

TIN (IV) OXIDE AND OXO-HYDROXIDE MODIFICATION AND INVESTIGATION OF THEIR PROPERTIES

Four series of tin (IV) oxide and oxo-hydroxide samples were modified by using microwave and mechanochemical treatments. Physical-chemical properties of all samples were studied by using the following techniques: XRD, differential thermal analysis, nitrogen adsorption-desorption, UV-Vis spectroscopy. The estimation of photocatalytic activity under visible irradiation was carried out by using degradation of textile dyes (safranin T, rhodamine B) in aqueous medium. Investigations have shown that a specific surface area decreases as a result of mechanochemical treatment of samples of the first three series in air, and remains almost unchanged after milling in water. The specific surface area increases and the crystal structure of the latter are improved as a result of microwave treatment.

Meso-macroporous structure is formed in all cases. All samples showed high photocatalytic activity in the degradation of rhodamine B and safranin T.

Keywords: tin (IV) oxide and oxo-hydroxide, mechanochemical treatment, microwave treatment, pore volume, specific surface area, photocatalytic activity.

Introduction

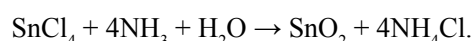
Tin (IV) oxide and hydroxide are important versatile materials, which have high chemical stability and excellent physical-chemical properties. For example, tin (IV) oxide and hydroxide used as adsorbents [1; 2], catalysts [3], photocatalysts [4], gas sensors [5] etc.

It is well known that crystal, porous and surface structure, thermal and mechanical stability, the ability to granulation are determined sorption and catalytic properties of solids. Therefore, it is very important to develop ways for regulation of these parameters both on the stage of synthesis and next modification. Tin (IV) oxide and hydroxide have been synthesized by various methods such as chemical vapor deposition [2], thermal decomposition of tin chloride [4], sol-gel [6], hydrothermal synthesis [7] and others. These synthesis methods sufficiently well studied and widely used, but not always using them allow to achieve the desired properties. Therefore, there is a need to improve synthesis and modification procedures for preparation tin (IV) dioxide and hydroxide. To overcome most of existing shortcomings, microwave and mechanochemical treatments, which showed efficiency for others oxides and hydroxides, can be used.

Materials and methods

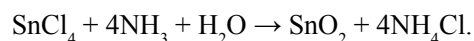
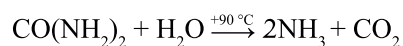
We modified four series of samples: 2 laboratory xerogels and 2 commercial powders. Laboratory xerogel of *series 1* was heterogeneously precipitated

from aqueous stannic tetrachloride solutions with ammonia solutions:



The resulting precipitate was washed and dried.

Laboratory xerogel of *series 2* was homogeneously precipitated using aqueous stannic tetrachloride solutions and urea:



Aging of wet gel was performed at room temperature for 25 h by pH = 1. The obtained gel-like precipitate was washed, filtered and divided into parts. First part reserved as a wet gel and second part dried at $t = 20^\circ\text{C}$ for preparation of xerogel.

The commercial powders were: high-dispersed porous powder (*series 3*) with specific surface area $S = 198 \text{ m}^2/\text{g}$, low-dispersed and low-porous powder (*series 4*) with specific surface area $S = 6 \text{ m}^2/\text{g}$.

All samples were subjected to mechanochemical treatment **MChT** in air and water at 300, 600 and 850 rpm for 0.5 h using a planetary ball mill "Pulverisette-7" ("Fritsch", German). Microwave treatment **MWT** was carried out in the form of wet gel and dry xerogel for 0.5 h using high-pressure reactor "NANO 2000" ("Plazmotronika", Poland).

Physical-chemical parameters of 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. Parameters of porous structure (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 analyzer ASAP 2405N (“Micromeritics Instrument Corp”). Electron (UV-Vis) spectra of powders were registered on Lambda 35 UV-Vis spectrometer (Labsphere RSA-PE-20 diffuse reflectance and transmittance accessory, Perkin-Elmer Instruments).

The testing of photocatalytic activity in visible region was carried out using degradation of textile dyes (safranin T, rhodamine B) in aqueous medium ($0.5 \cdot 10^{-5}$ mol·L⁻¹ solution). The calculation of photodegradation rate constants K_d was based on the concentration change of the dyes solution after establishment of adsorption/desorption equilibrium.

Results and discussion

According to DTA–TG data, the first three initial samples correspond to composition SnO(OH)₂, the latter – SnO₂ (Fig. 1). Influence of mechanochemical treatment of all samples leads to partial removal of OH-groups. It is accompanied by transformation of initial SnO(OH)₂ into SnO₂. Chemical composition of SnO₂ does not change under milling.

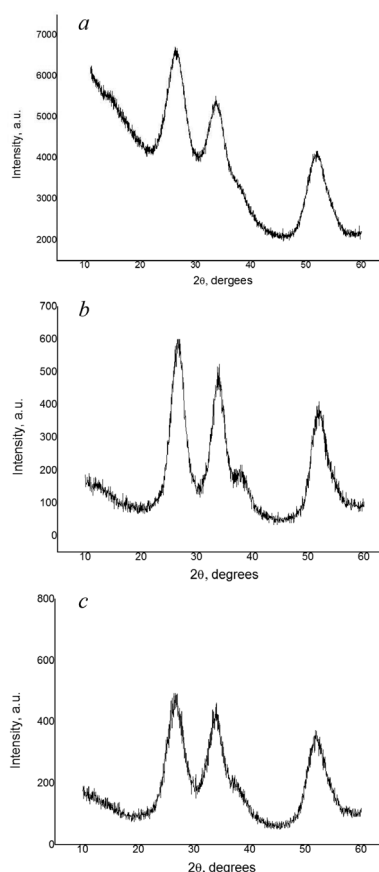


Fig. 2. XRD for samples: *a* – SnO(OH)₂ heterogeneously precipitate initial; *b* – SnO(OH)₂ heterogeneously precipitate after MWT; *c* – SnO(OH)₂ heterogeneously precipitate after MChT

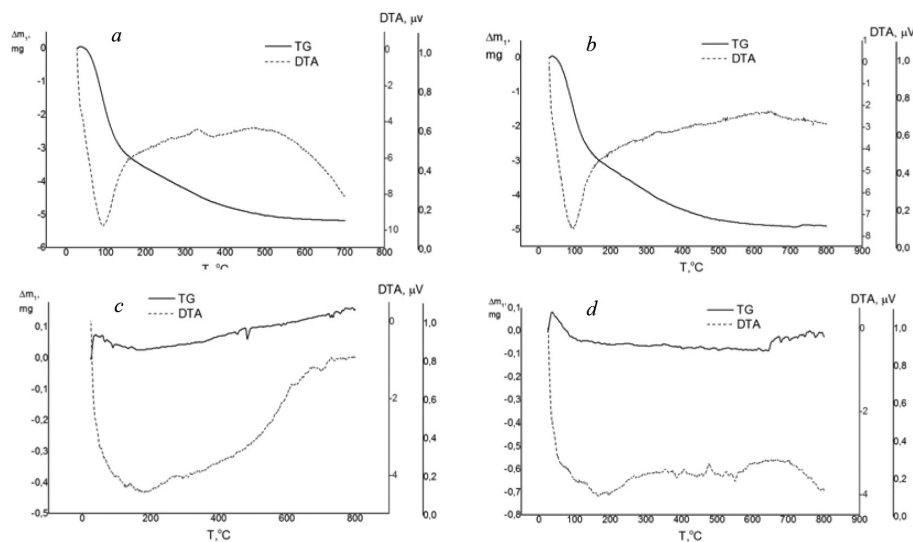


Fig. 1. DTA–TG curves for samples: *a* – SnO(OH)₂ homogeneously precipitate; *b* – SnO(OH)₂ homogeneously precipitate MChT air 600 rpm; *c* – SnO₂ powder initial; *d* – SnO₂ powder MChT air 600 rpm

Laboratory xerogels have X-ray amorphous structure and commercial powders are crystalline. The crystal structure of latter is partially destroyed after mechanochemical treatment, but on the contrary, improved as a result of microwave treatment (Fig. 2).

The first three initial samples are high-dispersed and porous (Table). They have high content of micropores. The total pore volume V_Σ and specific surface area S of samples with higher initial values of these parameters (series 2 and 3) decrease during

Table. Tin (IV) oxide and oxo-hydroxide porous structure parameters

N	Samples	S_s , m ² /g	V_s , cm ³ /g	V_p , cm ³ /g	V_{me} , cm ³ /g	V_{mi} , cm ³ /g
series 1	SnO(OH) ₂ heterogeneously precipitated	108	0.05	0.05	0.02	0.02
	SnO(OH) ₂ MChT air 300 rpm	138	0.08	0.08	0.03	0.04
	SnO(OH) ₂ MChT water 300 rpm	163	0.33	0.10	0.05	0.04
	SnO(OH) ₂ gel MChT 300 rpm	180	0.17	0.09	0.04	0.04
	SnO(OH) ₂ xerogel MWT	166	0.17	0.17	0.17	–
	SnO(OH) ₂ gel MWT	183	0.31	0.11	0.08	–
series 2	SnO(OH) ₂ homogeneously precipitated	177	0.08	0.08	0.01	0.04
	SnO(OH) ₂ MChT air 300 rpm	142	0.23	0.07	0.02	0.04
	SnO(OH) ₂ MChT air 600 rpm	135	0.16	0.07	0.02	0.04
	SnO(OH) ₂ MChT water 300 rpm	164	0.45	0.10	0.03	0.06
	SnO(OH) ₂ MChT water 600 rpm	159	0.27	0.08	0.02	0.02
	SnO(OH) ₂ gel MChT 300rpm	179	0.10	0.09	0.02	0.03
	SnO(OH) ₂ gel MChT 600rpm	182	0.13	0.09	0.03	0.04
series 3	SnO(OH) ₂ initial	198	0.10	0.10	0.06	0.04
	SnO(OH) ₂ MChT air 300 rpm	177	0.10	0.09	0.08	0.04
	SnO(OH) ₂ MChT air 600 rpm	144	0.08	0.07	0.02	0.04
	SnO(OH) ₂ MChT air 850 rpm	130	0.07	0.07	0.04	0.00
	SnO(OH) ₂ MChT water 300 rpm	185	0.18	0.10	0.06	0.02
	SnO(OH) ₂ MChT water 600 rpm	192	0.19	0.10	0.06	0.03
	SnO(OH) ₂ MChT water 850 rpm	187	0.10	0.09	0.06	0.03
series 4	SnO ₂ powder initial	6	0.025	0.02	0.02	0.0008
	SnO ₂ MChT air 300 rpm	8	0.07	0.06	0.06	0.0004
	SnO ₂ MChT air 600 rpm	11	0.07	0.06	0.06	0.0006
	SnO ₂ MChT air 850 rpm	13	0.05	0.05	0.05	0.0000
	SnO ₂ MChT water 600 rpm	10	0.20	0.07	0.07	0.0005
	SnO ₂ MChT water 850 rpm	8	0.23	0.05	0.05	0.0011

milling in air while the mechanochemical treatment in water does not almost change them.

However, all porous structure parameters increase as a result of MChT and MWT of sample with minimal S (series 1). The formation of the secondary porosity that presented by macropores is a feature of milling in water. Therefore, meso-macroporous structure are formed which is the most requested in adsorption and catalytic processes. Specific surface area increases during mechanochemical treatment of low-dispersed powder (series 4) in air and water. Additionally, porosity also arises: mesoporosity in the first case and meso- and macroporosity – in the second case.

UV-Vis spectra (Fig. 3) show that the changes of absorption in visible region (> 400 nm) do not occur as a result of MChT and MWT of powders and xerogels.

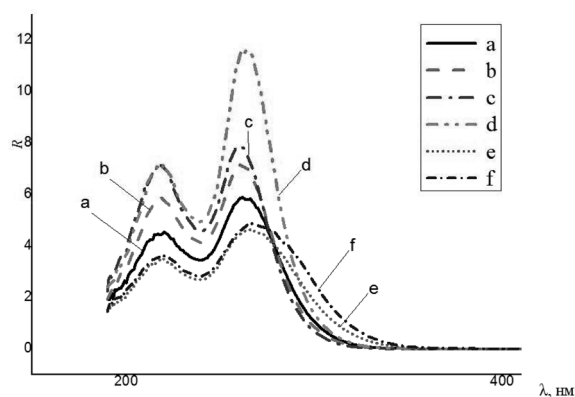


Fig. 3. UV-Vis spectra for samples SnO(OH)₂ heterogeneously precipitated: a – initial; b – MChT xerogel air 300 rpm; c – MChT xerogel water 300 rpm; d – MChT gel air 300 rpm; e – MWT gel 185 °C; f – MWT xerogel 165 °C

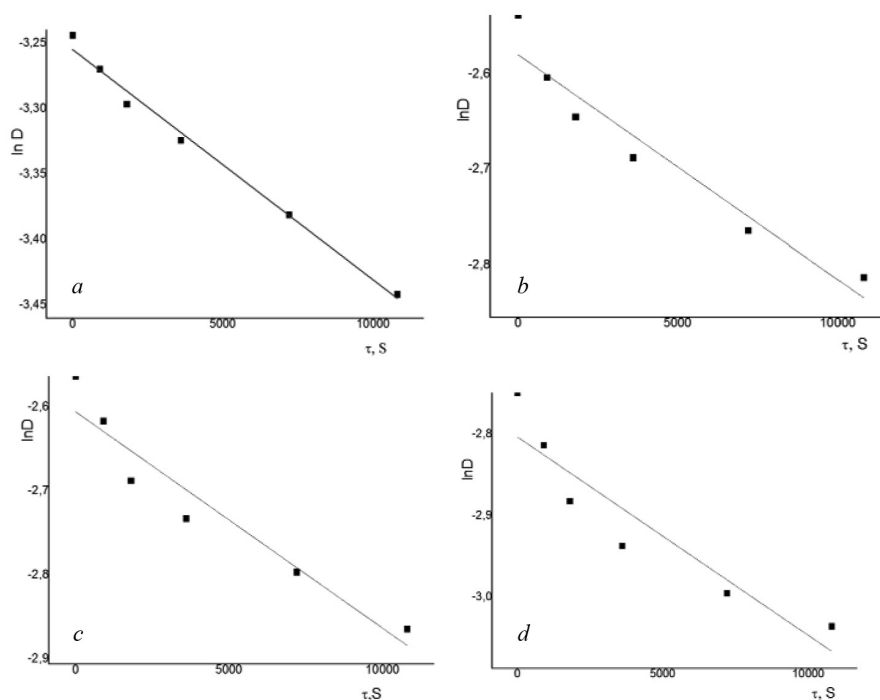


Fig. 4. Photocatalytic activity modified samples in processes of rhodamine B degradation in aqueous medium:

- a* – $\text{SnO}(\text{OH})_2$ heterogeneously precipitated initial $K_d = 1.76 \cdot 10^{-5} \text{ s}^{-1}$;
b – $\text{SnO}(\text{OH})_2$ heterogeneously precipitated MWT $K_d = 2.36 \cdot 10^{-5} \text{ s}^{-1}$;
c – $\text{SnO}(\text{OH})_2$ heterogeneously precipitated MChT gel $K_d = 2.57 \cdot 10^{-5} \text{ s}^{-1}$;
d – $\text{SnO}(\text{OH})_2$ heterogeneously precipitated MChT xerogel $K_d = 2.44 \cdot 10^{-5} \text{ s}^{-1}$

The hypsochromic shift (the same regardless of the intensity of the treatment) of absorption edge shifts from 335 (initial sample) to 309 nm (modified samples) is observed for all milled samples. The latter indicates broadening of the band gap E_g from 3.70 to 4.01 eV and from 4.09 to 4.17–4.25 eV for samples of *series 3* and *series 1*, respectively. In contrast, MWT results in bathochromic effect and corresponding narrowing of band gap for modified samples of *series 1*: from 4.09 to 3.8–3.9 eV.

All modified samples exhibit higher photocatalytic activity in processes of dyes (rhodamine B, safranin T) degradation in aqueous medium compared with initial samples. Thus, rate constant of dye degradation K_d achieves of magnitudes $3.6\text{--}8.8 \cdot 10^{-5} \text{ s}^{-1}$ for modified samples of *series 3* under visible irradiation. The samples of *series 1* are less active in the same

conditions: value of K_d is equaled $2\text{--}3 \cdot 10^{-5} \text{ s}^{-1}$ (Fig. 4). However, their activity sharply improves under UV-illumination: rate constant of dye degradation increases 3–5 times.

Under mechanocatalytic degradation, K_d is maximal and achieves $3 \cdot 10^{-4} \text{ s}^{-1}$ but decreases after preliminary milling of initial $\text{SnO}(\text{OH})_2$.

Conclusions

Thus, tin (IV) oxide and oxo-hydroxide modification by means of mechanochemical and microwave treatments allows to regulate of porous structure parameters and improve their photocatalytic properties in process of rhodamine B and safranin T degradation under UV- and visible light.

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МОДИФІКУВАННЯ ТА ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ ОКСИДУ ТА ОКСИГІДРОКСИДУ ОЛОВА (IV)

Чотири серії зразків оксиду та оксигідроксиду олова (IV) було модифіковано за допомогою механохімічної та мікрохвильової обробки. Досліджено фізико-хімічні властивості всіх зразків за допомогою рентгенофазового аналізу, диференційного термічного аналізу, методів дослідження пористої структури, електронної (UV-Vis) спектроскопії. Фотокаталітичні властивості дослідних зразків вивчалися в реакціях фотодеструкції водних розчинів барвників (Сафранін Т, Родамін Б) при опроміненні у видимій області. Дослідження показали, що після проведення механохімічної обробки перших трьох серій зразків в атмосфері повітря питома поверхня знижується, а у воді залишається майже незмінною. У результаті мікрохвильової обробки питома поверхня зростає, спостерігається упорядкування кристалічної структури.

В усіх випадках формується мезо-макропорувата структура. Усі зразки показали високу фотокаталітичну активність при фотодеструкції Родаміну Б та Сафраніну Т.

Ключові слова: оксид та оксигідроксид олова (IV), механохімічна обробка, мікрохвильова обробка, об'єм пор, питома поверхня, фотокаталітична активність.

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ОСОБЛИВОСТІ УТВОРЕННЯ КОМПЛЕКСІВ ТИПУ «ГІСТЬ–ГОСПОДАР» МІЖ ДВОШАРОВИМИ КАРБОНОВИМИ НАНОТРУБКАМИ ТА БІС(η⁵-ЦИКЛОПЕНТАДІЄНІЛ)КОБАЛЬТОМ

З використанням методів молекулярної механіки ММ+, напівемпіричного квантово-хімічного РМЗ та Monte-Carlo досліджено характер розташування молекул біс(η⁵-циклопентадієніл)кобальту у двошаровій (5,5)@(10,10) карбоновій нанотрубці (ДКНТ) залежно від концентрації інтеркаляту і температури інтеркалювання. Зі зростанням температури (понад ~490 К) відбувається поступове руйнування утворених зв'язків з екструзією міжтрубного інтеркаляту. Подальше підвищення температури до 650–750 К характеризується зовнішньоповерхневою десорбцією інтеркаляту та вришті-решист стабілізує досліджувану наносистему загалом, зберігаючи лише внутрішньотрубний інтеркалят. Розраховано УФ-спектри (5,5)@(10,10) ДКНТ залежно від концентрації інтеркаляту та визначено константу асоціації системи, яка становить 76,8 л·моль⁻¹.

Ключові слова: інтеркалювання, кобальтоцен, двошарова карбонова нанотрубка, комплекс типу «гість–господар», сорбція, екструзія, термодинамічна стабільність, константа асоціації.

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