



UDC 544.2+544.057+544.723

PHYSICO-CHEMICAL PROPERTIES OF CERIUM- AND FERRIC-DOPED TITANIUM HYDROXIDES SYNTHESIZED BY TWO METHODS

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Received 25 May 2021; accepted 2 July 2021; available online 20 July 2021

Abstract

Two types of materials on the base of titanium hydroxides are synthesized by co-precipitation and sol-gel method using pure and technical precursors. The ratio of metals in the samples after thermal treatment is determined by XRF analysis. Morphology of the composites obtained is characterized by low-temperature nitrogen adsorption/desorption technique. Adsorption of phosphate ions which are considered to be serious water pollutants has been studied onto the individual titania samples and titania, doped by ceria and ferric oxides. The samples have been obtained by two methods and were studied in the wide region of pH. All the investigated samples have demonstrated the high removal ability for phosphate anions at pH = 2. The sample of titania, doped by cerium and ferric, obtained by sol-gel method exhibits the highest adsorption capacity towards the adsorbed ions of 3.6 mmol/g. The adsorption isotherms have been fitted to the Langmuir, Freundlich and Temkin models. The equilibrium data of non-cerium-doped samples agreed satisfactory with the Langmuir isotherm model. Temkin model of isotherm describes well the experimental data regardless the method used for synthesis with the highest values of the coefficient of determination.

Keywords: titania; composites, cerium and ferric doped; adsorption; phosphate ions.

ФІЗИКО-ХІМІЧНІ ВЛАСТИВОСТІ МАТЕРІАЛІВ НА ОСНОВІ ГІДРОКСИДІВ ТИТАНУ ДОПОВАНИХ ЦЕРІЄМ ТА ЗАЛІЗОМ СИНТЕЗОВАНИХ ДВОМА МЕТОДАМИ

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Анотація

Матеріали на основі гідроксиду титану синтезовано методами співосадження та золь-гель технології з використанням аналітичних та технологічних розчинів. Співвідношення металів у зразках після термічної обробки визначалось методом рентгено-флуоресцентного аналізу. Морфологію одержаних композитів досліджено методом низькотемпературної адсорбції/десорбції азоту. Процес сорбції фосфат-іонів, які визнані одними з основних забруднювачів води, вивчено на індивідуальних зразках гідроксидів титану та композитах, до складу яких входять також оксиди заліза та церію, у широкому діапазоні рН розчинів. Всі досліджені зразки виявили максимальну здатність до вилучення сорбованих іонів при рН = 2. Композит на основі гідратованих оксидів титану, феруму та церію, синтезований золь-гель методом, має максимальну адсорбційну ємність, що складає 3.6 ммоль/г. Для математичної обробки ізотерм адсорбції використано теоретичні моделі Ленгмюра, Фрейндліха та Тьомкіна. Виявилось, що модель Ленгмюра найкраще підходить для обробки ізотерм, одержаних на індивідуальних зразках гідроксиду титану. Модель Тьомкіна можна використовувати для обробки всіх експериментальних ізотерм, незалежно від складу композитів та методу, застосованого для їх синтезу.

Ключові слова: оксид титану; композити, доповані оксидами церію та феруму; адсорбція; фосфат-іони.

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doi: 10.15421/jchemtech.v29i2.232199

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА МАТЕРИАЛОВ НА ОСНОВЕ ГИДРОКСИДОВ ТИТАНА ДОПИРОВАННЫХ ЦЕРИЕМ И ЖЕЛЕЗОМ СИНТЕЗИРОВАННЫЕ ДВУМЯ МЕТОДАМИ

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Аннотация

Материалы на основе гидроксида титана синтезованы методами соосаждения и золь-гель технологии с использованием аналитических и технологических растворов. Соотношение металлов в образцах после термической обработки определялось методом рентгено-флуоресцентного анализа. Морфология полученных композитов исследована методом низкотемпературной адсорбции/десорбции азота. Процесс сорбции фосфат-ионов, которые признаны одними из основных загрязнителей воды, изучено на образцах индивидуальных гидроксидов титана и композитах, в состав которых входят оксиды железа и церия, в широком диапазоне pH растворов. Все исследованные образцы показали максимальную сорбционную способность по отношению к сорбируемому иону при pH = 2. Композит на основе гидратированных оксидов титана, железа и церия, синтезованный золь-гель методом, обладает максимальной сорбционной емкостью, которая составляет 3.6 ммоль/г. Для математической обработки изотерм адсорбции использовано теоретические модели Ленгмюра, Фрейндлиха и Темкина. Оказалось, что модель Ленгмюра наилучшим образом подходит к описанию изотерм, полученных на индивидуальных образцах гидроксида титана. Модель Темкина можно использовать для обработки всех экспериментальных изотерм, независимо от состава композитов и метода, использованного для их синтеза.

Ключевые слова: оксид титана, композиты, допированные оксидами железа и церия, адсорбция, фосфат-ионы.

Introduction

Titanium dioxide (titania, TiO_2) has been extensively investigated over the past few decades due to its potential using in the many different areas. First of all, TiO_2 has high refractive index and ultraviolet (UV) light absorption and can be used as a white pigment in paint, food coloring, personal care products and as a UV-absorber in sunscreens [1]. Numerous works are devoted to investigation the titania and composites on the base of titania as photovoltaic cells and photocatalysts for hydrogen production and environmental remediation [2–3]. Titania and TiO_2 -containing nanomaterials are successfully applied in the medical and biological fields, where they have been used for in vivo imaging, cancer therapy and protein separation/ purification and as bactericides [4–5].

Pollution of ground water by phosphate-ions is considered as a serious problem worldwide. Numerous methods have been developed and used in the process of water treatment such as magnetic filtration, electro-coagulation, biological and sorption purification [6–9]. Among a number of materials, hydrated mixed oxides of group-II-IV metals, especially Ti, Fe and Al, synthesized by the most popular method of co-precipitation are suggested for removal of phosphorus and arsenic compounds [10–13]. It is well known that physico-chemical properties of functional materials largely depend on the synthesis conditions [14–16]. For example, the main advantage of sol-gel method that also is widely

used for obtaining the various composites is the possibility to control the textural and surface properties of target materials. According to the studies published early, adding the reagents on the stage of mixing solutions could significantly change the morphology and sorption properties of final products [14].

In this paper, the aim of the study is to investigate the physico-chemical properties of cerium- and ferric-doped titania synthesized by co-precipitation and sol-gel methods with the focus on comparing the composition, morphology of materials obtained and their ability to remove the phosphate ions from water solution.

Experimental section

All chemicals used for the sorption tests ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, HCl, NaOH) were of analytical grade (Makhrohim, Ukraine) and were used without purification. Starting compounds for preparing of the materials on the base of titania were TiOSO_4 , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and NH_4OH . Sorbitol ($\text{C}_6\text{H}_{14}\text{O}_6$) and lactic acid ($\text{C}_3\text{H}_6\text{O}_3$) were used as complexing agents for sol-gel synthesis. Pure solution of TiOSO_4 was prepared by replacing Cl⁻ with SO_4^{2-} in TiCl_4 . The metals content in the prepared solution was controlled by a complexometric titration [17]. Technical solution of TiOSO_4 was bought from the Ukrainian enterprises and consists of TiO_2 (200 g/l), FeO (80 g/l), H_2SO_4 (500 g/l).

Titania samples were synthesized by two methods: co-precipitation (CP) and sol-gel (SG) technology. Co-precipitation process was realized

by dropwise adding to the solution of pure TiOSO_4 ($C = 3 \text{ mol/L}$) the NH_4OH solution (6 mol/L) with intensive stirring at room temperature (sample Ti CP). For obtaining the cerium-doped titania, the solution of cerium nitrate ($C = 1.5 \text{ mol/l}$) was added in desired quantities (initial ratio $\text{Ti}:\text{Ce}=5:1$) on the stage of mixing solutions (sample TiCe CP). After isolation, the obtained solid products were washed with distilled water and then were dried in the air for 24 h at 100°C .

For synthesis of the titanium-based materials by sol-gel method, only technical solution of TiOSO_4 has been used. Gel was prepared by mixing of TiOSO_4 ($C = 3 \text{ mol/L}$) with sorbitol and lactic acid (40 w. % to TiO_2 , according to the data [18]) and then the calculated quantities of NH_4OH (6 mol/L) were added. The ratio of the metals $\text{Ti} : \text{Fe}$ was $5 : 2$ (sample Ti SG). Sample TiFeCe SG was synthesized with the ratio of components of $\text{Ti} : \text{Fe} : \text{Ce}=5 : 2 : 1$. The time of gel formation was 10 sec that was required to obtain the homogenies mixture of reagents. After that, the prepared gels were hydrothermally treated in the steel autoclaves with Teflon beakers under autogenous pressure at 180°C for 24h, and the synthesized titania gels were rinsed with water and dried at 80°C .

Thermogravimetric analysis (TG-DTA) was carried out in the interval of $20\text{--}900^\circ\text{C}$ in the air with a rate of temperature increase of $10/\text{min}$ on a Derivatograph - Q equipment (Hungary). The chemical composition of the obtained titania samples was performed with XRF-spectrometer ELVAX CEP-01 (Ukraine). Specific surface areas and pore size distributions for the synthesized samples were calculated from nitrogen adsorption/desorption curves (NOVA 2200e, Quantachrome, USA) using the Nova Win 2.0 software. Specific surface areas and total pore volumes were found using the Brunauer-Emmett-Teller (BET) method. To acquire the volume of mesopores and micropores, Barrett-Joyner-Halenda (BJH) and t -methods, respectively, were used. Pore radii distributions were obtained from isotherms in terms of the density functional theory (DFT).

Sorption of phosphate ions was examined under static conditions in $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ solutions acidified with hydrochloric acid, if necessary. The sorbent (100 mg) was added to 25 ml of the solution ($V:m = 250$), and the system was equilibrated under shaking for 4 h at 25°C . The mixture was left to stand for 24 h, after which the precipitate was filtered off, and the content of phosphate ions in the filtrates was

determined photocolometrically on a KFK-2 colorimeter (UKL, Russia) in the form of vanadium phosphomolybdate complex [19]. Adsorption capacity (q) was calculated using the following equations:

Adsorption capacity: $qe = \Delta C V/m$, (1)
where $\Delta C = C_0 - C_e$, and C_0 and C_e are the initial concentration and the concentration of phosphate in the solution after sorption (mmol/L); V is the aliquot volume (L); and m is the mass of the adsorbent (g).

The influence of pH on the adsorption capacity in the solutions was evaluated at a pH range of 2–10 with initial PO_4^- concentration of 50 mmol/L .

Experimental data were fitted into the Langmuir, Freundlich and Temkin models, which are commonly used to describe liquid–solid systems [20, 21] by the following equations

Langmuir: $qe = Q_0 K_L C_e / (1 + K_L C_e)$, (2)
where q_e is the adsorption capacity (mmol/g); C_e is the equilibrium concentration of the adsorbate (mmol/L); Q_0 is the maximum adsorption capacity of the adsorbent (mmol/g); and K_L is the Langmuir sorption equilibrium constant (L/mmol).

Freundlich: $qe = K_F C_e^{1/n}$, (3)
where K_F ($(\text{mmol/g})/(\text{L/mmol})^n$) and n are the Freundlich adsorption constants.

Temkin: $qe = (RT/bT) \ln AT C_e$, (4)
where A_T (L/mol) and b_T are the Temkin isotherm equilibrium binding constant, R – universal gas constant (8.314 J/mol K), T – temperature (K).

To evaluate the correlation between the experimental data and theoretical models, the coefficient of determination (R^2) was calculated [20].

Results and discussion

All the obtained materials are amorphous hydrated oxides of titanium or composites on titanium base. The first stage of investigation is the determination of the minimal temperatures needed for decomposition of hydrated oxides to oxides. As follows from the TG curves (Fig.1) after 400°C treatment for the sample synthesized by co-precipitation method and 450°C treatment by the sol-gel method the loss of mass cannot be fixed.

This fact means the TiO_2 is formed at this temperature in the case of TiCP sample (experimental mass loss is 18.9 %, theoretical – 18.9 %). For the sample obtained by sol-gel method (TiFe SG) the process is more difficult and consists of the stage of the organic part

decomposition.

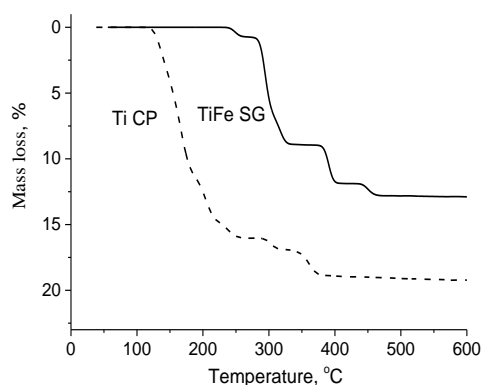


Fig. 1. Thermal analysis (TG curves) of samples obtained by co-precipitation Ti CP and sol-gel method TiFe SG.

After thermal treatment of the samples at these temperatures the metals content is analysed by XRF method. The ratio of the metals calculated in the samples is presented in the Table 1. It should be mentioned that the content of the doped metals in the final products is less than the ratio taken for synthesis (5 : 2 : 1). Nitrogen adsorption-desorption isotherms of all the samples obtained are similar and in accord with the IUPAC classification [22] belong to the II type with the hysteresis loop of the H3 type. The specific surface areas and total pore volumes of initial and doped materials do not differ significantly. A summary of porosimetry data for two modified titania samples is given in Table 1.

Table 1. Composition and porosity data for cerium- and ferric-doped titania synthesized by co-precipitation and sol-gel method.

Sample	Ratio of Ti : Fe : Ce	S _{BET} m ² /g	V _{total} cm ³ /g	V _{BJH} cm ³ /g	V _{t-method} cm ³ /g	R _{BJH} nm	R _{DFT} nm
TiCe CP	5:0:0.5	367	0.26	0.09	0.07	1.71	2.36
TiFeCe SG	5:1.8:0.1	310	0.19	0.04	0.11	1.72	1.25

Such parameters as specific surface area, total pore volume and volume of mesopores (V_{BJH}) for titania, doped by ceria and obtained by co-precipitation method, are greater than those for the second one presented. It has been found that in the structure of all samples mesopores (R_{BJH}) of approx. 1.7 nm radii prevail. Pore volume of micropore ($V_{t-method}$) increases in the case the sample is obtained by sol-gel method. Pore size distributions calculated by the DFT method (Fig. 2) demonstrate the two-mode character for all titania samples

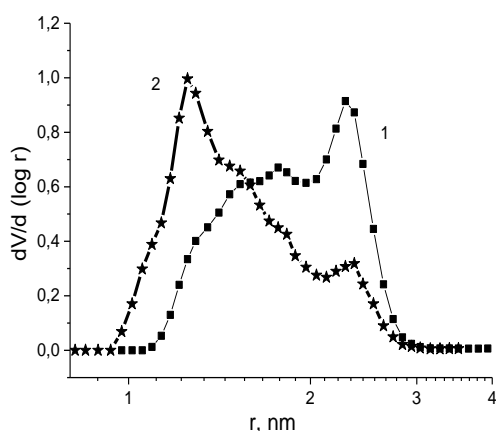


Fig. 2. Pore size distributions obtained in term of DFT method for the samples TiCe CP (1) and TiFeCe SG (2).

The presence of the smaller sized pore in the structure of the titania obtained by the sol-gel method is associated with the more homogeneous distribution of ferric and cerium ions in the structure of the final composite. This result could be explained by using the sorbitol and lactic acid that delay the process of gel formation which guarantee to obtain the uniform mixture of reagents on the first stage of the synthesis, according to complex formation with metals, which was investigated. [23-24].

The first step of the adsorption experiments is to determine the ability of the synthesized materials to remove phosphate ions from 50 mmol/L solution within a pH range from 2 to 10 (Fig. 3). It was found that all titania samples can remove PO_4^{3-} within an extended range of pH (2-10) with the highest adsorption capacity at pH=2. This dependence is typical for the process of sorption the anions by hydrated oxides of transition metals [25]. Mechanism of sorption proposed by authors includes the ion exchange process and formation of the surface complexes with $H_2PO_4^-$ ions that dominated in this region of pH.

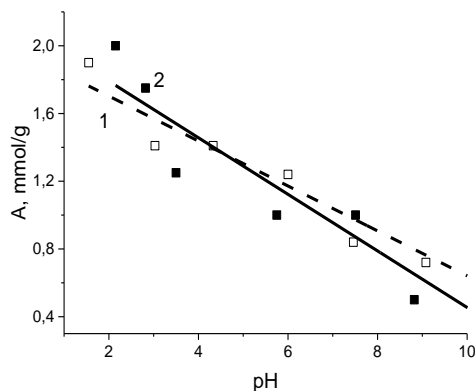


Fig. 3. Dependency of adsorption capacity on the pH for the samples TiCe CP (1) and TiFeCe SG (2). $C_0 = 50$ mmol/L.

According to data represented in Figure 2 the sample synthesized by sol-gel method (TiFeCe SG) has the higher value of capacity in acidic medium than the composite obtained by co-precipitation method.

The second step includes the adsorption isotherms obtained at pH=2 for initial titania and titania doped by ferric and cerium oxides synthesized by two methods, experimental data are represented on Fig. 4 and 5. For all investigated materials, the value of adsorption capacity in a case of the doped titania is greater than for individual titania without reference to the method used. This result could be explained by the contribution of cerium and ferric ions to the process of formation of the complexes with phosphate ions on the surface of composites. The sample TiFeCe SG exhibits the highest adsorption capacity towards phosphate ions of 3.6 mmol/g (Table 2). The equilibrium data have been fitted to the theoretical models: Langmuir, Freundlich and Temkin. Experimental data, calculated curves and parameters for all models are presented in Fig. 4, 5 and in the Table 2.

First model of the Langmuir isotherm refers to homogeneous adsorption, where the each molecule possess constant enthalpies and sorption activation energy (so all sites possess equal affinity for the adsorbate). Table 2 demonstrates that the equilibrium data of non-doped by cerium samples (Ti CP and TiFe SG) correspond satisfactory with the Langmuir isotherm model, with coefficients of determination $R^2=0.996$ and 0.991 , respectively. The correlation coefficient, R^2 calculated for the Freundlich isotherm model is found lower than the one calculated for the Langmuir isotherm model (Table 2).

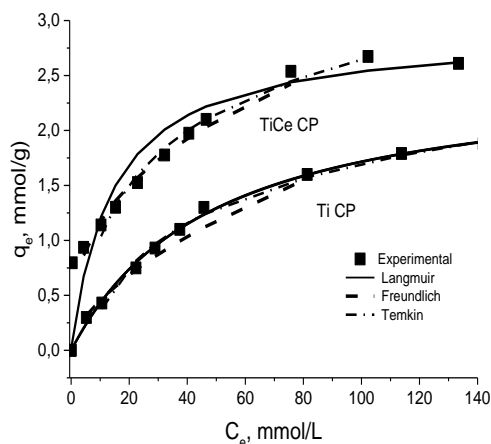


Fig. 4. Experimental data, plots of Langmuir, Freundlich and Temkin isotherm models for the adsorption of phosphate onto the titania and cerium-doped titania obtained by co-precipitation at 25 °C.

Freundlich isotherm is the earliest known correlation describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be better applied to adsorption onto the TiCe CP and TiFeCe SG samples ($R^2=0.997$ and 0.971), than the Langmuir model. The slope ranges between 0 and 1 ($1/n$) and it is a measure of adsorption intensity or surface heterogeneity. The surface becomes more heterogeneous as the slope value gets closer to zero.

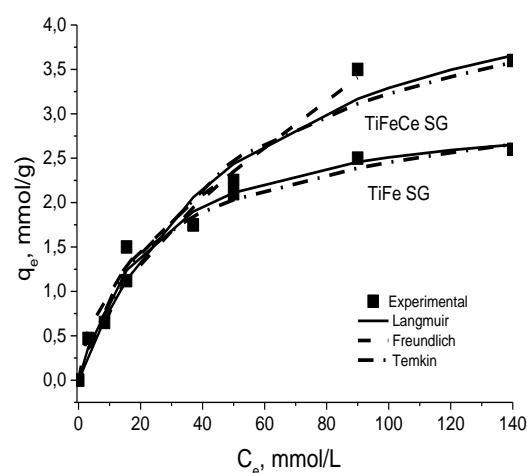


Fig. 5. Experimental data, plots of Langmuir, Freundlich and Temkin isotherm models for the adsorption of phosphate onto the titania and cerium- and ferric-doped titania obtained by sol-gel method at 25 °C.

Langmuir, Freundlich and Temkin isotherm constants for the adsorption of phosphate ions onto titania and ferric- and cerium-doped titania synthesized by two methods.

Samples q_{exp} , mmol/g	Ti CP 1.88	TiCe CP 2.61	TiFe SG 2.65	TiFeCe SG 3.60
Langmuir				
Q_0 (mmol/g)	2.51	2.97	3.09	5.07
K_L (L/mmol)	0.008	0.019	0.043	0.019
R^2	0.996	0.887	0.991	0.967
Freundlich				
K_F (mmol/g)(L/mmol) ^{1/n}	0.121	0.514	0.32	0.2
1/n	0.58	0.36	0.51	0.63
R^2	0.989	0.997	0.971	0.971
Temkin				
A(L/g)	0.18	0.42	0.58	1.1
b_T	43,22	35.84	41.94	24.43
R^2	0.998	0.997	0.986	0.977

The Temkin isotherm contains the factor that explicitly takes into the account the adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that the heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly, rather than in the logarithmic way, with the surface coverage. This type of model describes well the experimental data regardless the method used for synthesis with the highest average value of $R^2=0.99$ (Table 2).

Conclusion

Two types of titania materials are synthesized by co-precipitation and sol-gel method using pure and technical precursors. It has been found that the ratio of the metals and porous structure of materials depends on the peculiarities of synthesis. Presence of pore of the smaller size in the structure of the sample, obtained by the sol-gel method, is associated with a more homogeneous distribution of ferric and cerium ions in the structure of the final composite. It is shown that the sample synthesized by sol-gel method (TiFeCe SG) has the higher value of capacity in acidic medium than the composite obtained by co-precipitation method. The highest adsorption capacity towards phosphate ions shows the sample TiFeCe SG 3.6 mmol/g obtained from technical solution. Temkin model of isotherm describes well the experimental data regardless the method used for synthesis with the highest values of the coefficient of determination.

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