METHOD OF COMPETING IONS FOR SOL-GEL PROCESSING OF SORBENTS AND CATALYSTS IN AQUEOUS SOLUTIONS OF INORGANIC SALTS

VLADIMIR V. STRELKO*
Institute for Sorption and Endoecology Problems of National Academy of Sciences of Ukraine, General Naumov Str. 13, Kyiv-164

Abstract. An original method of competing ions has been proposed and experimentally tested permitting a sol-gel process to be conducted only with water solutions of simplest salts, alkalis and acids without using chelating reagents.

The data are also presented on the "oil-drop" and "air-drop" technologies for continuous sol-gel production of spherically granulated inorganic ion exchangers such as titanium and zirconium phosphates as well as solid high-porous acid catalysts based on sulfonated zirconium and titanium dioxide. The information is given about selective sorption of trace amounts of heavy metals, radionuclides, and uranium from a variety of technological solutions and drinking water on the prepared titanium and zirconium phosphates.

Keywords: Sol-gel processing, aqueous salt solutions, continuous granulation, inorganic ion exchangers, titanium and zirconium phosphates, titanium silicates, heavy metals, uranium and radionuclides, hard solid acids.

1. Introduction

Today the sol-gel approaches have realized their potentials in the preparation of a new generation of advanced materials: ceramic powders, membranes, glasses, fibers and monodisperse particles, coatings, biomaterials and sensors, electronic materials, and even untraditional sorbents and catalysts.[1]

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[*] To whom correspondence should be addressed: Vladimir strelko; e-mail: vstrelko@ispe.org.ua

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Two main sol-gel techniques are used nowadays. The first one involves aqueous solutions of salts as precursors and the second one is based on hydrolysis of metal-organic molecular precursors, such as metal alkoxides (mostly in alcohols as solvents).

The aqueous solutions of salt precursors free from any additives are employed only in sol-gel methods of processing silica gels and amorphous aluminosilicates (especially on industrial scale) using sodium silicate and aluminate as well as mineral acids. As regards water solutions of other polyvalent metal salts, the sol-gel process can be realized, as a rule, by chelating metal ions by organic ligands such as citrates or oxalates thus forming polymeric gel precursors.

The traditional method of sol-gel synthesis using polyvalent metal alkoxides may have a variety of modifications, for instance, the use of non-hydrolytic sol-gel techniques.

It should be, however, noted that in spite of many attractive prospects of using alkoxides in the sol-gel synthesis of materials (mild chemical conditions, easy miscibility of different metals, easily controlled homogeneous doping, high purity of products, use of functionalized precursors, etc.), this widespread method possesses a number of limitations. Indeed, alkoxides are not always available and easy to handle, and they are also quite expensive and volatile, sensitive to atmospheric moisture; moreover, application of usual organic solvents (e.g., alcohol) in the sol-gel method on an industrial scale is very dangerous due to their flammability.

In the above context, this paper presents the data on development of new continuous sol-gel methods for the synthesis of spherically granulated dispersed individual and mixed oxides (inorganic ion exchangers, solid catalysts, and catalyst supports) with controlled porosity and surface chemistry. An important feature of these sol-gel methods is the use of convenient and accessible water solutions of inorganic salts, alkalis (hydroxides), and acids as precursors without addition of chelating organic ligands.

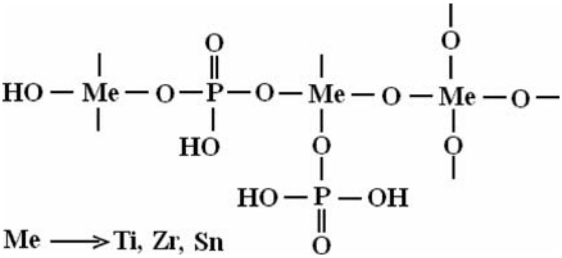
In other words, the present study demonstrates possibility to realize the sol-gel process only with metal salt precursors using no alkoxides or organic chelating ligands. The emphasis will be on the description of an original method of sol-gel synthesis, mostly focusing on preparation of porous dispersed materials with spherical granulation, namely, inorganic ion exchangers and catalysts.

It is well known that the methods of wet chemistry (precipitation and co-precipitation, sol-gel synthesis from alkoxides, etc.) are widely practiced now for production of sorbents, catalysts, and catalyst supports. However, they have some grave drawbacks: the impossibility of continuous technological process, necessity of the granulation step (tableting, extrusion with a binder, etc.), and poor control of porometric characteristics.

A pivot concept of the approach stems from the fact that precipitation occurs always more rapidly than sol or gel formation in the course of dispersed oxide preparation. Accordingly, the sol-gel process can be realized using water solutions of metal salts with the addition of organic ligands, as the chelation of metal ions slows down the solid phase formation (generation of sol particles and their coagulation to gels).

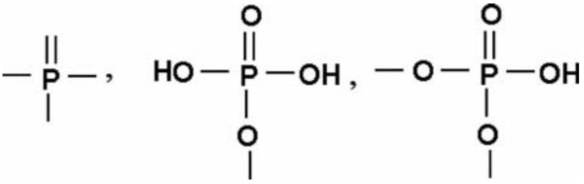
From our point of view, the slowing down of solid phase formation (sol-gel preparation from water solutions of metal salts) can also be caused by the competition of cations and anions added to one of starting precursors.

For experimental confirmation of the developed concepts, it is appropriate to consider the possibility of the occurrence of sol-gel processes in formation of classical inorganic ion exchangers, namely, acidic titanium phosphates (TiP) and zirconium phosphates (ZrP).[2,3] These materials are inorganic polymers consisting of individual or cross-linked chains as shown in the following scheme:



(1)

It is assumed that such polymer species are partially or entirely globule-folded preserving their ion-exchanging properties. As an example, Figure 1 shows the molecular structure of ZrP and the corresponding ^{31}P NMR spectrum which indicates the relative contents of the groups in the ion exchanger matrix and some amount of H_3PO_4 occluded in the synthesis.[4] TiP has a similar molecular structure.



One can obtain such ion exchangers with much developed porosity; they are known for thermal, chemical, and radiation stability and manifest, due to surface complexing, high absorption selectivity even with respect to traces of heavy metals, radionuclides, and transuranium elements to be extracted from solutions of complex composition.[2,3]

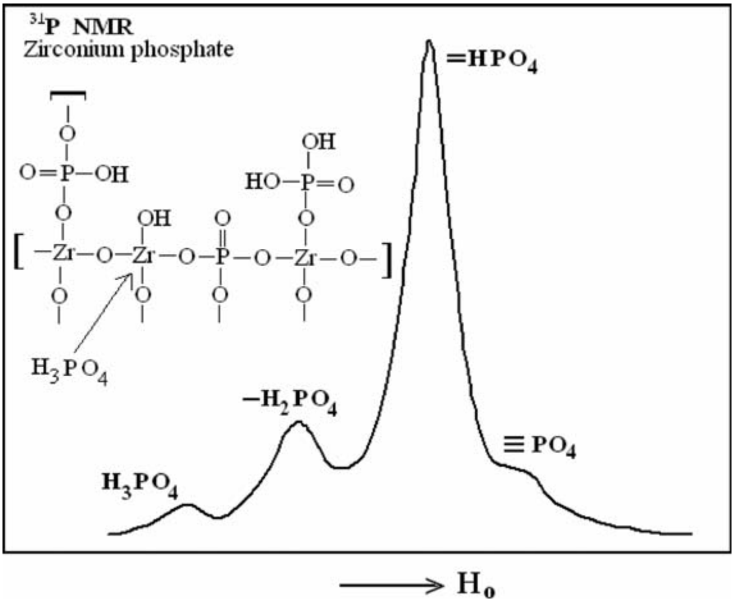


Figure 1. The suggested molecular structure and the ^{31}P NMR spectrum for a typical sample of zirconium phosphate.[4]

As a rule, these materials are obtained as precipitates, according to the equation:

$$TiCl_4(ZrOCl_2) + nH_3PO_4 \rightarrow \underbrace{Ti_x(HPO_4)_y{\cdot}nH_2O + Zr_v(HPO_4)_w{\cdot}nH_2O}_{\text{precipitates}} + mHCl \quad (2)$$

By addition of Ti- and Zr-chelating organic ligands (e.g., urea or acetate and lactate anions) to the initial salt solution, we succeeded, under certain regimes, to obtain TiP and ZrP gels rather than precipitates, just as in the sol-gel preparation of Ti and Zr oxides when the metal complexes with the mentioned ligands are treated with ammonia.[5]

2. Competing ions as a Control Factor in the Sol-Gel Synthesis Based on Aqueous Salt Solutions

In our opinion, the solid phase generation in reaction (2) can also be slowed down by preliminary addition of some cations and anions to one of the components of the reaction medium; these ions are also capable of forming a solid phase (precipitate) or a stable soluble compound with Ti (Zr) or phosphoric acid. In this case, competing interaction should occur which can essentially influence the formation of a solid phase (sol). As an example, the following reactions can proceed in the reaction system presented by (2) if SO_4^{2-} anions (competing with H_3PO_4) are introduced into it:

– The traditional reaction producing the TiP precipitate

$$TiCl_4 + H_3PO_4 + H_2O \rightarrow \underset{\text{precipitate}}{Ti_x(H_2PO_4)_y \cdot nH_2O} + HCl \qquad (3)$$

– The competing reaction producing the stable soluble $TiOSO_4$ compound

$$TiCl_4 + H_2SO_4 + H_2O \rightarrow TiOSO_4 + 4HCl, \qquad (4)$$

– TiP gelation induced by the addition of SO_4^{2-} anions:

$$TiCl_4 + H_3PO_4 + H_2SO_4 + H_2O \ \rightarrow\ \underset{\text{gel}}{Ti_x(H_2PO_4)_y \cdot (HSO_4)_z^{*}} + nHCl.$$

If SO_4^{2-} anions compete with phosphate anions in the reaction medium (5), the formation time of the solid phase (sol and gel) rises and grows almost linearly with the increasing SO_4^{2-} content in the system (Figure 2).

It is interesting to note that the variation of $SO_4/TiCl_4$ ratio in the reaction medium allows to regulate, in a certain range, the volume of sorption pores, V_s (measured by benzene vapor sorption), the specific surface area, S_{sp} (Figure 3), and the mesopore volumes distribution per radii of the corresponding xerogels (Figure 4).

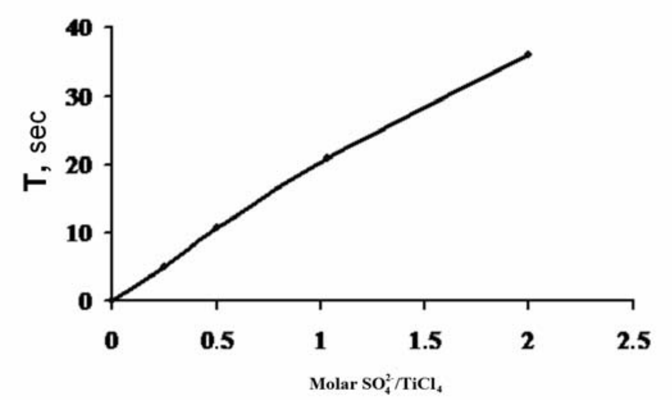


Figure 2. The effect of the $SO_4^{2-}/TiCl_4$ molar ratio in the reaction mixture on the TiP gelation time ($T = -10^0C$).

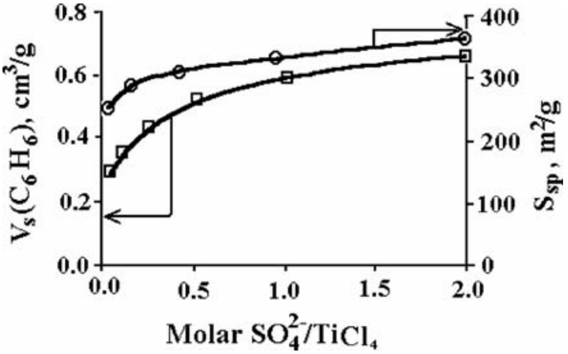


Figure 3. The effect of the $SO_4^{2-}/TiCl_4$ molar ratio in the reaction mixture on TiP xerogel porometric characteristics.

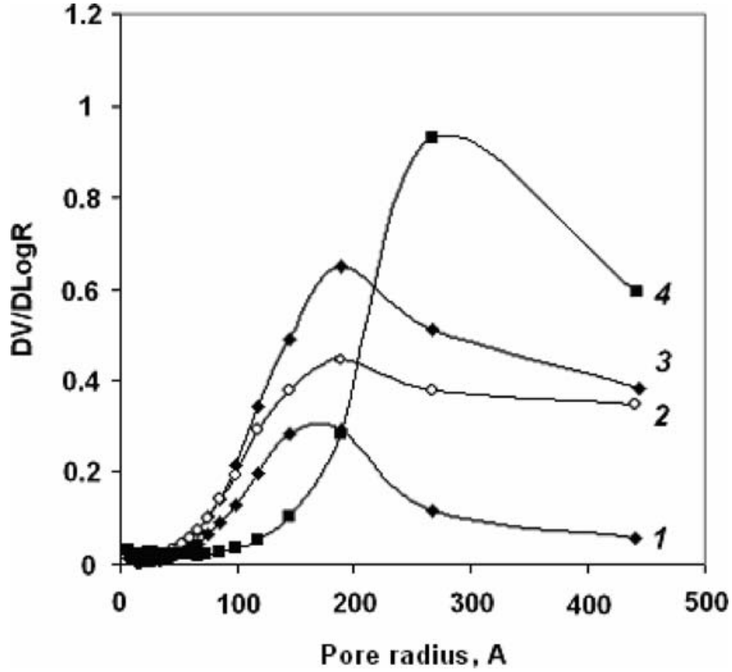


Figure 4. The distribution of pore volumes per radii for TiP samples synthesized from $TiCl_4$ solutions with different SO_4^{2-} ion contents: 1 – SO_4^{2-}/Ti = 0.1; 2 – SO_4^{2-}/Ti = 0.5; 3 – SO_4^{2-}/Ti –1.0; 4 – SO_4^{2-}/Ti – 2.0.

A special investigation has been carried out in order to confirm (5), i.e., to insure that the TiP solid phase can be generated, though more slowly, by the reaction of H_3PO_4 with $TiOSO_4$. Titanyl sulfate arises in process (5) as an intermediate in the reactions of the sol-gel formation of TiP. The affinity of Ti (IV) to the phosphate anion is likely to be higher than to the sulfate anion, which is evidenced by the fact that TiP does form in a system containing H_2SO_4.

In the following, we shall demonstrate that not only phosphate groups but also some amount of sulfonic $-SO_3H$ groups are chemically immobilized on the titanium phosphate surface at the presence of SO_4^{2-} anions in the solution (5). For simplicity, this material is designated from here on as TiP.

In fact, the process occurs according to the following equation:

$$TiOSO_4 + H_3PO_4 \rightarrow \underset{\text{gel}}{Ti_x(H_2PO_4)_y(HSO_4)_n \cdot nH_2O}. \quad (6)$$

For this reaction, the temperature dependence of gelation time (Figure 5) and the time dependence of viscosity (Figure 6) were studied at varied P/Ti molar ratios. As it can be seen from Figure 6, the gelation time increases with the increasing $TiOSO_4$ content (the decreasing P/Ti molar ratio) in the system, thus corroborating the assumption represented by (5) and (6). Clearly exponential increase of viscosity in the system (Figure 6) results in formation of gel with various TiP content.

On the other hand, it is well known that Fe^{3+}, Al^{3+}, Cr^{3+}, Ti^{3+}, and other triple-charged cations, as well as Ti (IV), form insoluble phosphates in the reaction with phosphoric acid. That is why one would expect that the addition of these cations to the reaction medium presented by (2) can cause the competition between them and Ti, Zr(IV) for the interaction with phosphate anions

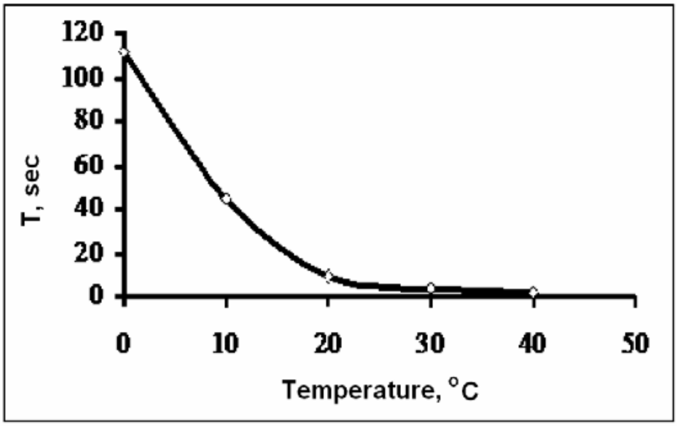


Figure 5. Gelation time of the synthesized TiP samples as a function of temperature (for the initial molar ratio P/Ti = 1).

(phosphoric acid). Finally, this should also slow down the process and hence may lead, under certain conditions, to the formation of the TiP sol and gel with the matrix containing the chemically bound triple-charged cations added in the synthesis.

In this case, it is apparent from general principles that the sequence of adding triple-charged cations (Fe^{3+} as an example) to the reagents can notably effect the course of the process. It is known that $FeCl_3$ addition to H_3PO_4 immediately

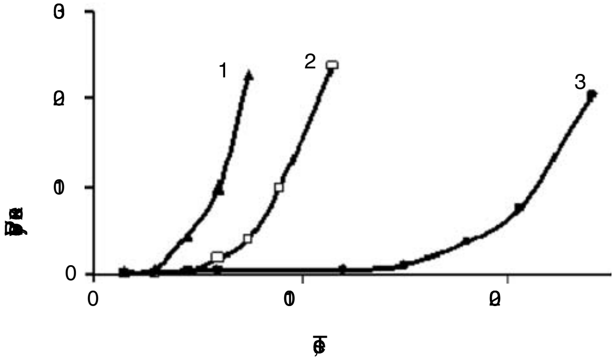


Figure 6. Effective viscosity plotted against reaction time for the TiP samples synthesized from $TiOSO_4$ at varied P/Ti molar ratios: 1 – 1.25; 2 – 1; 3 – 0.75.

$$[TiOSO_4 + FeCl_3] + H_3PO_4 \rightarrow \underline{TiP}\ (gel)\ (a)$$

$$TiOSO_4 + [FeCl_3 + H_3PO_4] \rightarrow \underline{TiP}\ (gel)\ (b)$$

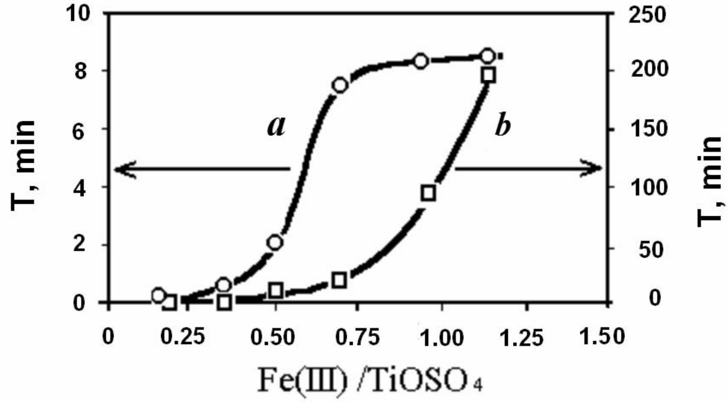


Figure 7. The effect of the sequence of the Fe(III) salt addition on the TiP gelation time at varied Fe(III)/$TiOSO_4$ molar ratios.

results in the soluble acidic phosphate, which should be destroyed in the reaction with $TiCl_4$. Indeed, we succeeded to demonstrate that adding Fe^{3+} to various precursors (a solution of $TiOSO_4$ or H_3PO_4) significantly changes the kinetic parameters of the process, as seen from the experimental data presented in Figure 7.

After drying the TiP hydrogels, the triple-charged cations involved in the sol-gel processing are almost completely removable from the ion exchanger matrix by washing with a mineral acid and then with water.

We have carried out an analogous study to assess the possibility that the ZrP sol-gel synthesis is induced by the addition of Al^{3+} ions competing with Zr(IV) to the starting precursors. The process occurs according the equation:

$$\mathrm{ZrOCl_2 + H_3PO_4} \xrightarrow{\mathrm{Al^{3+}}} \underset{\text{mixed AlZrP gel}}{\mathrm{Al_x^{3+}Zr_y(H_2PO_4)_z\cdot nH_2O}} \xrightarrow{\mathrm{H^+}} \underset{\text{pure ZrP gel}}{\mathrm{Zr(H_2PO_4)_2\cdot nH_2O}} + \mathrm{Al^{3+}} \qquad (7)$$

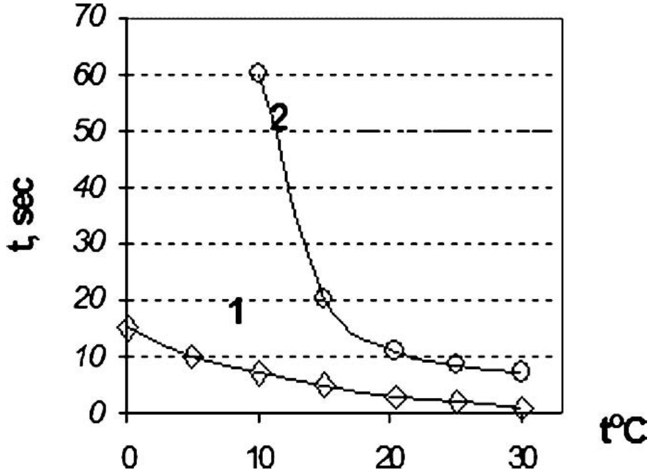


Figure 8. The temperature dependence of the ZrP gelation time at varied molar Al/Zr ratios: 1 – *0.5* and 2 – *1.0*.

Figure 8 shows the data testifying the essential influence of Al^{3+} ions on the ZrP gelation time at various temperatures.

We have been first to reveal not only the slowing-down effect of triply charged cations on TiP and ZrP gel synthesis but also their template action on the matrix of these materials. Indeed, the S_{sp} values of traditionally produced titanium and zirconium phosphates do not exceed 150–250 m^2/g. If they are prepared by the suggested procedure, i.e., by the sol-gel processing in the presence of triply charged cations, the S_{sp} values reach 300–700 m^2/g after desorption of these template cations from the matrix because they leave ultra-pores of comparable size (Figure 9):

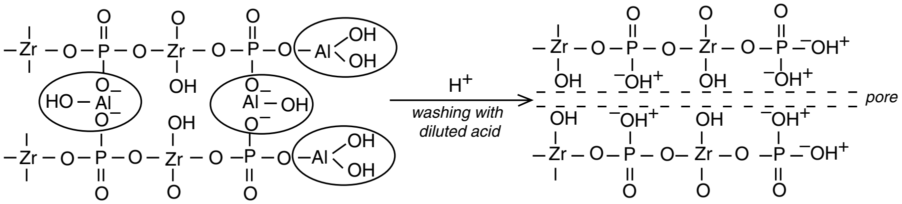


Figure 9. The scheme of the template action of Al^{3+} ions in the synthesis of ZrP cation exchangers.

It is essential that the TiP and ZrP samples synthesized in the presence of templating gel-forming cations (slowing down the process) exhibit much higher selectivity to d-metal cations. In the ZrP matrix, phosphate and hydroxyl groups oriented in the course of the synthesis and fixed in ultrapores (Figure 9) are spaced so that the coordination interaction with complexing cations is facilitated.

Figure 10 shows the isotherms of ion-exchange sorption for a series of d-metal cations. We notice from this figure that in the region of equilibrium near-zero concentrations, the isotherms start just at the ordinate axis, which unequivocally confirms high ion exchanger selectivity. Selectivity coefficients, K_d, for some cations have large values (10,000–20,000) and the selectivity series for ZrP is as follows:

$Th(IV)>Ce(III)>Fe^{3+}>Al^{3+}>Cr^{3+}>Pb^{2+}>>Cu^{2+},Zn^{2+},Cd^{2+},Co^{2+}\sim$
$Ni^{2+}>Ca^{2+}>Na^{+}$

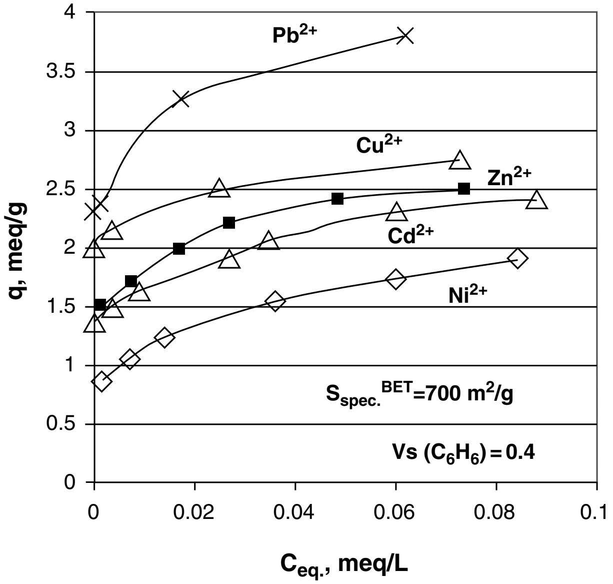


Figure 10. Typical isotherms of sorption of heavy metal cations onto the ZrP sample templated with Al^{3+} ions.

Summing up, it is appropriate to demonstrate (Figure 11) the appearance of solid transparent hydrogels containing various competing cations in the matrix; for comparison, gel-like precipitates (often misnamed gels) are also shown.

Figure 11. The appearance of gels and gel-like precipitates.

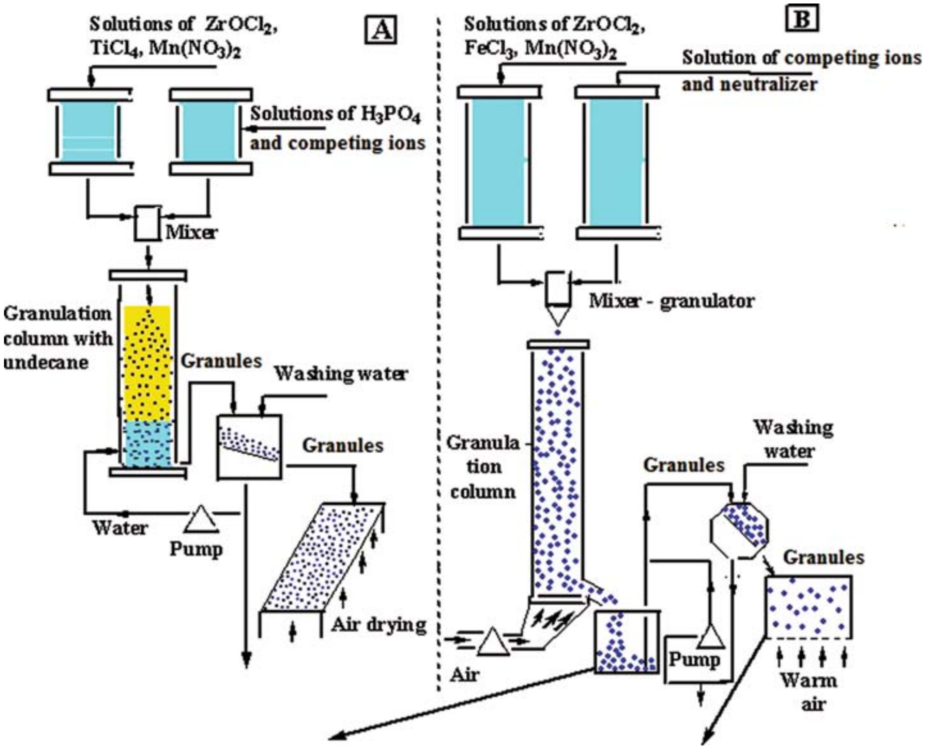


Figure 12. The schematic diagram of the “oil-drop” (A) and “air-drop” (B) sol-gel technologies to prepare spherically granulated hydrated oxides and phosphates of Ti and Zr by the method of competing ions.

By testing various reagent ratios, temperatures, pH values, and quantities of competing ions (mostly SO_4^{2-}), we managed to reduce the sol-gel conversion time to 3–5 sec. This allowed us to develop two semi-pilot technologies (the “oil-drop” and “air-drop” technologies) for the continuous preparation of individual and mixed hydrated oxides and phosphates of polyvalent metals (mostly Ti and Zr) obtained as highly porous spherical granules (Figure 12).

The “oil-drop” technology is based on fast injection of quickly mixed reagents into a column with oil or another water-immiscible liquid (like undecane). Entering the column, the reaction mixture stream is divided into spherical drops of controlled size which are transformed into hydrogel spherical granules within 3–5 sec during the slow movement through the organic liquid layer in the column.

The “air-drop” technology is organized in the same way; however, the drops of the reaction mixture enter the air stream (rather than organic liquid) blowing from the bottom of the column and controlling the air temperature and movement time of the hydrogel drops until they reach the flow of a washing solution or water.

The resulting spherical granules of hydrogels can be subjected to a number of different treatment schemes (washing with solutions of various pH values, substitution of intermicellar liquid, thermochemical and hydrothermal processing, etc.) which enable a wide-range variation of the porous structure and the surface chemistry of the materials obtained.

Figure 13 gives the appearance of the initial typical hydrogel produced by the continuous method and the corresponding dried xerogel with highly developed porosity and glass-like transparent granules of regular spherical shape.

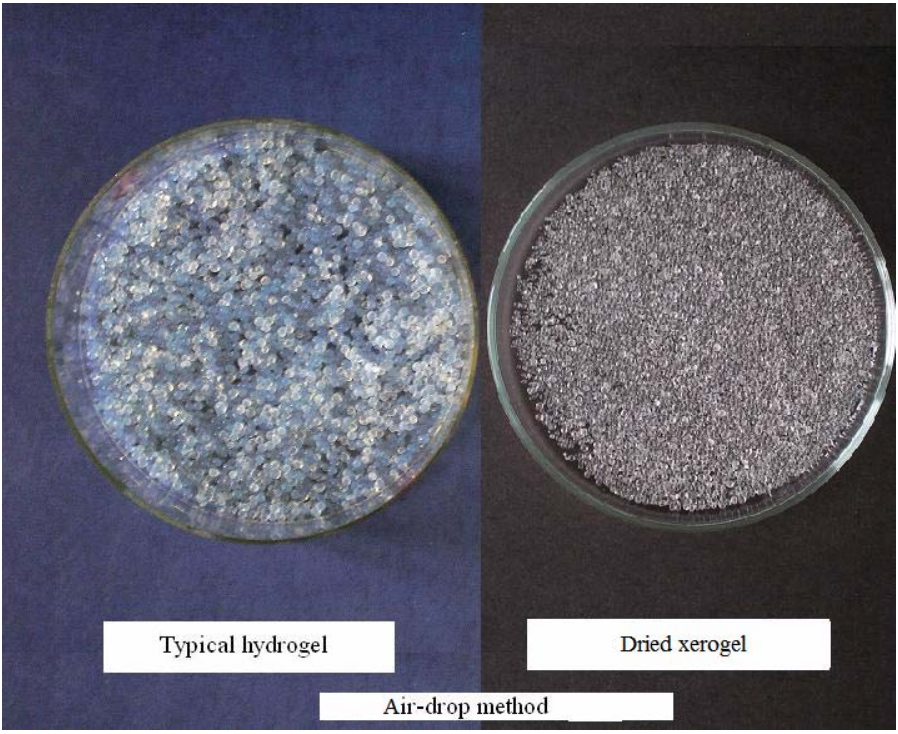


Figure 13. The appearance of the ZrP typical hydrogel and dried xerogel.

3. Porous Structure, Surface Chemistry, and Sorption Properties of Spherically Granulated TiP and ZrP Synthesized by the Sol-gel Method Using Competing Ions

Taking into account that $TiOSO_4$ is easier to handle and cheaper than $TiCl_4$, and also accessible as an industrial semi-product, we investigated thoroughly how the conditions of the sol-gel TiP synthesis with the $TiOSO_4$ precursor affect the physico-chemical properties of target materials.

This study addressed the effect caused by the P/Ti molar ratio in the synthesized ion exchanger on its porometric characteristics. Figure 14 demonstrates the N_2 adsorption-desorption isotherms for two TiP samples at –196^{0}C and the effective pore volumes distribution per radii. The mesoporous character of the samples with the P/Ti molar ratios 1 and 1.5 is evident from the figure.

It should be noted that the pore radius is ~120 Å, irrespective of the P/Ti molar ratio. The overall picture of how the P/Ti ratio affects the volume of sorption pores and $S_{sp.}$ values is judged from the data in Table 1. The Table lists also the corresponding data for the TiP sample obtained by the traditional

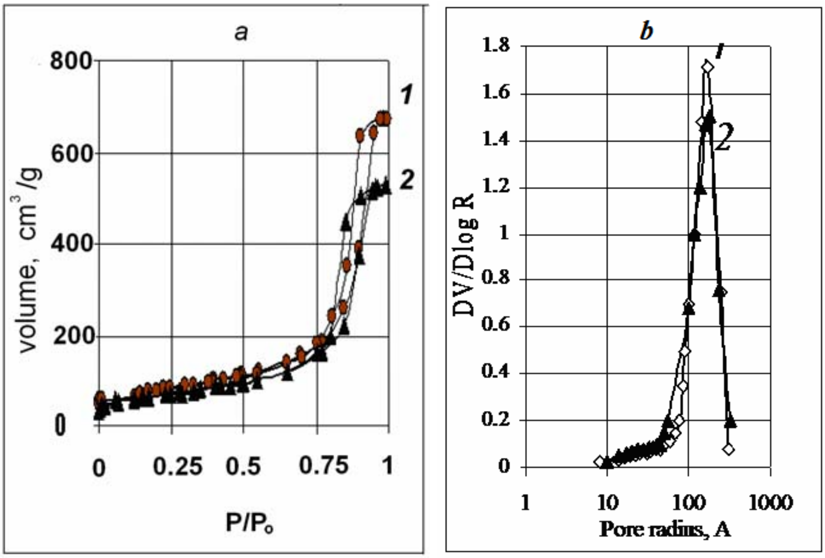


Figure 14. The N_2 adsorption-desoprtion isotherms (a) and pore volumes distribution per radii (b) for the TiP samples synthesized from $TiOSO_4$: TiP – 1.0 (1), TiP – 1.5 (2).

TABLE 1. Porometric characteristics of the synthesized TiP samples.

P/Ti ratios of TiP samples	Pore volume $V_s^{benzene}$ (cm^3/g)	Specific surface area S_{sp}^{Ar} (m^2/g)
0.75	0.89	295
1.00	0.72	280
1.25	0.84	285
1.50	0.66	240
1.65	0.65	255
2.00	0.42	210
2.50	0.46	185
TiP – $TiCl_4$	0.15	90

method based on $TiCl_4$. It is important to note that the porometric characteristics of this material are inferior to those of TiP produced from the $TiOSO_4$ precursor.

It is also worth noting that the TiP samples synthesized by the sol-gel method from the $TiSO_4$ precursor are characterized by a different kind of surface chemistry than ion exchangers produced on the $TiCl_4$ precursor. First and foremost, this can be deduced from the curves of potentiometric titration of the samples with a 0.01 M NaOH solution (Figure 15). As it can be seen, the TiP samples with different P/Ti ratios are very different from each other, especially on the initial portions of the curves (up to pH = 2.1). It can be assumed that the bending points on the curves occurring at pH ≈ 2 are caused by the presence of strongly acidic $-SO_3H$ surface groups which are fixed in the surface layer during the sol-gel synthesis. In this case, the contribution to sorption capacity from these groups rises, as the P/Ti ratio in ion exchangers decreases. Our supposition is supported by the fact that the bending point at pH ~ 2 is lacking on the titration curves of the TiP samples produced from $TiCl_4$. Thus, the molecular structure of the surface layer for the TiP samples synthe-sized by the sol-gel method from the $TiOSO_4$ precursor can be schematically represented as in Figure 16.

The thermal stability of functional phosphate and sulfate groups on the TiP surface is characterized by the data of Figure 17. It is seen that even after calination at 200°C, the ion-exchange capacity of the material does not decrease but even somewhat increases.

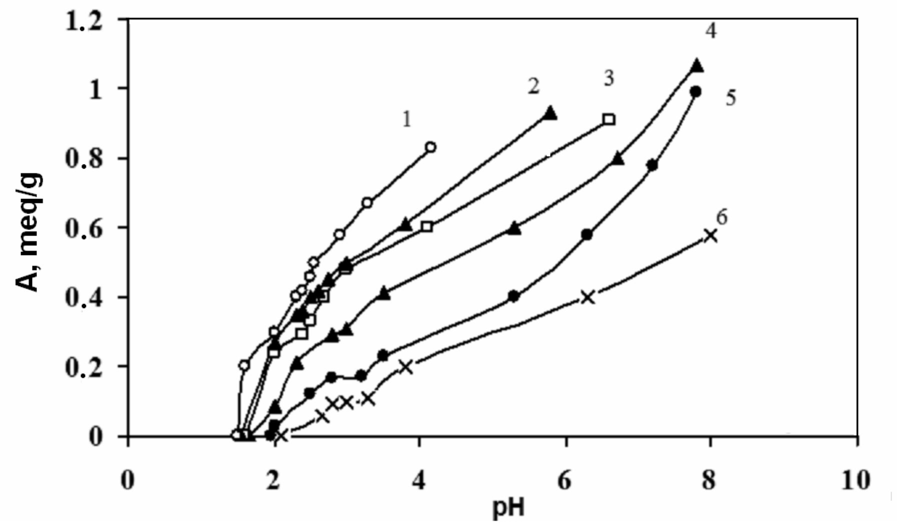


Figure 15. The pH-metric titration curves for the TiP samples synthesized from $TiOSO_4$ at different P/Ti ratios: P/Ti = 0.70 (1), 1.0 (1), 1.25 (3), 1.4 (4), 1.65 (5) and for the TiP sample synthesized from $TiCl_4$ at the molar ratio P/Ti = 1.5 (6).

With the above considerations, it makes sense to present the data demonstrating the peculiarities of the ion-exchange sorption on TiP and ZrP; in particular, it is appropriate to elucidate their sorption selectivity.[6] We have already noted that the isotherms of the ion-exchange sorption on templating ZrP (Figure 10) imply the high selectivity of this ion exchanger.

The same is evident from the data on TiP efficiency in the purification of water wastes containing a number of organic compounds and also Cd^{2+} ions (formed in the acetaldehyde production with the Cd catalyst) – see Table 2. On

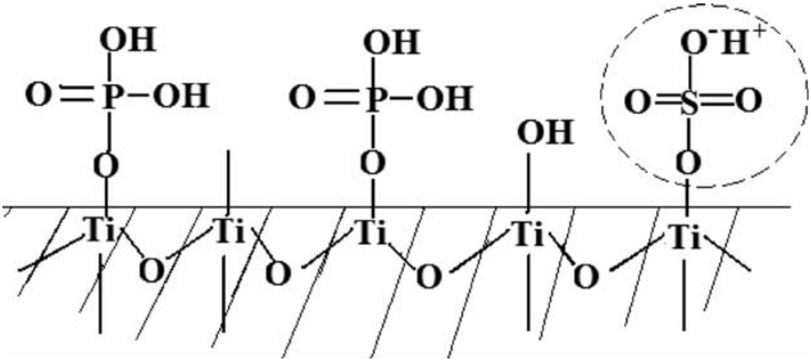


Figure 16. The molecular structure of the TiP surface synthesized from the $TiOSO_4$ precursor.

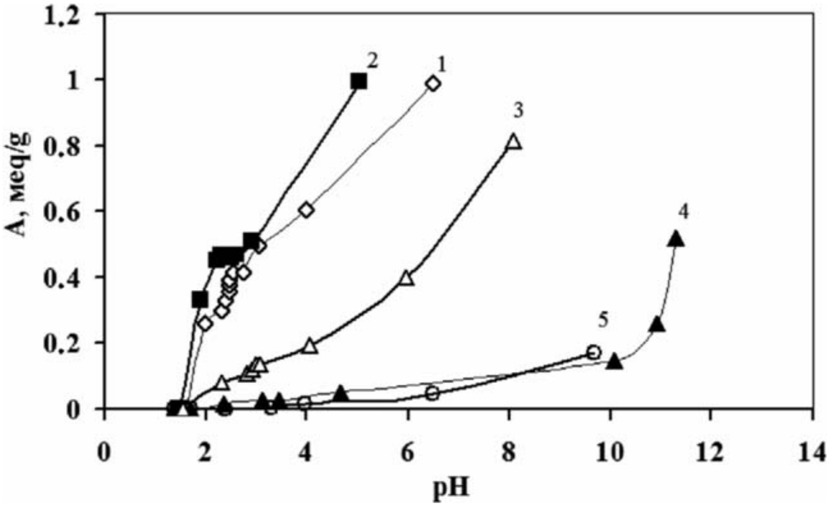


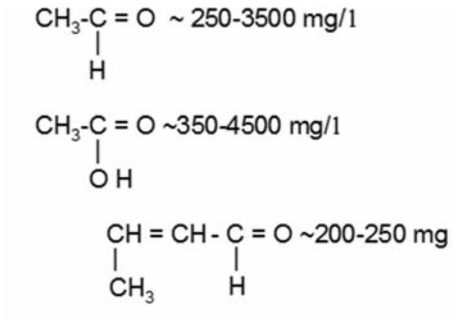
Figure 17. The pH-metric titration curves of the TiP samples calcinated at different temperatures: (1) before calcination; (2) 200°C; (3) 300°C; (4) 400°C; (5) 500°C.

purification, the content of toxic cadmium ions decreases from 0.05–10 to <0.002 mg/l.[7]

The data of the Table 2 (below) illustrate also the high efficiency of these ion exchangers in purification of some process solutions (concentrated salt solutions) which permits certain undesirable ion admixtures to be removed.

Finally, an essential advantage of TiP and ZrP is a potential possibility to use them in autonomous systems of drinking water purification.[8] In the known "Brita" system, the sorption column of the water-purifying unit contains a mixture of active carbon and carboxylic resin absorbing traces of heavy metals. In our system, spherically granulated TiP or ZrP are used instead of the synthetic resin.

TABLE 2. Application of TiP(ZrP) for deep purification of cadmium-containing wastes and some process solutions.

Technological process	Composition and content of undesirable admixture	
	Before purification	After purification
Cd removal from wastes of acetaldehyde production	 $CH_3\text{-}\underset{H}{\underset{\vert}{C}}=O$ ~ 250-3500 mg/l $CH_3\text{-}\underset{OH}{\underset{\vert}{C}}=O$ ~350-4500 mg/l $\underset{CH_3}{\underset{\vert}{CH}}=CH\text{-}\underset{H}{\underset{\vert}{C}}=O$ ~200-250 mg Cd ~ 0.05 – 10 mg/l	Cd < 0.002 mg/l
Fe removal from solution of mercury electrolysis	NaCl – saturated solution Fe – 5 mg/l	Fe < 0.02 mg/l
Cu^{2+} and Cd^{2+} removal from Zn-electrolyte	Zn^{2+} – 145 g/l Cu^{2+} – 2.0 g/l Cd^{2+} – 0.6 g/l	Cu^{2+} – 0.0005 g/l Cd^{2+} – 0.0015 g/l
Cu^{2+} removal from the electrolyte of nickelation	Ni^{2+} – 63 g/l Cu^{2+} – 0.1 g/l	Cu^{2+} – 0.0005 g/l

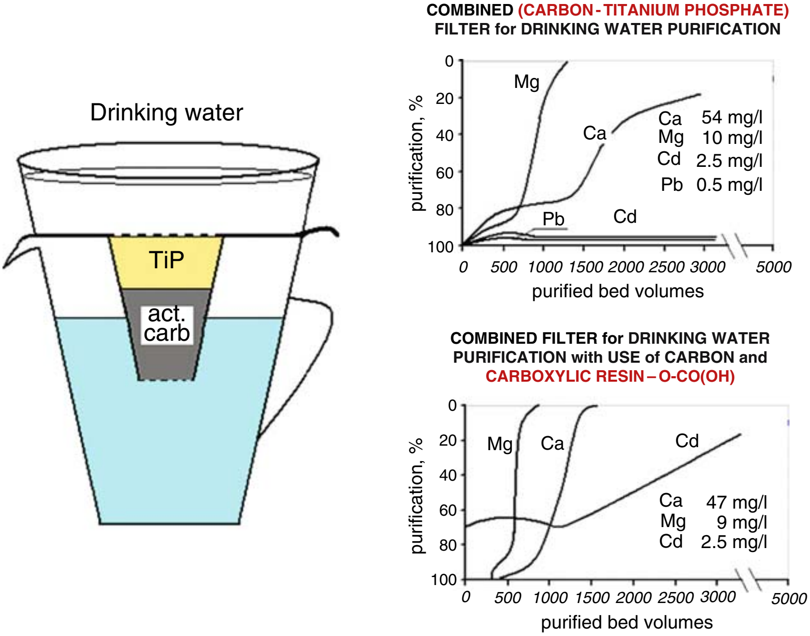


Figure 18. Sorption dynamics for Pb^{2+}, Cd^{2+}, Mg^{2+} and Ca^{2+} traces in drinking water purification on the combined sorption layers, viz., active carbon-titanium phosphate and active carbon-carboxylic resin.[8]

As Figure 18 suggests, it is possible to purify up to 5,000 column volumes of drinking water from lead and cadmium contaminants using combined sorption layer consisting of active carbon and titanium phosphate; at the same time, a breakthrough immediately occurs for biologically vital elements (such as Mg^{2+} and Ca^{2+} ions), i.e., they are not removed from drinking water. In contrast, in the case of the "Brita" system, the cadmium breakthrough is observed right after passing through the sorption layer, whereas Mg^{2+} and Ca^{2+} ions are completely absorbed in purification of the first 300–400 column volumes.

Of particular interest is the possibility to use inorganic ion exchangers for the absorption of uranium, cesium, and strontium radionuclides from liquid radioactive wastes, in particular, water solutions of complex composition. In a detailed study of this problem, we have revealed high sorption capacities (4–7 mg-eq/g) and unusually long times of sorption equilibration for most of TiP samples.

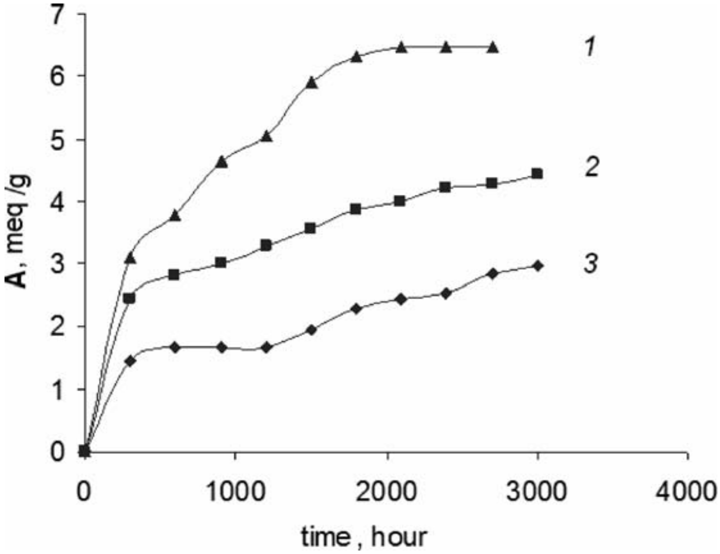


Figure 19. The kinetics of UO_2^{2+} sorption from a uranyl-acetate solution ($C_{in} = 1.5 \times 10^{-3}$ M) on TiP samples synthesized with different initial P/Ti molar ratios: 1 – 0.8; 2 – 1.0; 3 – 1.25.

As it is clear from Figure 19, the kinetic curves reach the plateau only within ~3,000 h, although their initial portions rather suggest fast saturation of some sorption centers.

Using the XPS method and X-ray analysis, it has been shown that the sorption process requiring such a long time to reach equilibrium is contributed not only by the ion exchange but also by formation of a new phase, $(UO_2)_3(PO_4)_2$. This phenomenon is probably due to the fact that the phosphate anion affinity to uranyl cations is higher than to Ti (IV).

In our opinion, the revealed features of uranium sorption on TiP make this sorbent also applicable in the so-called “capping method”[9] which implies binding of undesirable admixtures by placing a thin sorbent layer onto the ground sediments in cooling ponds or in natural reservoirs contaminated with uranium and transuranium elements. As a result, uranium and other radio-nuclides will be fixed on TiP in the bottom zone and its drainage into water horizons will be prevented.

As regards Cs-137 and Sr-90, the titanium silicate ion exchangers developed by us (produced by the sol-gel technique from the $TiOSO_4$ and Na_2SiO_3 precursors) appear to be most promising for selective adsorption of traces of these radionuclides. The synthesis of such ion exchangers can be generalized by the following equation:

$$\underset{\text{}}{TiOSO_4+Na_2SiO_3+NaOH} \rightarrow \underset{\text{amorphous hydrogel}}{Na_2O{\cdot}TiO_2{\cdot}SiO_2{\cdot}nH_2O} \rightarrow \underset{\text{semicrystalline product}}{Na_2Ti_2O_3SiO_4{\cdot}nH_2O} \quad (8)$$

As it is evident from the equation, this process permits preparation of ion exchangers in the semicrystalline form under mild conditions, contrary to the reported methods of hydrothermal action[10] leading to full material crystallization. At the same time, it has been found that the ion exchanger with the molar ratio Ti/Si = 1:1 is selective to Sr-90 and the material with Ti/Si = 2:1 is selective not only to Cs-137 but also to UO_2^{2+}. Selectivity coefficients being rather large: K_d(Cs-137) = 137,000; K_d(Sr-90) = 34,000, and $K_d(UO_2^{2+})$ = 310,000.

It is also significant that due to the small thermal expansion coefficient, this universal rationuclide absorber can be melted, after saturation with the Cs and Sr radioisotopes, as well as U, to chemically stable ceramics and then kept in special depositories.

4. Sulfated ZrO_2 and TiO_2 as Strong Solid Acid Catalysts

According to K. Tanabe et al.,[11] about 120 of 130 modern industrial processes are catalyzed by solid acids. Solid acid catalysts have many advantages over their liquid Broensted- and Lewis-acid counterparts, especially in liquid-phase processes: strong solid acids are non-corrosive and environmentally benign, create fewer disposal problems, are much easier in recycling and separation from liquid products, have a longer catalyst life, etc. In this context, solid catalysts are now regarded as most promising in view of the challenges of the green chemistry.

It should be noted that, along with solid acid catalysts of the zeolite type (mostly used in high-temperature large-scale processes like cracking or isomerization), much recent attention has also been paid to the solid acids derived from sulfated Zr, Ti, and Sn oxides.[12] The practical advantage of the latter catalyst type is exemplified by sulfated zirconia (ZrO_2/SO_4^{2-}) which is used as a solid acids catalyst in fine organic synthesis; it displays excellent activity and good selectivity for a variety of processes including those of commercial value. Among them are isomerization, hydration, dehydration, etherification and esterification (e.g. in the production of dibutyl and dioctylphthalate plasticizers, as well as numerous drugs and pharmaceuticals), the Friedel-Crafts alkylation of phenols with alkenes, alkanols, ethers and alkyl halides, etc.[13–15]

The synthesis of these new catalytical materials is rather simple and consists in covering the surface of porous oxides with 3–4% H_2SO_4 or $(NH_4)_2SO_4$, followed by drying and calcination at 500–700°C in the open air.

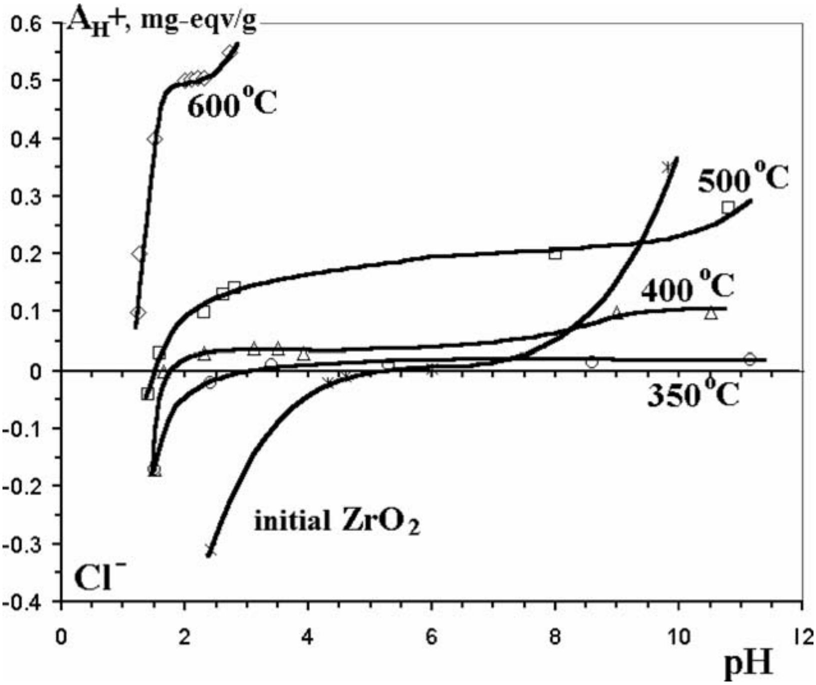


Figure 20. The curves of potentiometric titration for the initial ZrO_2 sample and for the samples treated with H_2SO_4 and calcinated at various temperatures .[16]

Previously we proposed a mechanism for strong-acid center formation resulting from the mentioned treatment.[16] Leaving aside the details of this mechanism, such centers arise during thermally induced recrystallization of the material

(Figure 20); they are represented by stable sulfate groups chemically immobilized in the surface layer. As already mentioned, such sulfate groups are also fixed in the surface layer of TiP synthesized from $TiOSO_4$, as evidenced by the potentiometric titration curves plotted in Figures 15 and 17. One can thus infer that TiP samples even with a small P/Ti molar ratio display properties of strongly acidic mesoporous catalysts. It is just mesoporous materials free of kinetic restrictions that are necessary for liquid-phase catalysis.

On the other hand, the above-described semi-pilot technologies (Figures 12, 13) for the continuous sol-gel synthesis of Ti and Zr phosphates and oxides (obtained as easy-to-handle spherical granules of a controlled diameter) can be used in large-scale production of high-quality solid acid catalysts.

To conclude, the wet sol-gel method of competing ions pioneered by us represents a convenient, easy-to-handle, safe, and cheap technological strategy. It provides great potentialities for large-scale production of sorbents, selective inorganic ion exchangers and strong solid acid catalysts for fine organic synthesis. Moreover, a pronounced porosity and thermal stability of these materials make them applicable as stable catalyst supports.

5. Conclusions

- The original methods for sol-gel synthesis of hydrated oxides and phosphates of polyvalent metals have been proposed and experimentally tested. The methods are based on the use of simple salts, acids, and alkalis with the addition of competitive cations and anions affording the control of gelation time.
- Using the proposed method of competing ions, we have developed the “oil-drop” and “air-drop” semi-pilot technologies for the continuous production of spherically granulated sorbents derived from hydrated oxides and phosphates of polyvalent metals.
- The templating effect of competing M^{3+} cations in the sol-gel synthesis of TiP and ZrP has been discovered improving significantly the adsorption properties of inorganic cation exchangers.
- As demonstrated, inorganic ion exchangers synthesized by the sol-gel method remove efficiently the traces of radionuclides (including uranium) and heavy metals from waste and drinking water as well as from process solutions thus enabling their deep purification.
- It has been found that spherically granulated Ti and Zr oxides can be used in the preparation of strong solid acid catalysts with controlled porosity and surface chemistry.

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