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STUDY OF THE PHYSICAL-CHEMICAL AND SORPTION PROPERTIES OF SnO₂ PREPARED BY MECHANOCHEMICAL AND MICROWAVE ROUTES

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There are many methods for synthesis of tin dioxide SnO₂, namely sol-gel, precipitation. However, these methods do not allow to regulate the physical-chemical properties in wide limits in the synthesis stage. The most commonly obtained samples are predominantly microporous as a rule. On the other hand, the meso-macroporous structure is required for the effective use of tin dioxide in sorption processes. The mechanochemical and microwave treatments can be used for eliminating mentioned above disadvantages. Therefore, the purpose of this work was to study the influence of the mechanochemical and microwave treatments on the physical-chemical and sorption properties of SnO₂ prepared by heterogeneous precipitation.

SnO₂ gels and xerogels have been obtained by heterogeneous precipitation. The mechanochemical treatment was carried out in air and water at 300 rpm for 0.5 h in the form of dried xerogel as well as wet gel using a planetary ball mill Pulverisette-7. Initial wet gel was subjected to microwave treatment for 1 h using a high-pressure reactor «NANO 2000». We used XRD and DTA-TG analysis, FTIR spectroscopy, adsorption-desorption of nitrogen for characterization of initial and modified samples.

The initial sample corresponds to the composition tin oxohydroxide with gross formula Sn₃O₄(OH)₄. For the modified samples a partial removal of the structural OH groups occurs. The initial sample is characterized by high values of specific surface area and high content of micropores. The specific surface area, total volume of pores, mesoporous size are increased as a result of the mechanochemical and microwave treatments. Formation of the secondary porosity that presented by meso- and macropores is peculiarity of xerogel milling in water.

The cation exchange capacity under the most optimal conditions for the sorption of U(VI) ions (pH = 5–6, no background, cationic forms of uranium) for the initial sample was 0.82 mEq/g UO₂²⁺. The mechanochemical and microwave treatments result in drastic increase in sorption capacity of tin oxohydroxide in relation to U(VI) ions. The greatest effect was observed for sample milled in the form of wet gel, the sorption capacity *A* of which increases almost in three times while distribution coefficient *K_d* increases almost 70 times. In case of sorption on the background of 0.1 M NaHCO₃ (pH 8, model of block water of the Chernobyl Nuclear Power Plant), the sorption capacity of sample after mechanochemical treatment of gel increases by 43 % compared to initial sample from 0.31 to 0.43 mEq/g UO₂²⁺. Thus, modified samples can remove both cationic and anionic forms of U(VI) ions in the solution. At the same time, for sorption of Cs(I) and Sr(II) ions, it has been found, that in both cases the mechanochemical and microwave treatments negatively affect to their removal in comparison with initial sample.

Keywords: SnO₂, mechanochemical and microwave treatments, porous structure, sorption, uranium, cesium, strontium

INTRODUCTION

As well known, tin dioxide belongs to inorganic ion-exchangers [1] and, dependent on the conditions, it can exhibit both cation- and anion-exchange properties [2–4]. Effective use of tin dioxide in these processes is determined by the following characteristics: crystal and porous structure, surface structure, namely nature and content of adsorption sites [1, 2, 5–7]. The SnO₂ structure, in turn, is formed at the stage of its

preparation. There are many methods for synthesis of tin dioxide, namely sol-gel, precipitation [3, 8, 9]. However, these methods do not allow to regulate the physical-chemical properties in wide limits. Moreover, the most commonly obtained samples are predominantly microporous as a rule [2, 9]. On the other hand, the meso-macroporous structure is required for the effective use of tin dioxide in sorption processes. Thus, there is a need to improve the

synthesis methods of tin dioxide. The mechanochemical (MChT) and microwave (MWT) treatments can be used for eliminating the mentioned above disadvantages. Their efficiency has been demonstrated for other oxides and hydroxides [10–13]. Particularly, formation of meso-macroporous structure was found as a result of tin oxohydroxide powders milling [14]. However, published studies that cover these modification methods for tin dioxide are not numerous and insufficiently informative.

Therefore, the purpose of this work was to study the influence of the MChT and MWT on the physical-chemical and, consequently, on ion-exchange properties of precipitated SnO₂.

EXPERIMENTAL

Initial SnO₂ was obtained by dissolving SnCl₄·5H₂O in water and adding ammonia solutions to the gel-like precipitate formation. Aging of wet gel was performed at room temperature for 25 h. Then precipitate was washed, filtered. The part of gel was dried at 20 °C for preparation of xerogel.

The SnO₂ samples were subjected to mechanochemical treatment MChT in air and water at 300 rpm for 0.5 h in the form of dried xerogel as well as wet gel using a planetary ball mill «Pulverisette-7» («Fritsch», Germany). Microwave treatment MWT was carried out in the form of wet gel for 1 h using a high-pressure reactor «NANO 2000» («Plazmotronika», Poland).

Physical-chemical parameters of initial and modified samples were determined using the following techniques. XRD analysis was done on a diffractometer Philips PW 1830 with CuK_α-radiation. Curves of differential thermal analysis (DTA – TG) were obtained using apparatus Derivatograph-C (F. Paulik, J. Paulik, L. Erdey) in the range of temperature 20 – 600 °C at the heating rate 10°/min. FTIR spectra were obtained using a spectrophotometer «Spectrum-One» (Perkin-Elmer, USA) in reflection mode. For this measurements, a mixtures of powders with KBr in ratio a sample/KBr = 1 : 20 were used. Parameters of porous structure, namely specific surface area *S*, sorption pore volume *V_s*, micropores volume *V_{mi}*, mesopores volume *V_{me}*, were determined from isotherms of low-temperature nitrogen adsorption obtained with the help of an analyzer ASAP 2405N («Micromeritics Instrument Corp») using BET,

t- and the BJH methods. The mesopores diameter *d_{me}* is calculated from the pore size distribution (PSD) curves plotted using desorption branches of isotherms. The total pore volume *V_Σ* was determined by ethanol impregnation of granules of the samples dried at 150 °C. The volume of macropores *V_{ma}* was calculated as the difference between *V_Σ* and *V_s*.

The sorption properties of the tin(IV) oxide were characterized by sorption capacity *A* and distribution coefficient *K_d*. The studies were performed under static conditions, ratio solid : liquid was 1 : 2000. The pH value was adjusted to 5.4 (no background) during sorption of ions U(VI), Cs(I) and Sr(II). During sorption of ions U(VI) from a solution, that simulates «block» waters of the ChNPP, the pH value was 8 (on the background of 0.1 M NaHCO₃). The uranium concentration in solution was determined on a KFK-3 photometer by the technique based on formation by UO₂²⁺ ion of a stable colored complex with arsenazo III at pH 1.0–3.0 [15]. The concentrations of Cs and Sr in solution were determined on an atomic absorption spectrophotometer AA-6300 (Shimadzu).

RESULTS AND DISCUSSION

According to these data DTA–TG (Fig. 1), the initial sample corresponds to composition tin oxohydroxide (with gross formula – Sn₃O₄(OH)₄). Similar results were obtained by the other authors [16] for tin dioxide prepared by sol–gel method. Mechanochemical treatment of samples in air and water leads to partial removal of OH groups. This process is accompanied by partial transformation of Sn₃O₄(OH)₄ into SnO₂. Moreover, ratio the number of structural OH groups/Sn is changed from 1.114 to 0.908, depending on the conditions of MChT. In turn, the similar processes occur at MWT of gel.

On the FTIR spectra (Fig. 2) of samples after MChT is observed decrease in the intensity of several absorption bands, namely: in the region of stretching vibrations of OH groups (3000–3500 cm⁻¹) and bending vibrations of OH groups (1235 cm⁻¹). This correlates with the results of thermogravimetric analysis, namely with a partial removal of OH groups during milling. It should be noted that the largest removal of OH-groups occurs in MChT of gel.

The diffractograms for initial and modified samples are depicted in Fig. 3. It should be noted

that positions of diffraction peaks, which correspond to the planes (110), (101), (200) and (211) for tetragonal modification of cassiterite/rutile (JCPDS N 41-1445), are identical for tin dioxide and hydroxide [17].

These reflexes differ only in width, which is a measure of crystallinity. The patterns from these planes are observed for all studied samples that have an imperfect crystal structure.

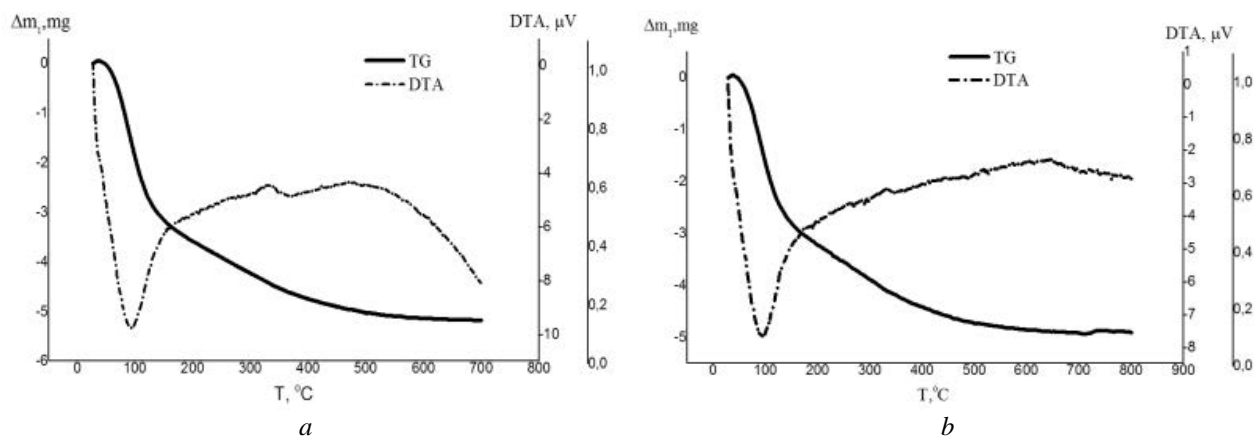


Fig. 1. DTA–TG curves for tin oxohydroxide: initial xerogel (a) and that after MChT in air (b)

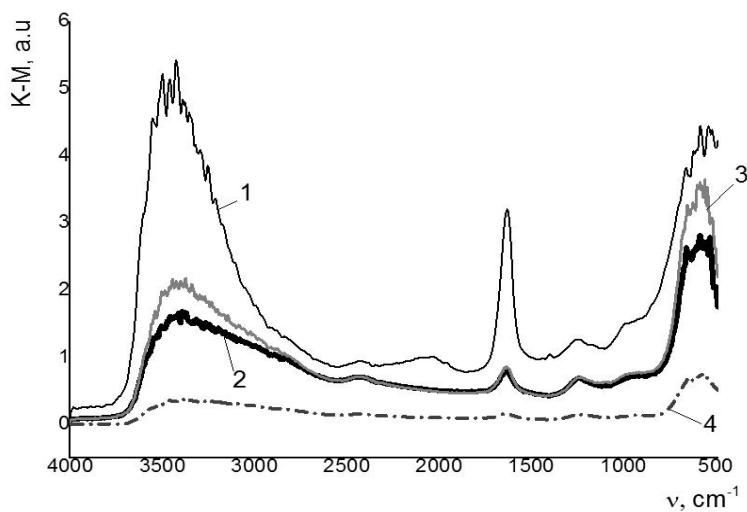


Fig. 2. FTIR-spectra of samples of the initial (1) tin oxohydroxide, as well as those after MChT of xerogel in water at 300 rpm (2), in air at 300 rpm (3) and MChT of gel at 300 rpm (4)

The MChT almost does not change the crystal structure. But a decrease takes place in the intensity of reflexes and an increase in the values of full width at half maximum (FWHM), which corresponds to 110 plane, from 3.86 degree (initial sample) to 3.97 degree (for xerogel milled in water). On the contrary, MWT contributes to the formation of a more perfect crystal structure and the value of FWHM for reflex from this plane decreases almost twice.

Isotherms of nitrogen adsorption - desorption for the initial sample close to type I (Fig. 4) although this sample also contains the smallest mesopores with a size of 2.3 nm (Table 1). In turn, the isotherms for modified samples belong to different types. Thus, isotherms of samples after MChT are similar to that for initial sample, but there is insignificant rise in the region of values of $P/P_0 > 0.95$, which corresponds to filling of macropores. The isotherm for sample

after MWT is close to type IV and shows the presence of a hysteresis loop in the region of average values of P/P_0 (0.4–0.8). It is evidence for formation of mesoporous structure at MWT, which is characterized by significant volume and larger size of mesopores (4.3 nm).

Parameters of the porous structure for all samples, calculated from the isotherms, are given in Table 1. The initial sample is characterized by high values of the surface area ($178 \text{ m}^2/\text{g}$) and high content of micropores (60 % of the total pore volume V_Σ). The values of V_Σ and V_{me} (and fractions of the latter) as well as size of mesoporous (Table 1) increase as a result of MChT and MWT. The feature of wet MChT, namely milling of gel and xerogel in water, is the formation of secondary porosity, that presented by large mesopores and macropores. As a result of MWT of wet gels, uniform mesoporous structure is formed, as demonstrated by the isotherm, PSD curve and the data given in the Table 1. Such a structure is the most requested in adsorption.

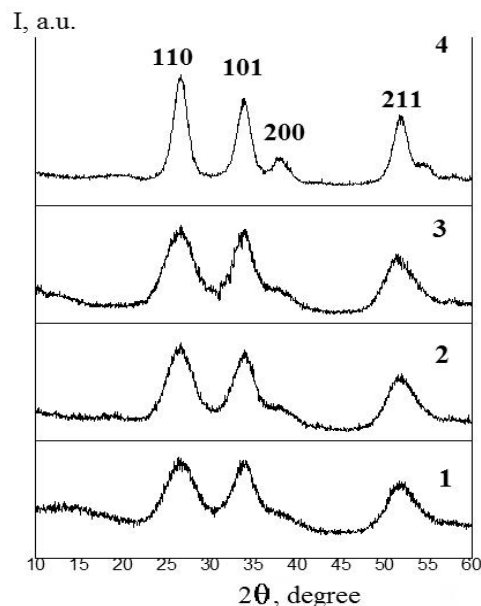


Fig. 3. XRD for samples tin oxohydroxide: initial (1) and MChT in air at 300 rpm (2), MChT in water at 300 rpm (3); MWT of gel at 235 °C (4)

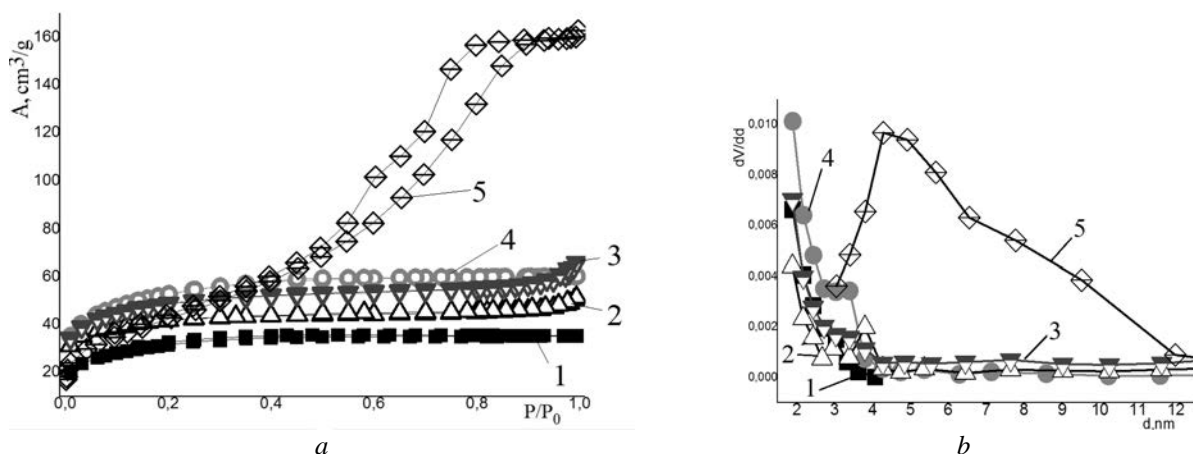


Fig. 4. Isotherms of nitrogen adsorption–desorption (a) and curves of PSD (b) for samples tin oxohydroxide: initial (1), and after MChT in air at 300 rpm (2), MChT in water at 300 rpm (3), MChT of gel at 300 rpm (4), and after MWT of gel at 235 °C (5)

Table 1. Porous structure parameters of initial and modified samples of tin oxohydroxide

Modification conditions		$S, \text{ m}^2/\text{g}$	$V_\Sigma, \text{ cm}^3/\text{g}$	$V_S, \text{ cm}^3/\text{g}$	$V_{mi}, \text{ cm}^3/\text{g}$	$V_{me}, \text{ cm}^3/\text{g}$	$V_{ma}, \text{ cm}^3/\text{g}$	$d_{me}, \text{ nm}$
Tin oxo- hydroxide	Initial xerogel	178	0.05	0.05	0.03	0.02	–	2.3
	MChT xerogel air 300 rpm	138	0.08	0.08	0.04	0.03	–	4.1
	MChT xerogel H ₂ O 300 rpm	163	0.33	0.10	0.04	0.05	0.23	4.3
	MChT gel 300 rpm	180	0.17	0.09	0.04	0.04	0.08	3.4
	MWT gel 235 °C	156	–	0.25	–	0.25	–	4.3

Sorption properties of initial and modified samples were investigated by the example ions of stable isotopes of U(VI), Cs(I) and Sr(II). Radioactive isotopes of these elements form the main part of the activity of the «block» waters of the Chernobyl Nuclear Power Plant [18] and other liquid radioactive wastes.

Among the above-mentioned elements, U(VI) has features that make it difficult to extract, in particular the variability of its soluble forms. Up to pH = 5, U(VI) is present predominantly in the form of uranyl ions (UO₂²⁺) in the solution while hydroxides and anionic carbonate complexes are formed at higher pH. It

should be noted that vast majority of these complexes are polymeric (bi- and more nuclear complex) [19].

The results of investigations of the sorption properties for tin oxohydroxide samples in relation to the ions U(VI), Cs(I) and Sr(II) are summarized in Table 2. In order to study the cation exchange properties of samples, sorption of ions U(VI) were performed in the most favorable (reference) conditions at pH = 5.4 in the absence of background. Sorption of Cs(I) and Sr(II) ions was also carried out according to the same conditions for correct comparative analysis (including under the same pH value).

Table 2. Estimation of sorption properties of initial and modified samples of tin oxohydroxide

Sample	Extractive elements	Solution	C ₀ , (mEq/L)	A, mEq/g	K _d , L/g
Initial				0.82	0.75
MChT gel 300 rpm		No background, pH = 5.4	1.5	2.90	51.50
MChT air 300 rpm				1.53	2.10
MChT H ₂ O 300 rpm	U(VI)			1.80	2.85
MWT gel 235 °C				1.57	2.15
Initial				0.1 M NaHCO ₃ (pH = 8)	1.0
MChT gel 300 rpm				0.43	0.51
Initial				0.21	2.27
MChT gel 300 rpm	Cs	No background, pH = 5.4	0.2	0.01	0.66
Initial				0.26	2.6
MChT gel 300 rpm	Sr			0.03	0.14

It has been found, that MChT and MWT result in drastic increase in sorption capacity of tin oxohydroxide in relation to U(VI) ions to a level characteristic of the most common cation exchange resins [20]. The greatest effect was observed for sample milled in the form of wet gel, the sorption capacity *A* of which increases almost in three times while distribution coefficient *K_d* increases almost 70 times. Samples milled as xerogels in water and air, as well as that after MWT of wet gel also show higher (compared with initial sample) values of *A* and *K_d* for sorption for U(VI) ions (Table 2). The favorable effect of MChT and MWT is related to the formation of mesoporous or meso-macroporous structure. It is obvious that such a structure is more accessible for various ionic species of U(VI), the size of which is within 0.4–1.0 nm [21, 22] while kinetic diameter of nitrogen is 0.36 nm [23, 24]. The accessibility of pores can be determined not so much by their size, calculated from the PSD curves, as by the

size of the entrances to the pores: so-called «ink-bottle effect» [25]. It is necessary to pay attention to the fact that sample milled in the form of wet gel has practically the same specific surface area and somewhat larger mesopore size compared to the initial sample. Nevertheless, this sample shows significantly higher, namely maximum values of sorption capacity. On the other hand, this is the only sample, during the modification of which the complete repacking of globules in the framework occurs. As a result, the shape and size of entrances to the pores can be changed and «ink-bottle effect» can be eliminated. Therefore, uranium sorption is very sensitive to the pore size. This sample is also distinguished by the presence of macropores in the structure (Table 1). The latter ensures the acceleration of diffusion processes, as for xerogel milled in water, which also contains macropores.

Next studies of sorption of ions U(VI) were carried out from a solution that simulates

«block» waters of the ChNPP (background 0.1 M NaHCO_3 , $\text{pH} \approx 8$). Under these conditions, U(VI) is present in the solution in the form of anionic carbonate complexes [18] and SnO_2 samples demonstrate their anion exchange properties, which are determined by the number of anion-exchange centers, presumably Sn-OH groups [26, 27]. Under these conditions, a positive effect was also obtained as result of MChT (Table 2). In particular, the sorption capacity of sample after MChT of gel at 300 rpm increases by 43 % compared to initial sample. Thus, sorbents based on modified samples can remove both cationic and anionic forms of U(VI) ions in the solution. In other words, these samples demonstrate the ampholytic properties. This makes it more versatile, for example, in comparison with titanium phosphates, cation exchange and anion exchange resins.

At the same time, for sorption of Cs(I) and Sr(II) ions, it has been found that MChT and MWT negatively affect to their removal in comparison with initial sample. This can be explained by the collapse of the microporous structure during MChT and MWT (Table 1). According to modern notions about sorption processes, pores comparable in size with the removed ions can be regarded as adsorption centers for them. This hypothesis was first proposed by the authors of work [28] and later confirmed in many studies on the sorption of alkali and alkaline earth cations by phosphates, heteropoly compounds, titanosilicates [7, 29, 30]. It should be noted that the size of the Cs(I) and Sr(II) ions is 0.2–0.4 nm [31], which corresponds to micropores size.

This feature of modified SnO_2 , namely its indifference to the Cs(I) and Sr(II) ions in combination with the significant sorption capacity of the U(VI) ions, is rather unique, since

the most sorbents are capable of one or another way adsorbing ions of Cs(I), Sr(II), and U(VI). Thus, even a classical crystalline titanium silicate, which is considered as high-specialized sorbent for extraction of isotopes Cs(I), together with it, accumulates certain amount of ions U(VI) [32].

Thus, MChT of gels allows to significantly improve the sorption properties of tin oxohydroxide. Particularly, it facilitates increasing the selectivity of the extraction of long-lived isotopes of U(VI) from: 1) mixtures with the intermediate-living Cs(I) and Sr(II) for further separate utilization; 2) including on the background of cations Na^+ and Ca^{2+} , adsorption of which can also be complicated by analogy with ions of Cs(I) and Sr(II).

CONCLUSIONS

It has been studied the influence of mechanochemical and microwave treatments on the physical-chemical and sorption properties of precipitated tin oxohydroxide. It has been found that MChT of xerogel in water promotes to the formation of meso-macroporous structure. MChT and MWT in the form of wet gels promote to the formation of a homogeneous mesoporous structure with high values of the specific surface, pore volume and diameter of mesopores. Mechanochemical and microwave treatments improve the sorption characteristics of the samples with respect to the sorption of U(VI) ions from aqueous solutions. This is the result of the formation of a more accessible for hydrated uranium ions surface. But on the other hand, both types of treatment negatively affect to removal of Cs(I) and Sr(II) ions, in comparison with initial sample. This can be explained by the collapse of the microporous structure during MChT and MWT.

Вивчення фізико-хімічних та сорбційних властивостей SnO₂, отриманих шляхом механохімічної та мікрохвильової обробок

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Існує багато методів синтезу діоксиду олова SnO₂, зокрема золь-гель та осадження. Проте ці методи не дозволяють регулювати фізико-хімічні властивості в широких межах на етапі синтезу. Як правило, отримані зразки є переважно мікропористими. З іншого боку, для ефективного використання діоксиду олова в сорбційних процесах потрібна мезо-макропорувата структура. Механохімічна і мікрохвильова обробки можуть бути використані для усунення зазначених вище недоліків. Тому метою цієї роботи було вивчення впливу механохімічної і мікрохвильової обробок на фізико-хімічні та сорбційні властивості SnO₂, отриманого шляхом гетерогенного осадження.

SnO₂ гелі та ксерогелі були отримані шляхом гетерогенного осадження з використанням розчину аміаку. Механохімічну обробку сухого ксерогелю, а також вологого гелю проводили на повітрі (суха МХО) та у воді при 300 об/хв протягом 0.5 год з використанням планетарного кулькового млина Pulverisette-7. Вихідний вологий гель був підданий мікрохвильовій обробці протягом 1 год за допомогою реактора високого тиску «NANO 2000». Для характеристики вихідних та модифікованих зразків використовували рентгенофазовий аналіз, диференційно-термічний аналіз, ІЧ-спектроскопію з Фур'є перетворенням, адсорбцію-десорбцію азоту. Сорбційні властивості досліджувалися в процесі сорбції іонів U(VI), Cs(I) та Sr(II).

Вихідний зразок відповідає складу оксогідроксиду олова з брутто формулою Sn₃O₄(OH)₄. При модифікуванні відбувається часткове видалення структурних -ОН груп. Вихідний зразок характеризується високими значеннями питомої поверхні та високим вмістом мікропор. Значення питомої поверхні, загальний об'єм пор та розміри мезопор збільшуються в результаті механохімічної і мікрохвильової обробок. Особливістю механохімічної обробки сухого ксерогелю у воді є утворення вторинної поруватості, що представлена мезо- та макропорами.

Сорбційна ємність у найбільш оптимальних умовах для сорбції іонів U(VI) (рН = 5–6, без фону, катіонні форми іонів урану) для вихідного зразка становила 0.82 мг-екв/г UO₂²⁺. Механохімічна та мікрохвильова обробки приводять до різкого збільшення сорбційної ємності оксогідроксиду олова по відношенню до іонів U(VI). Найбільший ефект спостерігався при механохімічній обробці вологого гелю, сорбційна ємність (А) цього зразка збільшилася майже в три рази, тоді як коефіцієнт розподілу K_d збільшився майже в 70 разів. У разі сорбції на фоні 0.1М NaHCO₃ (рН = 8, модель «блочних» вод Чорнобильської АЕС) сорбційна ємність (А) зразка після механохімічної обробки вологого гелю збільшилася на 43 %, у порівнянні з вихідним зразком, від 0.31 до 0.43 мг-екв/г UO₂²⁺.

Таким чином, модифіковані зразки можуть видаляти з розчинів як катіонні, так і аніонні форми U(VI). У той же час, було виявлено, що механохімічна і мікрохвильова обробки негативно впливають на сорбцію іонів Cs(I) та Sr(II), у порівнянні з вихідним зразком.

Ключові слова: SnO₂, механохімічна та мікрохвильова обробки, порувата структура, сорбція, уран, цезій, стронцій

Изучение физико-химических и сорбционных свойств SnO₂, полученных путем механохимической и микроволновой обработок

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Существует много методов синтеза диоксида олова SnO₂, в частности золь-гель и осаждение. Однако эти методы не позволяют регулировать физико-химические свойства в широких пределах на этапе синтеза. Как правило, полученные образцы являются преимущественно микропористыми. С другой стороны, для эффективного использования диоксида олова в сорбционных процессах нужна мезо-макропористая структура. Механохимическая и микроволновая обработки могут быть использованы для устранения указанных выше недостатков. Поэтому целью настоящей работы было изучение влияния механохимической и микроволновой обработок на физико-химические и сорбционные свойства SnO₂, полученного путем гетерогенного осаждения.

SnO₂ гели и ксерогели были получены путем гетерогенного осаждения с использованием раствора аммиака. Механохимическую обработку сухого ксерогеля, а также влажного геля проводили на воздухе (сухая МХО) и в воде при 300 об/мин в течение 0.5 ч с использованием планетарной шаровой мельницы Pulverisette-7. Исходный влажный гель был подвергнут микроволновой обработке в течение 1 ч с помощью реактора высокого давления «NANO 2000». Для характеристики исходных и модифицированных образцов использовали рентгенофазовый анализ, дифференциально-термический анализ, ИК-спектроскопию с Фурье преобразованием, адсорбцию-десорбцию азота. Сорбционные свойства исследовались в процессе сорбции ионов U(VI), Cs(I) и Sr(II).

Исходный образец соответствует составу оксигидроксида олова с брутто формулой Sn₃O₄(OH)₄. При модифицировании происходит частичное удаление структурных -ОН групп. Исходный образец характеризуется высокими значениями удельной поверхности и высоким содержанием микропор. Значение удельной поверхности, общий объем пор и размеры мезопор увеличиваются в результате механохимической и микроволновой обработок. Особенностью механохимической обработки сухого ксерогеля в воде является образование вторичной пористости, которая представлена мезо- и макропорами.

Сорбционная емкость в наиболее оптимальных условиях для сорбции ионов U(VI) (pH = 5–6, без фона, катионные формы ионов урана) для исходного образца составляла 0.82 мг-экв/г UO₂²⁺. Механохимическая и микроволновая обработки приводят к резкому увеличению сорбционной емкости оксигидроксида олова по отношению к ионам U(VI). Наибольший эффект наблюдался при механохимической обработке влажного геля, сорбционная емкость (A) этого образца увеличилась почти в три раза, тогда как коэффициент распределения K_d увеличился почти в 70 раз. В случае сорбции на фоне 0.1M NaHCO₃ (pH = 8, модель «блочных» вод Чернобыльской АЭС) сорбционная емкость (A) образца после механохимической обработки влажного геля увеличилась на 43 % по сравнению с исходным образцом, от 0.31 до 0.43 мг-экв/г UO₂²⁺.

Таким образом, модифицированные образцы могут выделять из растворов как катионные, так и анионные формы U(VI). В то же время, было обнаружено, что механохимическая и микроволновая обработки негативно влияют на сорбцию ионов Cs(I) и Sr(II), по сравнению с исходным образцом.

Ключевые слова: SnO₂, механохимическая и микроволновая обработки, пористая структура, сорбция, уран, цезий, стронций

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