

CRYSTALLIZATION OF THE FRAME-STRUCTURED TITANOSILICATE IN A HIGHLY ALKALINE MEDIUM

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Abstract

The conditions for the crystallization of the frame-structured titanosilicate with the use of a solution of Ti^{4+} sulfate with the addition of alkali in the form of liquid glass and sodium alkali to a pH of 12.5–13.5 have been studied. The optimum molar ratio of TiO_2 : SiO_2 is 1: 4.5. To increase hydrolysis stability, partial reduction of initial solution has been fulfilled by electrochemical method with Ti^{4+} conversion to Ti^{3+} (content of Ti_2O_3 in the solution after reduction is 30–45 g/l). This expedient allows avoiding premature generation of a titanium amorphous phase and directing the process to creation of crystalline precipitate in a form of two structural modifications: trigonal ($Na_4(TiO)_4(SiO_4)_3 \cdot 6H_2O$) and cubic ($Na_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$); the precipitate crystallinity degree is 90–95%. Both structures are similar to the structure of the ivanyukite mineral. Crystallization proceeds under significant oversaturation system by alkaline components. Determined have been optimal conditions for titanium - siliceous precursor sol-gel obtaining and consequent hydrothermal transformation of the obtained gel to crystalline phase. It has been shown that the pore system (total volume of pores) of crystalline ivanyukite particles is approximately 1.5 times larger than that of X-ray amorphous samples and that it is mainly represented by mesopores of medium size, which are characterized by the most activity in sorption processes. Sodium and potassium ions situated in the ivanyukite frame space along with water provide high exchange velocity of cations absorption in sorption processes due to minimal diffusive obstacles. The reported preliminary data on sorption allow to describe the frame-structured crystalline alkaline titanosilicates as effective sorbents of one or two charge cations, as shown by the example of the sorption of strontium, caesium and non-ferrous metals.

Keywords: crystallization, frame-worked titanosilicates, synthesis, sol-gel process, sorbent, sorption processes

INTRODUCTION

Actual economic circumstances in Russia connected with the needs of domestic market in import-substituting production, brings to the fore the question of developing new functional materials. At present, demand for them is considerable, but their manufacturing in Russia is almost lacking. Among these materials are titanium-containing sorbents, which are represented by wide class of compounds with different composition and structure — amorphous and crystalline titanium phosphates, frame-structured titanosilicates, titanium oxyhydroxides and so on. Investigations in the area of synthesis and study on the properties of such sorbents are carried out quite intensively. Titanic reagents in the form of sulphate and fluoride salts of titanium (IV), tetrachlorated titanium [1–3], titanium hydroxide [4] as well as titanium- containing industrial waste products arising, for example, as a result of apatite-nepheline ores processing [5, 6] are used as a raw material for producing such sorbents. In the latter case cost of the sorbents significantly comes down. Advantages of synthetic titanium-containing sorbents over traditional ion exchange resins consists in higher temperature and radiation steadiness, and in a number of cases, selectivity as well, which is especially important during liquid radioactive waste processing and subsequent reagentless utilization of spent sorbents in the form of mineral-like ceramics [7]. Preliminary estimation of titanium-containing sorbents appropriateness for extracting toxic cations of heavy non-ferrous metals is also of practical interest.

The problem of wastewater treatment at enterprises of non-ferrous metallurgy is especially acute, since

toxicity of these wastes is injurious to animate nature. Usage of such inorganic sorbents as titanium phosphates and hydroxides for purification is well known. Their synthesis and properties are clearly understood in contrast to the sorbents based on framework titanosilicates. The investigations, implemented in the latest years, has showed that sorptive activity of titanium phosphates is stipulated by functional groups with complexing properties, presented in them. In other words, sorption of cations proceeds due to exchange for gegenions, which neutralize a charge of phosphate groups [8]. As it is shown by crystallographic research, framework titanosilicates, ivanyukite-group minerals in particular, form an open microcellular framework $[\text{Ti}_4\text{O}_3(\text{OH})(\text{SiO}_4)_3]_3$ – with a system of three groups of mutually perpendicular channels, defined by 8-membered rings with an effective channel width of 3.5 Å, in which Na^+ , K^+ extra framework cations and H_2O molecules are localizing [7].

Exchange of these cations for cations of non-ferrous metals should determine sorptive behaviour of titanosilicates. Model procedure of synthesizing alkaline titanosilicates (Ti – Si) with a structure similar to that of natural minerals consists in mixing silicate and titanium-containing solutions with formation of a gel, which is held in autoclave at high temperature. Various technological and physicochemical aspects of synthesis are discussed in the literature: selection of initial structure-forming titanic and silicon reagents, their molar ratio and pH indicator of a reaction blend, temperature and time behaviour of technological stages [9, 10]. At the same time, it is noticed that the phase content of crystalline products being formed in a process of hydrothermal synthesis depends upon velocity of silicon and titanium compounds hydrolysis at a sol-gel stage of the titanosilicate gel-like precursor formation. Uncontrolled hydrolysis may cause formation of the phases, enriched in silicon or titanium. This corrects the solid phase structure formation, in particular, causes arising a multiphases precipitate which crucially affects technical properties of the final product. The most widespread way of adjusting the process of titanosilicates structure formation is adding into a reaction mass the inorganic compounds, which suppress or accelerate reaction activity of the structure-forming components of the blend [11].

Materials of the present article contain results of the investigations of synthesizing Ti – Si with an ivanyukite-type structure [12]. For directional ivanyukite synthesis it is necessary to suppress reaction ability of titanium component. Authors of the papers [15] add hydrogen peroxide into titanium chloride (IV) solution in order to form a hydrolysis-resistant titanium peroxycomplex (IV), which allows to control a solid phase formation rate. Adding an organic complexon, acetylacetone for example, pursues the same goals. Process of the solid phase formation (sol particles) during sol-gel synthesis can be slowed down by metal powders (zinc, iron) addition into acid titanium liquor as well. Hydrogen arising with this going on reduces titanium (IV) to more hydrolysis-resistant titanium (III). In a sol-gel process, cations-dopants take part in generating the colloid titanosilicate particles, and on consequent hydrothermal action they penetrate into a solid titanosilicate phase structure, provoking its deformation, which doesn't allow getting stability of the final product sorption behaviour. In this connection search of new reagentless technoques of titanium (IV) stabilization, which guarantee a directional synthesis of titanosilicate with ivanyukite-type structure is interesting as scientific and practical matters.

MATERIALS AND METHODS

To implement the experiments there has been used a titanium salt - ammonium titanyl sulphate, out of which a solution has been prepared. Further, partial Ti^{4+} reduction until Ti^{3+} has been carried out by electrochemical technique. The reduction plant is depicted below (in section).

Experimental procedure involves the following sequential operations:

- preparing titanium (IV) solution of titanium salt with composition $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ by its dilution in water without forced heating with the salt consumption in an amount so that the solution with concentration of 80 g/l by TiO_2 would be obtained. Acidic factor, or ratio of H_2SO_4 concentration in the solution to TiO_2 corresponds to 1.45–1.5.
- electrochemical reduction of titanium (IV) to trivalent state at current density on electrodes of 0.1

A/cm². Time of reduction processes has been controlled by achieving the given Ti³⁺ concentration in a solution.

- preparing a titanium-silicate mixture (gel) for hydrothermal synthesis. For this purpose, solution of liquid glass (density 1.46 g/cm³, content of SiO₂ – 30%) has been gradually introduced into the reduced titanium solution until achieving the ratio TiO₂:SiO₂ = 1:0.75–4.5, then a sodium alkali solution has been added to a ratio of TiO₂:Na₂O = 1:4 (a pH indicator is 12.5–13.5). The blend has been mixed for 0.5–1 h and kept at rest for 2 h.
- conducting the gel-like mass hydrothermal synthesis in autoclave during 5 days at the temperature of 200°C.
- the obtained suspension filtering under vacuum.
- the precipitate ablation of mother waters on a filter.
- the washed precipitate drying at the temperature of 70–75°C.

Solid phases has been studied by a Siemens/Bruker D5000 X-ray Diffractometer with monochrome CuK α radiation (λ = 1.5418 Å), UR-20 Carl Zeiss Jena spectro- photometer, Cameca MS-46 electron microanalyzer and Carl Zeiss LEO-1450VP Scanning Electron Microscope with a QUANTAX Energy-dispersive X-ray spectrometer. To characterize a surface behaviour of synthesized titanosilicates a Micromeritics TriStar 3020 surface area and porosity analyzer has been used. The specific surface area and total volume of pores has been determined by a BET method through the nitrogen sorption/desorption isotherms. Size distribution of pores has been calculated by nitrogen thermal desorption method (BJH-method), the structure porosity has been determined by the adsorbed nitrogen volume dependence on adsorbate film thickness (t-plot method).

Sorption capacity of obtained materials with respect to some uni- and bivalent cations has been established in static conditions at a solid to liquid phase ratio of 1:200 and a sorbent and sorbate contacting time of 24 hours. The cations concentration in solutions has been determined by mass-spectrometry with inductive-connected plasma (MS-ICP) on a PerkinElmer Elan 9000 quadrupole ICP-mass spectrometer (Perkin Elmer, USA) [13].

RESULTS AND DISCUSSION

Two sulphate-ammonium solutions with a trivalent titanium concentration of 30 and 45 g/l by Ti₂O₃ respectively have been used for research. When implementing the experiments by the procedure outlined above, precipitates have been obtained, the phase composition of which according to X-ray phase analysis is aggregated in Table 1.

The solid phase characteristics, % (wt.)	Experiment 1 30 g/l Ti ₂ O ₃	Experiment 2 30 g/l Ti ₂ O ₃	Experiment 3 45 g/l Ti ₂ O ₃	Experiment 4 45 g/l Ti ₂ O ₃
	TiO ₂ :SiO ₂ =1:0.75	TiO ₂ :SiO ₂ =1:4.5	TiO ₂ :SiO ₂ =1:0.75	TiO ₂ :SiO ₂ =1:4.5
Amorphous phase	65	5	65	10
Anatase with low crystallinity degree	35	-	35	-
Ivanyukite – C + Ivanyukite – T	-	95	-	90

Table 1. Experiments conditions and phase composition of the synthesized solids

Nucleation for structuring titanosilicate has started in a multicomponent sol-gel system. During the consequent high-temperature hydrothermal reaction on a gel-like mass under autoclave conditions, regulating the solid phase particles structural order takes place. In experiments with stoichiometric for ivanyukite molar titanium to silicon ratio TiO₂:SiO₂ = 1:0.75, an X-ray amorphous precipitate with crystallinity degree is forming (experiment 1 and 3 in Table 1). This is because the Ti₂O₃ presence in

an initial solution slows down a Ti^{4+} hydrolysis, initiating by this the silicon hydrolysis with formation of amorphous silica. Titanium hydrolysis with an X-ray amorphous phase formation as well is beginning at significant shortage of silicon in dissolved state. The following hydrothermal process leads to structure consolidation and appearing of the phase (anatase) with low crystallinity degree. In a case of the heightened silicon content $\text{TiO}_2:\text{SiO}_2 = 1:4.5$, in other words, on the system satiety by silicon- containing reagent in analogous experiment conditions, two structurally close crystalline phases of ivanyukite are forming: trigonal — $\text{Na}_4(\text{TiO})_4(\text{SiO}_4)_3 \cdot 6\text{H}_2\text{O}$ (T) and cubic — $\text{Na}_3\text{H}(\text{TiO})_4(\text{SiO}_4)_3 \cdot 4\text{H}_2\text{O}$ (C) (experiments 2 and 4). The excess silicon content provides keeping the stoichiometric ratio of the components over the course of both stages of the titanosilicate structure formation and promotes production of crystalline precipitate – ivanyukite (crystallinity degree is 90–95%). The initial Ti^{3+} concentration on Ti_2O_3 in titanium solution in either case have insignificant effect on the precipitate structure.

Since TiSi (samples of experiments 2 and 4) have approximately similar phase content, the authors cite data only on one of them (Fig. 1). An intensive peak of the synthetical ivanyukite main phase on the X-ray photo- graph has coordinates 2θ — 11.31 (Ref. Code 01-078-3450). Low-intensity refelexes with coordinates 2θ — 24.40, 32.14, 48.38, 62.84 have been attributed to a titanium phase $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (Code 00-047-0124). Low sensitivity of X-ray phase analysis and presence of X-ray amorphous phase don't permit to completely describe composition of synthesized products. Presence of X-ray amorphous phase (silica) is attested by unclearness of peaks at 2θ more than 35.

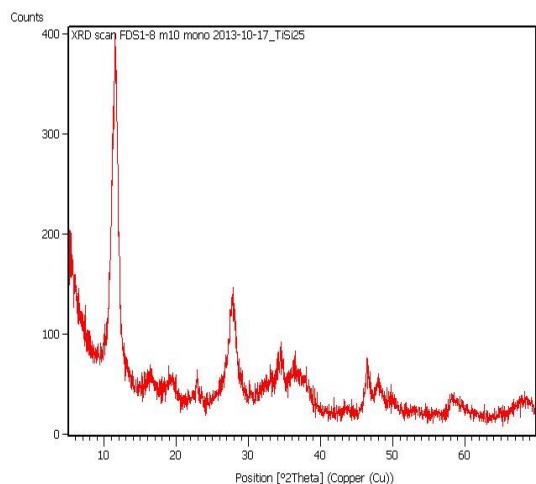


Fig. 1. XRD pattern of the sample 2

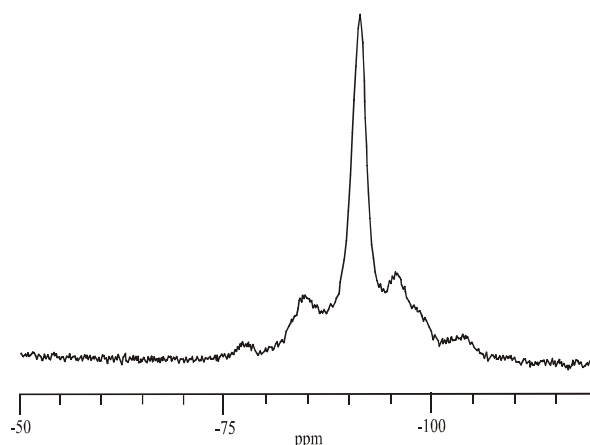


Fig. 2. ^{29}Si NMR spectrum of the sample 2

Nuclear magnetic resonance data of the sample study (for ^{29}Si) has showed that principal peaks at – 94.3 and – 97.5 ppm refer to $3\text{Si}1\text{Ti}$ environment (Fig. 2). This implies that three silicon are bounded with titanium and SiO_4 tetrahedron are perpendicular to $\text{Ti} - \text{O} - \text{Ti}$ chains. Small peak at – 104.5 ppm corresponds to $4\text{Si}0\text{Ti}$ environment, in which the central atom of silicon is tetrahedrally connected with 4 other structural blocks of silicon. Frequencies in a zone around – 87.5 ppm witness about presence of a small number of free groups = $\text{Si}(\text{OH})_2$ in the analyzed assay.

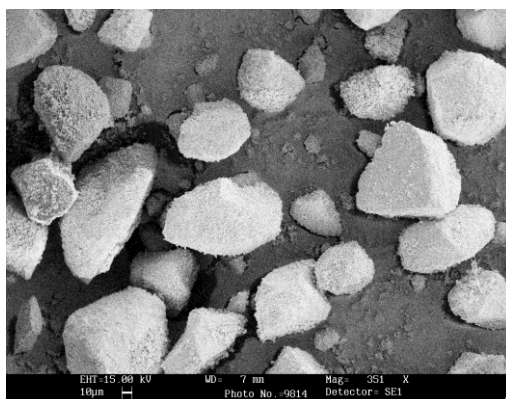


Fig. 3. A SEM image of the synthetic ivanyukite particles (sample 2)

Particles of ivanyukite in a sample are predominantly represented by fraction of 5–20 μm. Individual crystals of size up to 100 μm are also contained (Fig. 3).

The ivanyukite mineral crystalline structure is inherited for its synthetic analogue as well. Values of specific surface area and average pore size of the particles of investigated samples are given in Table 2.

Experiment	Ssp, m ² /g	Vpore, cm ³ /g	D pore, nm (average)
1	216.9	0.445	11.4
2	197.3	0.619	4.2
3	281.27	0.405	14.2
4	187.57	0.625	4.9

Table 2. Surface properties of the synthesized samples

Values of a specific surface area of the powder particles, mainly consisting of X-ray amorphous phase and anatase phase with low crystallinity degree, significantly exceed that of the samples with dominating content of crystalline ivanyukite (about 1.5 times). On the contrary, total pore volume of ivanyukite particles is 1.5 times higher. Since pore diameter in that case is essentially smaller than that of the samples of experiments 1 and 3, it can be assumed that the pore system of ivanyukite particles is represented by narrow but deep mesopores, which can guarantee transportation of ions deep into the particles thus rising sorptive ability. This assumption is confirmed by the data given in Table 3.

Experiment	E _{Co} , mg/g	E _{Ni} , mg/g	E _{Cu} , mg/g	E _{Sr} , mg/g	E _{Cs} , mg/g
1	47.4	52.6	62.3	72.1	166.0
3	28.0	34.7	46.0	62.5	144.8
2	68.9	101.1	144.6	152.0	450.6
4	67.0	94.8	140.9	160.3	438.5

Table 3. Sorption capacity of the samples toward mono and divalent cations

Sorption properties of Ti – Si products have been determined in static conditions with the proviso that sorbent:sorbate = 1:200 [14]. Model solutions have been used as sorbates.

Element	Co	Ni	Cu	Sr	Cs
Origin concentration of cations, g/l	0.45	0.83	0.89	1.17	2.06
pH of model solutions	6.3	6.5	5.15	6.59	6.94

Table 4. Characteristics of model solutions

Thus, it can be stated that ivanyukite samples have higher sorptive capacity over cations of caesium and strontium in comparison with X-ray amorphous or weakly crystalline anatase samples. Distinction of the investigated samples sorptive capacity over cations of non-ferrous metals becomes apparent to a lesser degree. Absorption of cations by sorbents proceeds according to different mechanisms. For X-ray amorphous samples and the ones with low crystalline degree (1 and 3), which practically don't contain ivanyukite, a cation absorption mechanism is based on surface complexing for the most part and on ion exchange to a smaller extent. For ivanyukite (experiments 2 and 4) with crystalline frame structure of the particles, filled by cations of sodium and potassium, the sorption mechanism is based on ion exchange.

Table 5 shows the pH values of the obtained samples of titanosilicate and filtrates after sorption with their participation.

Experiment	pH Ti-Si	pH filtrates after sorption				
		Co	Ni	Cu	Sr	Cs
1	8.56	6.70	6.75	4.93	7.05	8.01
3	8.35	6.71	6.69	5.01	6.98	7.76
2	11.2	7.18	7.14	5.55	8.03	10.30
4	11.5	7.55	7.33	5.58	8.01	10.06

Table 5. Characterization of the conditions (pH of the medium) of the sorption of mono and divalent cations.

Synthesized titanosilicates have different pH values. The samples containing several phases-amorphous (apparently silica), anatase with low crystallinity degree, as well as an impurity titanosilicate phase, have a pH of about 8.5, and samples with crystalline titanosilicate in the form of ivanyukite-11.3. The absorption of cations by sorbents occurs by a different mechanism. For samples 1 and 3 experiments, in which there is practically no ivanyukite, the sorption is mainly due to the high activity of the particle surface, and for the ivanyukite (experiments 2 and 4) with the crystal framework structure of the particles filled with sodium and potassium cations, the sorption mechanism is based on ion exchange. The medium in which the sorption process proceeds, the pH of the sorbent and sorbate is determined.

The kinetics of sorption of cations on a crystalline titanosilicate was studied (experiment 2). It is shown that the exchange processes involving the caesium cation proceed at a faster rate than with the strontium cation. This fact can be explained by the fact that the strontium ion, as well as the cations of non-ferrous metals, has a hydrate shell under these sorption conditions, which creates steric difficulties for its transport into the interior of the sorbent particles. Therefore, the process speed decreases (Fig. 4).

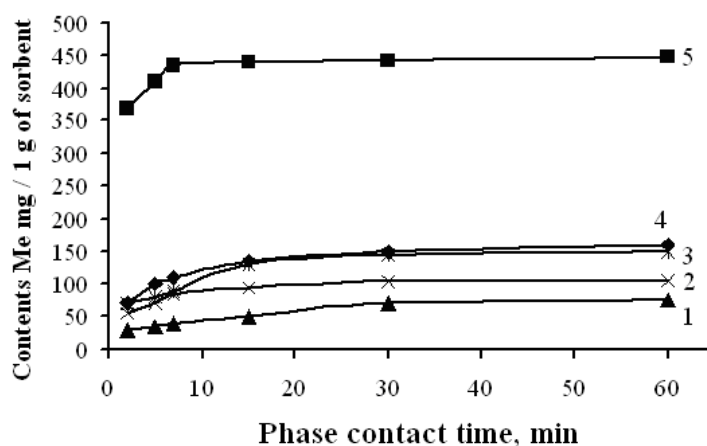


Fig. 4. Kinetics of the solid toward cations: 1 - Co, 2 - Ni, 3 - Cu, 4 - Sr, 5 - Cs.

CONCLUSIONS

The conditions of crystallization frame-structured titanasilicate with the use of a solution, prepared of ammonium titanyl sulphate have been investigated. To increase titanium(IV) hydrolysis stability, partial reduction of initial solution has been fulfilled by electrochemical method with Ti^{4+} conversion to Ti^{3+} . This expedient allows one to avoid an amorphous phase generation and to direct the process to creation of crystalline ivanyukite in a form of two structural modifications: trigonal $(Na_4(TiO)_4(SiO_4)_3 \cdot 6H_2O)$ and cubic $(Na_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O)$; the precipitate crystallinity degree is 90–95%. Determined have been optimum conditions for titanium- silicon precursor sol-gel synthesis and consequent hydrothermal transformation of the obtained gel to crystalline phase: content of Ti_2O_3 in the solution after reduction is 30–45 g/l, molar ratio $TiO_2:SiO_2 = 1:4.5$. It has been shown that total volume of pores of the crystalline titanasilicate particles is approximately 1.5 times larger than that of X-ray amorphous samples and that the pore system is represented by mesopores of medium size, which are characterized by the most activity in sorption processes. Located in the framework of crystalline titanasilicate, sodium, potassium and water ions provide a high rate of cation absorption in sorption processes due to minimal diffusion barriers. The reported preliminary data on sorption allow one to describe the frame-structured crystalline alkaline titanosilicates as effective sorbents of non-ferrous metals, strontium and caesium ions. Based on the absorption kinetics of the cations can be said that the exchange processes involving the caesium cation proceed at a higher rate than with the cation of strontium and non-ferrous metals. This fact can be explained by the fact that two charge cations under the indicated sorption conditions (pH) have a hydrated shell, which creates steric difficulties for their transport into the interior of the sorbent particles. The sorption activity of amorphous and slightly crystallized samples is much lower.

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