосування. Аерогелі $\text{ZrO}_2\text{-SiO}_2$ завдяки великій енергії зв'язку Zr-O-Si , дуже низькій теплопровідності та наявності кислотних та основних центрів виявляють чудові властивості, такі як аерокосмічні теплоізолятори, селективні сорбенти, каталізатори та носії каталізаторів для високотемпературних реакцій. Традиційним шляхом отримання аерогелів є формування розгалуженої, тривимірної, нерегулярної мережі вологих гелів, методом золь-гель синтезу з алкоксидів елементів, старіння гелів, заміна інтерміцелярної води на органічні рідини з низьким поверхневим натягом і обережне видалення розчинника шляхом сушіння в надкритичних умовах або при атмосферному тиску. Але алкоксиди елементів є дорогими та токсичними, сушка при підвищеному тиску вимагає спеціального обладнання, а також дорога і енергоємна, а сушка при атмосферному тиску вимагає складних і тривалих модифікацій гелю. У цій роботі було поставлено задачу на основі прямого методу широкомасштабного золь-гель синтезу високопоруватих, наноструктурованих, сферично гранульованих силікатів цирконію з водних розчинів дешевих, доступних солей, не вдаючись до тривалих технічно та хімічно складних методів попередньої обробки одержаних гідрогелів. Гелі готували шляхом утворення карбонатного комплексу цирконію з водних розчинів ZrOCl_2 і K_2CO_3 і його подальшої взаємодії з розчином Na_2SiO_3 методом їх коагуляції в краплі. Отримані міцні сферичні гранули гідрогелю $\text{ZrO}_2\text{-SiO}_2\text{-nH}_2\text{O}$ ретельно відмивали від сторонніх домішок дистильованою водою і піддавали гідротермальній обробці в різний час, подальшій декантації етанолом з домішкою бензину або алкотермальній обробці в цій суміші в щільно закритих контейнерах при суперкритичній температурі для етанолу. Термостійкість зразків вимірювали шляхом прожарювання їх на повітрі при високій температурі. За допомогою методів СЕМ, РФА та адсорбції / десорбції N_2 було визначено, що отримані аморфні Zr-Si матеріали, що містять 45 мас. % ZrO_2 , мають питому поверхню понад $500 \text{ м}^2/\text{г}$, об'єм пор $> 2 \text{ см}^3/\text{г}$, середній діаметр пор $\sim 18 \text{ нм}$, широкі мезопори діаметром $\sim 28 \text{ нм}$, насипну густиною менше $0.3 \text{ г}/\text{см}^3$, характерну для аерогелів на основі оксиду металу і оксиду кремнію, і проявляють високу термічну стабільність.

Ключові слова: $\text{ZrO}_2\text{-SiO}_2$ аерогелі, золь-гель синтез, суперкритична сушка, алкотермальна обробка, мезопоруваті матеріали

Получение цирконийсиликатных материалов типа аэрогелей из водных растворов солей Na_2SiO_3 и ZrOCl_2

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Аэрогели – это гели, в которых жидкая фаза полностью заменена газообразной. Они образуют новый класс твердых веществ с очень низкой плотностью, большой площадью удельной поверхности и высокой пористостью, что открывает им широкие возможности практического применения. $\text{ZrO}_2\text{-SiO}_2$ аэрогели, благодаря сильной энергии связи Zr-O-Si , очень низкой теплопроводности, наличию кислотных и основных центров, проявляют превосходные свойства, как аэрокосмические теплоизоляторы, селективные сорбенты, катализаторы и носители катализаторов для высокотемпературных реакций. Традиционным путем получения аэрогелей являются формирование разветвленной, трехмерной, нерегулярной сети влажных гелей, методом золь-гель синтеза из алкоксидов элементов, старение гелей, замена интермицеллярной воды на органические жидкости с низким поверхностным натяжением и осторожное удаление растворителя сушкой при сверхкритических условиях или при давлении окружающей среды. Но алкоксиды элементов дороги и токсичны, сушка при повышенных давлениях требует специального оборудования и также дорога и энергозатратна, а сушка при атмосферном давлении требует сложной и длительной модификации гелей. В этой работе была поставлена задача, на основании метода прямого масштабного золь-гель синтеза высокопористых, наноструктурированных, сферически гранулированных цирконийсиликатов из водных растворов дешевых, доступных солей получить материалы типа аэрогелей, не прибегая к длительным аппаратно и химически сложным методам обработки получаемых гидрогелей. Гели готовили путем образования карбонатного комплекса циркония из водных растворов ZrOCl_2 , и K_2CO_3 и его последующего взаимодействия с раствором Na_2SiO_3 методом их коагуляции в капле. Полученные прочные сферические гранулы гидрогеля $\text{ZrO}_2\text{-SiO}_2\text{-nH}_2\text{O}$ тщательно отмывали от посторонних примесей дистиллированной водой и подвергали гидротермальной обработке разное время, последующей декантацией этанолом с примесью бензина или алкотермальной обработке в этой смеси в плотно закрытых контейнерах при сверхкритической температуре для этанола. Термостойкость образцов определяли путем прокаливания их на воздухе при высокой температуре. С помощью методов СЭМ, РФА и адсорбции/десорбции N_2 было определено, что полученные аморфные Zr-Si материалы, содержащие 45 масс. % ZrO_2 , имеют удельную поверхность более $500 \text{ м}^2/\text{г}$, объем пор $> 2 \text{ см}^3/\text{г}$, средний диаметр пор $\sim 18 \text{ нм}$, широкие мезопоры диаметром $\sim 28 \text{ нм}$, плотность менее $0.3 \text{ г}/\text{см}^3$, характерную для аэрогелей на основе оксида металла и оксида кремния, и проявляют высокую термическую стабильность.

Ключевые слова: $\text{ZrO}_2\text{-SiO}_2$ аэрогели, золь-гель синтез, сверхкритическая сушка, алкотермальная обработка, мезопористые материалы

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