

Synthesis of Framework Complex Zirconium Phosphates via Mechanochemical Activation of Mixed Solid Salts

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Abstract

Results of systematic studies of framework zirconium phosphates synthesis via mechanical activation (MA) of the mixture of solid salts followed by the hydrothermal treatment (HTT) in the presence of surfactants, drying and calcination in air are considered. Application of modern physical methods sensitive to the state of bulk and surface of nanosystems (XPD, SAXS, TEM, EXAFS, FTIRS, SIMS, UV-vis) allowed to elucidate genesis of those complex systems containing different stabilizing/modifying cations and anions. The local structure of zirconium phosphate nuclei formed in the course of MA and spatial distribution of guest cations within those nanoparticles strongly depend on the composition of starting solid reagents, which determines a mode of the acid-base interaction in the activated mixture. These properties determine in turn realization of different mechanisms of complex framework phosphates crystallization under HTT - either *via* oriented stacking of primary particles (occurs even in neutral or alkaline solutions) or by dissolution-precipitation route in acid solutions. Factors determining the structural type, thermal stability, surface composition and solubility of crystalline complex zirconium phosphates prepared *via* MA route were elucidated and analyzed as dependent upon the composition and genesis of those systems.

INTRODUCTION

Framework zirconium phosphate of the NASICON (NZP) type with a basic composition corresponding to $\text{Me}_2^{+1}\text{Zr}_4\text{P}_6\text{O}_{24}$ are now attracting attention of researches from different branches of physics, chemistry and materials science. These materials possess a high ion (including proton) conductivity [1, 2], high radiation and corrosion stability, ultra-low thermal expansion [3–5]. Due to these features, they are

used as refractory materials in the car and space industry, as solid electrolytes, crystalline matrix for immobilization of radionuclides [6].

Basic rhombohedral structure presented *i. e.* by prototype $\text{NaZr}_2(\text{PO}_4)_3$ is formed by the skeleton $[\text{Zr}_{2n}(\text{PO}_4)_{3n}]^{m-}$ built up by two chemical groups: the octahedral ZrO_6 units and the tetrahedral PO_4 units that share corners only through strong covalent bonds $\text{Zr}-\text{O}-\text{P}$ [5, 6]. The $\text{Zr}_2(\text{PO}_4)_3$ groups repeat along the three-fold axis and the so-formed columns connect

together in a hexagonal array. Three types of interstices in this framework with octahedral ($M\phi$), 14-coordinated oxygen environment ($M\psi$) and trigonal prismatic ($M\pi$) can be filled by counter-cations of a different nature and charges stabilizing this structure. A flexible framework structure of complex zirconium phosphates allows to carry out the aliovalent substitutions in both cationic and anionic positions without substantial variation of the lattice characteristics [5–8]. As the result, strength of the Lewis and Brønsted acid sites can be tuned. Along with the rhombohedral phase, the monoclinic phase with the similar architecture [5] and cubic phase with a higher coordination number for $M\psi$ position (9) exist [9]. Hydrogen forms of framework phosphates possessing a high proton conductivity can be considered as solid superacids promising for application in petrochemical processes instead of zeolites. Indeed, complex inorganic phosphates are now considered promising as catalysts for the acid-base (isomerization, dehydration) [10–12] and red-ox (selective oxidation of paraffins into olefins or oxygenates) [13–15] processes.

For all these applications, crystallinity and phase/spatial uniformity of nanoparticles packed into dense ceramics or shaped catalysts are required. Traditional sol-gel or ceramic methods [3, 16] failed to achieve this goal, and we decided to apply the soft mechanochemistry methods for this purpose [16–21]. Apart from mechanical activation of the mixture of solid salts (usually, crystallohydrates) [17, 18], it includes also subsequent thermal treatment, which in our case is comprised of the hydrothermal treatment in the presence of surfactants which increased the dispersion of zirconium phosphates [16–18] followed by washing, drying and calcination. This approach allowed us to elucidate main features of the genesis of those systems starting from the structure of nanoparticles – nuclei of framework phosphates and follow the process of their aggregation into mesoscopic structures which at present is one of the most intensively developing trends in the materials science and solid state chemistry. As modifying cations, NH_4 , Na, Ca, Mn, Co, Al, La, F and W were used.

EXPERIMENTAL

To synthesize zirconium phosphates with substitutions of the type $M_kZr_m(PO_4)_nY$ (where $M = NH_4$, Na, Ca, Co, Mn, La, Al; $Y = F$, W; $k = 1/3$ –2; $m = 2$ –4; $n = 3$ –6) different starting compounds were used: zirconium oxide, oxonitrate, oxochloride, ammonium phosphates with different acidity, cobalt, manganese, lanthanum and aluminium nitrates, NaH_2PO_4 , $La_2(CO_3)_3$, $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$.

The mechanochemical activation of the stoichiometric mixture of starting compounds was carried out by 8-mm diameter titanium balls in a planetary mill of the EI-2 150 type, equipped with 2 zirconium drums of 150 cm³ volume each (drum rotation frequency 850 rpm). At this rotation frequency, the ball pressure can reach 1–6 GPa. Suspensions of activated mechanical mixtures in distilled water with addition of polyethylene oxide (PEO) were loaded into teflon-lined Parr bombs and kept at 175–200 °C for 5–7 days. After hydrothermal treatment, solids were separated by centrifugation, washed with ethanol and distilled water, dried at 120 °C and calcined at 400 °C.

To find the optimum conditions of highly dispersed crystalline systems synthesis, time of activation was varied, and parameters of the hydrothermal treatment were changed as well. The details of the preparation procedures were described earlier [21–32].

The bulk structure of samples was characterized by EXAFS (spectra were acquired at the EXAFS Station of the Siberian Center of Synchrotron Radiation, Novosibirsk) combined with the X-ray diffraction method with CuK_α radiation (XRD, a URD-63 diffractometer). The microstructure of samples was studied using transmission electron microscopy (TEM, JEM 2010, 200 kV). ³¹P MAS NMR (CXP-300 Bruker spectrometer, 121.47 MHz, 3.2 kHz spinning rate) was used to characterize a local coordination of phosphate groups. The isotropic chemical shift values (δ_{iso}) were calculated relative to 85 % H_3PO_4 . FTIRS was used to follow the acidity and symmetry of phosphate groups as well.

SAXS – Small Angle X-ray Scattering data were obtained with CuK_α radiation (a KPM-1

camera) in the $7\frac{1}{2}$ – 4° range of angles using a nickel filter and an amplitude analyzer. Particle size distribution in the range up to 200 Å was calculated from the scattering intensity using a hard spheres approximation.

RESULTS AND DISCUSSION

Effect of the chemical composition of mixture, its mechanical activation and subsequent thermal treatment on the nature of phases obtained

Simple annealing of the salts mixture up to 900 °C in all cases produced only Zr pyrophosphate phase. Annealing at 900 °C of activated mixture containing bulky cations of alkaline, alkaline-earth and rare-earth metals produced low surface area rhombohedral framework zirconium phosphates. For smaller Mn and Co cations and thermally unstable ammonium cation, only zirconium pyrophosphate phase was obtained after activated mixture annealing. Hence, stabilization of the framework zirconium phosphate structure requires presence of bulky cations in the cation-exchange positions. When ammonium tungstate is present in the activated mixture, a framework-type phase with a partial substitution of phosphorus for tungsten was obtained after calcination [32]. Hence, tungsten is able to stabilize the framework structure as well probably due to its high charge. Similarly, for lanthanum-modified fluorine-containing sample (one phosphorus was replaced by three fluorine atoms), high-temperature annealing leads to formation of rhombohedral framework zirconium phosphate with a partial anion substitution in the lattice [32].

Only hydrothermal treatment of the water suspension of MA products allowed to obtain highly dispersed crystalline phases of complex framework zirconium phosphates for such substituting cations as NH_4 , Co, Mn. The type of crystal structure (rhombohedral or cubic) [21–31] is determined by such synthesis parameters as the nature of the initial compounds, pH of suspensions, the presence of PEO.

Structure of nanosized precursors of framework zirconium phosphates generated under soft mechanical activation of the solid salts mixture

Mechanical activation of solid salt mixtures comprising zirconium oxonitrate or oxochloride and $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ produces crystalline ammonium salts (chloride or nitrate) and an amorphous phase revealed by a halo in the X-ray diffraction pattern (Fig. 1, spectrum 1). After hydrothermal treatment of MA products as suspensions in neutral solutions (pH 7) at temperatures not exceeding 200 °C, the crystalline phase of a complex zirconium phosphate of a cubic type is formed in the case of the system considered (see Fig. 1, spectrum 2). Hence, X-ray amorphous phase corresponds to nuclei or nanoparticles of the framework zirconium phosphate precursors. The structure of those precursors was elucidated by using the spectral methods.

In the case of neutral ammonium phosphate as a starting compound, equidistant lines are

- NH_4NO_3
- ▽ $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$
- ✱ Orthorhombic phase

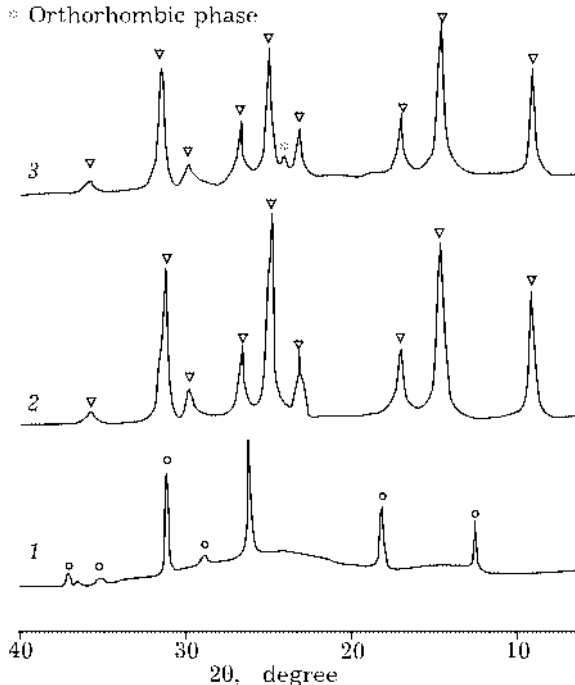


Fig. 1. X-ray diffraction pattern for the mixture of $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O} + \text{ZrO}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ at various stages of synthesis: 1 – after mechanical activation, 2 – after hydrothermal treatment at 200 °C, 3 – after calcination at 400 °C.

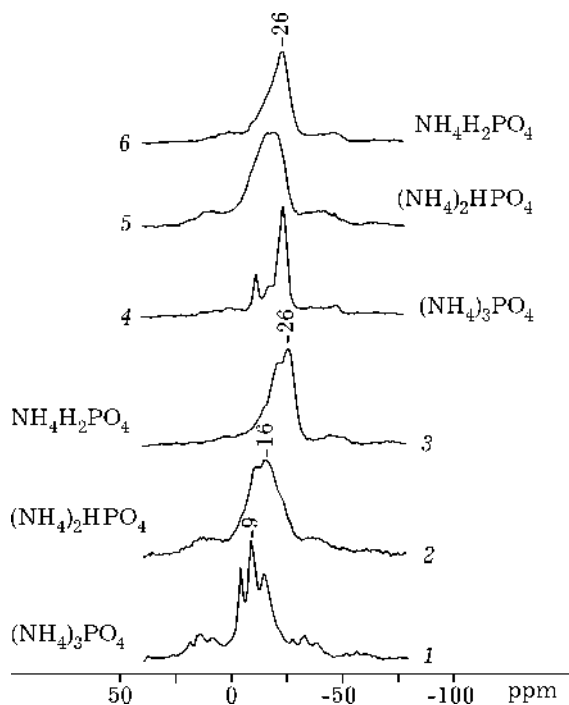


Fig. 2. ^{31}P MAS NMR spectra for the mixture of $\text{ZrOCl}_2 \times 8\text{H}_2\text{O}$ with different ammonium phosphate salts: 1–3 – after mechanical activation; 4–6 – after hydrothermal treatment at 200 °C.

observed in the ^{31}P MAS NMR spectra, which correspond to phosphate groups with a different degree of protons substitution for zirconium, higher substitution corresponding to a bigger shift into a strong field (Fig. 2). When more acidic $(\text{NH}_4)_2\text{HPO}_4$ is used, the local environment of phosphate groups in those nuclei approaches that in acid layer phosphates [33]. For the most acidic $\text{NH}_4\text{H}_2\text{PO}_4$ salt, the ^{31}P MAS NMR spectrum of the activated mixture is similar to that in crystalline framework zirconium phosphate, where each phosphate group is bound to 4 zirconium cations. However, in the activated mixture before hydrothermal treatment, the corresponding line at about -25 ppm is much broader than that in a crystalline sample (see Fig. 2), indicating strong disordering of the phosphate group environment similar to that in sols of zirconium phosphate [23]. With increasing acidity of starting phosphates, pronounced variation of the infra-red spectra of activated mixtures was observed as well (Fig. 3). Thus, a band at $\sim 1000\text{ cm}^{-1}$ corresponding to P–O stretching in phosphate groups is shifted to higher frequencies, which suggests a stronger bonding of those groups in emerg-

ing nuclei. In addition, a high frequency shoulder at $\sim 1100\text{--}1150\text{ cm}^{-1}$ corresponding to phosphate groups with attached protons decreases in intensity.

In the high-frequency range assigned to bridging hydrogen bound hydroxyls ($\sim 3200\text{ cm}^{-1}$), such as those typical to the structure of hydrated zirconium oxochloride [34], the intensity of bands also decreases with increasing acidity of starting ammonium phosphate salt. These results imply that in the course of mechanical activation, phosphate groups are incorporated between the layers of zirconium cations bound by bridging hydroxyls in the crystalline structure of zirconium salts, and protons of acid groups are responsible for hydrolysis of those bonds. The higher is the phosphate group acidity in the initial salt, the higher is the degree of the acid-base interaction leading to decrease of the sizes of oligomerized Zr oxocations. Since the size of precursor particles estimated by SAXS for water suspensions of activated mixtures is in the range of $10\text{--}15\text{ \AA}$, they include at least several Zr cations.

The degree of interaction between components during activation depends on the nature of starting zirconium salt as well. When zirconium oxonitrate is used in mixture with neutral ammonium phosphate, the ^{31}P MAS NMR data (Fig. 4) are in favour of a less pronounced interaction between phosphate groups and zir-

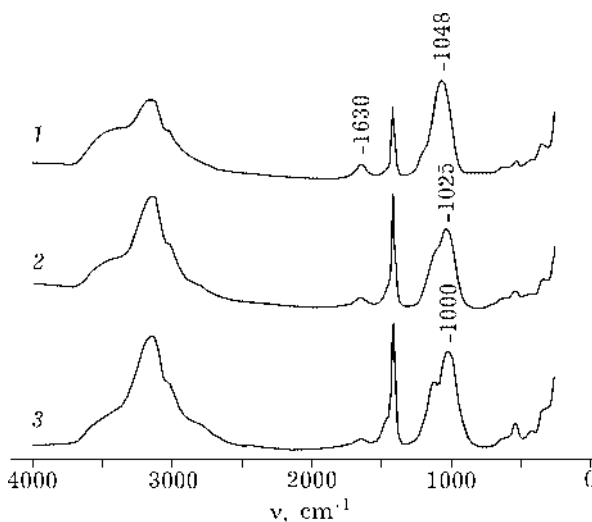


Fig. 3. FTIRS spectra for the mixture of $\text{ZrOCl}_2 \times 8\text{H}_2\text{O}$ with different ammonium phosphate salts after mechanical activation: 1 – $\text{NH}_4\text{H}_2\text{PO}_4$, 2 – $(\text{NH}_4)_2\text{HPO}_4$, 3 – $(\text{NH}_4)_3\text{PO}_4 \times 3\text{H}_2\text{O}$.

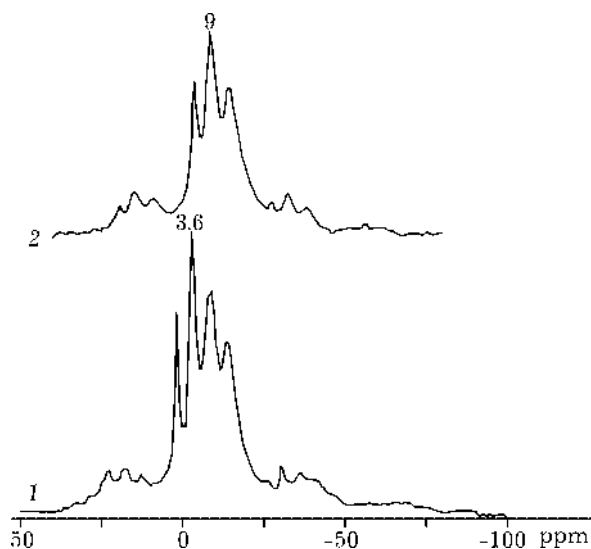


Fig. 4. ^{31}P MAS NMR spectra after mechanical activation of the mixtures: 1 – $(\text{NH}_4)_3\text{PO}_4 \times 3\text{H}_2\text{O} + \text{ZrO}(\text{NO}_3)_2 \times 8\text{H}_2\text{O}$, 2 – $(\text{NH}_4)_3\text{PO}_4 \times 3\text{H}_2\text{O} + \text{ZrOCl}_2 \times 8\text{H}_2\text{O}$.

conium cations, since more intense lines are situated at weaker fields. It can be explained by a stronger complexing ability of nitrate anions as compared with chloride anions. In such a way, interaction of phosphate groups with Zr cations seems to be retarded. As a result, the degree of Zr oxocations oligomerization in emerging nanoparticles of zirconium phosphate precursors as well as the relative concentration of bridging hydroxyls appear to be higher.

Peculiarities of zirconium phosphates crystallization in the course of hydrothermal treatment

When the products of mechanical activation are subjected to hydrothermal treatment in neutral solutions, their crystallization easily proceeds provided neutral ammonium phosphate salt is used [23–26].

In the case of more acidic phosphate salts, crystallization of MA products is hindered and proceeds only when more tough conditions (higher acidity and temperatures) are applied. After hydrothermal treatment in mild conditions of activated mixtures including acid ammonium phosphates, not only the long-range order is absent, but environment of phosphate groups remains rather disordered as well (see Fig. 2). The same is true for the hydrothermal treatment of zirconium phosphates sols obtained

via coprecipitation route, which are crystallized only in strong acid ($\text{pH} \sim 1$ or less). Hence, there is a strong resemblance between the reactivity of sols and products of salts coactivation with acidic phosphates, which seems to correlate with the similarity of their local structure as revealed by ^{31}P MAS NMR and FTIRS. In the case of sols, the difficulty of their crystallization is explained by the difficulty of their structure rearrangement in mild conditions into that of framework zirconium phosphates [23–26]. Hence, an important conclusion follows from these results: too strong and deep interaction between phosphate groups and oligomerized zirconium hydroxocations at the mechanical activation stage is not favourable for the subsequent easy crystallization of nanosized precursors into highly dispersed crystalline framework zirconium phosphates. This trend is apparently explained by the features of framework phosphates structure: in phases of all types (rhombohedral, cubic, monoclinic), there are strings formed by two octahedra occupied by zirconium cations and one face-sharing octahedron with a stabilizing cation (such as Na^+) situated between them. This group of three octahedra alternates with usually empty trigonal prismatic interstices formed by side faces of four phosphate groups located in the space between the strings. In the case of a too high degree of oligomerized zirconium cations hydrolysis in the course of activation (*vide supra*), each zirconium cation can in average be surrounded by up to six phosphate groups, and each phosphate group can be linked with up to four zirconium cations, as, *i. e.*, in amorphous glasses. Hence, rearrangement of such a precursor structure into that of a framework phosphate requires Zr-phosphate bonds to be broken and replaced by Zr–O–Me bonds (Zr–OH bonds in the case of ammonium zirconium phosphates).

Taking into account high strength of the former bonds as judged by low solubility of zirconium phosphates, this process appears to be rather energy demanding thus precluding an easy crystallization of those amorphous precursors in mild conditions. From this point of view, the presence of basic stabilizing cations such as those of alkaline, alkaline earth and rare-earth metals with a high strength of metal-

oxygen bonds favours formation of framework zirconium phosphates not only by stabilizing the final state of a lattice, but due to decreasing the transition energy barrier of the coordination sphere rearrangement as well.

The latter factor can be of importance in the case of both known mechanisms of amorphous precursors crystallization at aging and/or hydrothermal treatment – *via* dissolution-precipitation or oriented stacking of nanosized primary particles. Indeed, the product of the zirconium oxochloride coactivation with ammonium dihydrophosphate was found not to be crystallized by hydrothermal treatment even in acid solutions. However, when lanthanum salt is added to the mixture, crystallization occurs readily [31]. Certainly, such factors as the surface charge of precursor particles affected by the guest cations are also of importance for their easy dissolution in acid media.

In the case of HTT in neutral solutions where dissolution of zirconium phosphates is excluded, the mechanism of the oriented stacking of primary particles must operate. It agrees with increasing in time of the mean diameter of particles estimated by SAXS [25, 31]. To the contrary, crystallization of sols in acid solutions *via* dissolution-precipitation mechanism is accompanied by decline of the particle diameter. Hence, primary particles generated by mechanical co-activation, provided the process of oligomerized Zr cations hydrolysis is not too deep (*vide supra*), possess an increased reactivity due to specificity of their structure as discussed here.

Electron microscopy revealed an anisotropy of primary particles stacking forming first thin threads aligned into bundles and/or bands [23–26]. As HTT proceeds, these bands are juxtaposed forming platelets or bulky particles. Anisotropy of stacking at the initial stages of crystallization appears to naturally stem from the structure of primary particles corresponding to that of layer phosphates [33]. In those phosphates, the basal planes comprised of zirconium cations are coordinatively saturated due to strongly adsorbed triple coordinated phosphate groups situated over and under such planes. Here, only side faces contain coordinatively unsaturated Zr cations capable to form bonds with another primary particle. Certainly, in precursors, along

with phosphate groups, some hydroxyls (both bridging and terminal) are to be still present. The possibility of bands stacking by basal planes at latest stages of crystallization apparently correlates with restructuring of growing particles as revealed by EXAFS and ^{31}P MAS NMR [23–26]. Such a restructuring approaches Zr–P coordination number to 6 – a value typical for framework zirconium phosphates [3], and each phosphate group is bound with 4 Zr cations. Hence, restructuring of growing crystalline particles includes incorporation of phosphate groups into the layer of zirconium cations pushing them apart. This process increases coordination unsaturation and reactivity of the basal planes.

Simultaneously, incorporation of stabilizing cations into Zr-phosphate layers proceeds as was studied in details for Al-containing system [26]. In primary particles, aluminum cations are in the tetrahedral (^{27}Al MAS NMR line at about +46 ppm) and octahedral (about –10 ppm) environment similar to that in phosphated $\gamma\text{-Al}_2\text{O}_3$. Hence, in nanosized precursors, zirconium and aluminum cations are spatially separated, Al being mainly located at the external surface of Zr–P fragments. As crystallization proceeds, aluminum cations are shifted into positions with big coordination numbers typical for cubic framework zirconium phosphates formed in this case. For other cations, coordination certainly depends upon their nature. While for manganese cations similar bulky polyhedra are suggested by UV-vis data not shown here for brevity, for cobalt cations irrespective of the preparation route and type of structure, both tetrahedral and octahedral coordination is realized (Fig. 5).

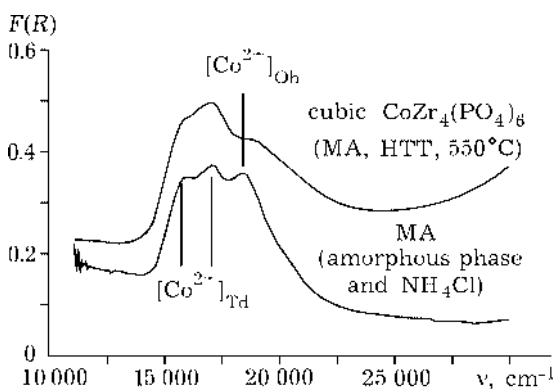


Fig. 5. Diffuse reflectance spectra of Co-containing MA products and $\text{CoZr}_2(\text{PO}_4)_3$ phase.

*The nature and some properties
of crystalline phases
obtained after hydrothermal crystallization
of the mechanical activation products*

After crystallization under mild conditions, mainly cubic phase of complex framework phosphates is formed. In addition, admixtures of layer phosphates and orthorhombic phases of zirconium hydroxophosphate ($b\text{-ZrPO}_4\text{OH}$ type, hydroxyls are bound with Zr cations) were observed, their amount depending upon the initial mixture composition and presence of surfactants in the water suspension. Thus, for zirconium oxochloride as starting compound, more pronounced acid-base interaction between Zr and phosphate groups at MA stage (vide supra) and cubic structure of the crystalline MA product – ammonium chloride (matrix effect [23–25]) certainly favours the cubic phase formation after calcination of hydrothermally treated sample (Fig. 6). For zirconium oxoni-

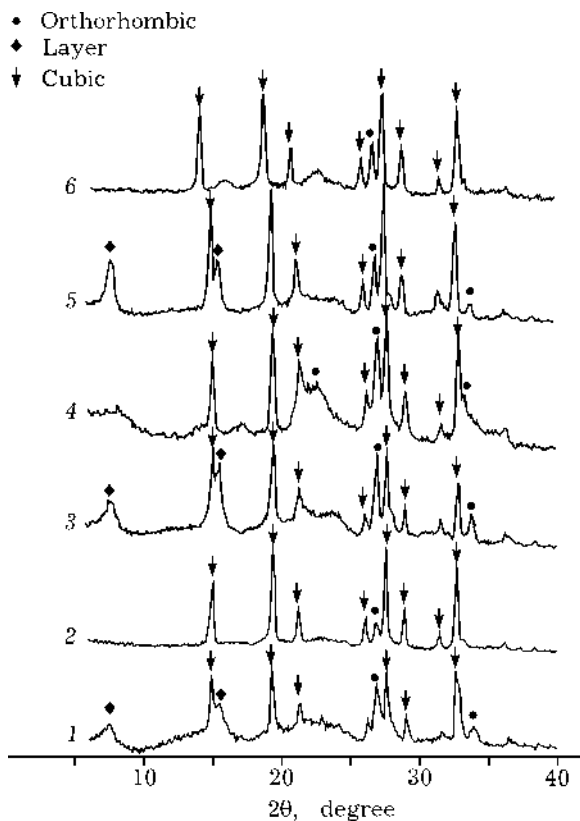


Fig. 6. X-ray diffraction pattern for mixtures of $(\text{NH}_4)_3\text{PO}_4 \times 3\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \times 8\text{H}_2\text{O}$ (1, 2), $\text{ZrO}(\text{NO}_3)_2 \times 8\text{H}_2\text{O}$ (3, 4), $\text{ZrO}(\text{NO}_3)_2 \times 8\text{H}_2\text{O} + \text{PEO}$ (5, 6): 1, 3, 5 – after hydrothermal treatment at 200 °C; 2, 4, 6 – after calcination at 400 °C.

trate, less strong interaction between Zr and phosphate groups during MA (more hydroxyls remain in a precursor and their structure is closer to a layer one) and orthorhombic structure of ammonium nitrate solid matrix are reflected in admixtures of a layer phosphate and orthorhombic phase. Polyethylene oxide as surfactant favours cubic phase formation, probably, *via* affecting the surface energy of nuclei (see Fig. 6).

When hydrothermal treatment is carried out in acid solutions, crystallization proceeds via dissolution-precipitation route irrespective of the mode of precursors synthesis – *via* MA route or sol-gel route yielding rhombohedral phase [23–25, 30, 31].

The specific surface area of crystalline phases can be as high as 100–200 m²/g. As revealed by SIMS, systems prepared *via* MA route are much more uniform by composition as compared with those prepared *via* sol-gel route. Their surface is predominantly covered by weakly acidic phosphate groups, and the density of the Lewis acid sites (coordinatively unsaturated cations) and Brønsted acid sites (Zr–OH groups) is usually not higher than several percent of monolayer [22, 28, 29]. As the result, solubility in mild acidic conditions of crystalline samples prepared *via* MA route is much lower as compared with those prepared by traditional sol-gel route (Fig. 7), which is vital for radionuclide immobilization.

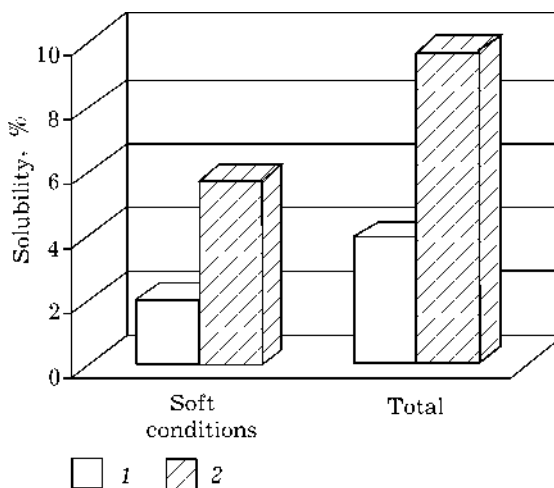


Fig. 7. Solubility of cobalt zirconium phosphate phases obtained by MA route at 550 °C (1) or sol-gel route at 900 °C (2) in diluted 1:10 HCl at room temperature in the flow of acid (soft conditions) or in static conditions (total solubility at room temperature).

Those systems containing V, Co and Mn were found to be promising as catalysts of paraffins oxidative dehydrogenation into olefins at short contact times [35]. Pt- and W-promoted complex framework zirconium phosphates possess promising activity and selectivity in skeletal isomerization of hexane [26–28]. An important specific feature of these systems is that they are not subjected to coking due to the surface shielding by phosphate groups.

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