

G.P. Tsintskaladze, T.M. Sharashenidze, L.G. Eprikashvili, M.G. Zautashvili,
T.N. Kordzakhia, M.A. Dzagania

STUDY ON THE STRUCTURE OF PHOSPHORUS-CONTAINING ZEOLITE ANIONIC NANOPOROUS MATERIALS

*Petre Melikishvili Institute of Physical and Organic Chemistry of the Iv. Javakhishvili Tbilisi State University
31 A. Politkovskaia Str., Tbilisi, 0186, Georgia (Saqartvelo), E-mail: giorgi.tsintskaladze@tsu.ge*

Phosphates are specific compounds of the composition of living organisms, that play a special role in plant and animal life. The skeleton of most living organisms consists mainly of calcium, sodium, magnesium and other phosphates. Because phosphorus plays an important role in supplying nutrients to the environment, it is central to all forms of life. Therefore, interest in this type of material is great, and the scope of application is enormous, from agriculture to medicine.

On the basis of clinoptilolite, a natural zeolite located in Georgia, zeolitic nanomaterials containing phosphates were obtained by two different methods. The first method is the introduction of mono-, di-, and tri-substituted sodium phosphates into the zeolite structure under conditions of boiling on a sand bath, where the introduction of phosphate ions is difficult. In the second method, phosphate ions almost completely occupy the inner structural area of the zeolite.

The zeolitic nanoporous materials of mono-substituted, di-substituted and tri-substituted phosphates obtained by these methods and subsequently studied by Fourier spectroscopic method.

The obtained materials have preserved the zeolitic structure, although their IR spectra are sharply different from each other, which can be explained by different anions occupying different positions in the zeolitic structure.

It should be noted that after washing the obtained material with water, phosphate ions are almost completely washed out of the zeolite structure. The importance of the received materials and the perspective of their use are given.

Keywords: *natural zeolites, phosphates, IR spectroscopy, anionic nanoporous materials, zeolite structure*

INTRODUCTION

A wide scientific field of use of natural zeolites, along with other properties, is determined by their ion-exchange capability. Study of zeolite sorbents behavior in ion-exchange processes (acid resistance, thermal stability, phase transformations) enables their purposeful modification [1, 2].

Most zeolites have a three-dimensional structure, so their parameters do not change significantly during ion exchange. The main and important feature of the zeolites structure is a system of intracrystalline pores and channels, where ion exchange, occlusion and release of small molecules are easily carried out, resulting in the zeolite having a greater capacity for adsorption and desorption [1, 3]. In addition, the activity of zeolites can be determined not only by the presence of acid centers in them, but also by the free energy of the entire system, which is possible due to additional polarization or ionization of occluded molecules and their placement in the structure [3].

The zeolite framework is characterized by a negative charge. If we modify the zeolite structure so that its charge becomes neutral or at

best positive, the area of zeolite application expands dramatically. When anionic forms are obtained, zeolites must have high affinity to ionic compounds, they must be easily occluded. In this system and in the intracrystalline structure of zeolite they must be arranged in such a way as to avoid excessive collision of like-charged ions. The role of zeolite structure in this process manifests itself not only in the fact that it is a system of symmetrically arranged pores and channels, but also in the fact that zeolite is a solid electrolyte in this process [4, 5].

Isomorphic substitution of phosphorus in the zeolite aluminosilicate framework makes it possible to change the total charge of the zeolite framework from negative to positive. Such zeolitic substances are anion-exchange nanoporous materials of great interest in terms of their use as selective, radiation- and thermal-resistant exchangers [6, 7]. Phosphates are specific compounds of the composition of living organisms, that play a special role in plant and animal life. The skeleton of most living organisms consists mainly of calcium, sodium, magnesium and other phosphates. Because

phosphorus plays an important role in supplying nutrients to the environment, it is central to all forms of life. Therefore, interest in this type of material is great, and the scope of application is enormous, from agriculture to medicine. Anion-containing zeolites, in the structure of which anions exist in the form of anionic acid salts [8–10], despite their great practical importance, are poorly studied.

When preparing anionic forms, zeolites must have a high affinity to ionic compounds, they must be easily occluded into this system. Salt cations and anions must be arranged in the zeolite intracrystalline structure in such a way as to avoid excessive collisions of like-charged ions. Occupation of the zeolite intracrystalline space by anions allows increasing the efficiency of acid hydrogen centers in the zeolite framework. In addition to the increase in concentration of acid centers, the free energy of the whole system decreases in such a system, which determines zeolite activity [1, 3].

MATERIALS AND METHODS

Both methods of preparing zeolite anionic nanomaterials make it possible to introduce anions with different properties and composition into the zeolite structure. In our case these are phosphate-ions (PO_4^{3-} , HPO_4^{2-} , H_2PO_4^-). The content of anions in materials prepared by different methods and with different salts is different and depends both on the method of synthesis and on the properties of the salt. The first method we use is based on boiling an aqueous solution of phosphates with zeolites in a sand bath for some time. After that, the solution is cooled, filtered, and then the resulting material is examined. It should be noted that this method is used mainly for preparing decationized [11] or various cation-substituted [12] forms of zeolites; phosphate-substituted forms of clinoptilolite were prepared by the same method earlier [13]. The concentration of anions in this prepared materials is relatively low.

The second method is based on melting the zeolite and the corresponding phosphorus salt at a certain temperature for a certain time. Later, the alloy cools down and becomes free-flowing. The concentration of anions in materials obtained by this method is high. For the experiment, we used natural zeolite-clinoptilolite from Georgia (Caspian region, Zemo Khandaki) and triple-substituted,

disubstituted, and monosubstituted sodium phosphates [14, 15].

For the research and characterization of phosphates, as well as for the research of the structures of aluminosilicates and the molecules and ions adsorbed on their surface, Fourier-transform infrared spectroscopy is widely used [16–18].

The phosphorus-substituted nanoporous materials prepared were studied in the mid-infrared range ($350\text{--}5000\text{ cm}^{-1}$) by Fourier-transform infrared spectroscopy. IR-spectroscopic studies were performed on an Agilent Cary 630 FTIR spectrometer(USA) in the range of $350\text{--}5000\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The structure of phosphates differs sharply from each other. They have low symmetry and crystallization or are at least amorphous, so it is difficult to analyze their structure. Infrared spectroscopy is the method by which these compounds can be identified and characterized.

The PO_4^{3-} ions are mainly characterized by four types of vibrations, namely, deformational vibrations ($500\text{--}560\text{ cm}^{-1}$) of the P–O–P bonds, the so-called scissoring deformational vibrations ($355\text{--}420\text{ cm}^{-1}$) of the P–O–P bond, and valence asymmetric vibrations of the P–O bond in the range of $1022\text{--}1080\text{ cm}^{-1}$ and symmetric vibrations in the range of $937\text{--}970\text{ cm}^{-1}$. In the IR spectrum of the sodium phosphate under study, three bands of the above vibrations are fixed at 420 , 561 and 1025 cm^{-1} . In addition to these bands in the spectrum there are two bands of medium intensity at 625 and 703 cm^{-1} , respectively. These could be the deformational vibrations of the P–O–P and P–O bonds (Table 1).

In the IR-spectrum of disubstituted sodium hydrophosphate (Table 1), the bands at 519 , at 537 , and 556 cm^{-1} are deformational vibrations of the O_3PO group; bands at 823 , 865 cm^{-1} are valence vibrations of the PO(H) group; bands at 1124 , 1139 cm^{-1} are the valence vibrations of PO_3 group, and the band at 1266 cm^{-1} is the deformation vibration of POH group. Vibrations at 959 , 993 , 1058 cm^{-1} are valence vibration bands of $[\text{PO}_4^{3-}]$ group [19, 20].

The bands at 422 , 500 , 522 and 537 cm^{-1} in the IR spectrum of monosubstituted sodium dihydrogen phosphate (Table 1) are deformational vibrations of O_2PO_2 groups.

Vibrational frequencies at 909, 965 cm^{-1} are valence vibrations of the $\text{PO}_2(\text{H}_2)$ group. And the band at 1144 cm^{-1} is the valence vibration of the PO_2 -group. The bands at 1252, 1287 cm^{-1}

belong to the deformational vibrations of the POH group. The valence vibrations of the $[\text{PO}_4^{3-}]$ group are at 630, 1051, 1026 cm^{-1} [19, 20].

Table 1. Vibrational assignment of the IR-spectrum of studied samples

IR-spectra of salts and assignment of frequencies, cm^{-1}		
Sodium phosphate	Sodium hydrophosphate	Sodium dihydrogen phosphate
$\nu_1[\text{PO}_4]^{3-}$ – 561	$\delta \text{O}_3 \text{PO}$ – 350; 570	$\delta \text{O}_2 \text{PO}_2$ – 422; 748
$\delta \text{P-O}$ – 703	$\nu \text{PO(H)}$ – 823; 865; 959; 993	$\nu \text{PO}_2(\text{H}_2)$ – 965; 1051
$\nu_3[\text{PO}_4]^{3-}$ – 1025	νPO_3 – 158; 1124	νPO_2 – 1144
	δPOH – 1266	δPOH – 1252; 1285

Table 2 shows the IR-spectrum of clinoptilolite. The spectrum corresponds to the literature data [17, 18]. Here we can clearly see two bands of high intensity, which correspond to deformation vibrations between Si–O–Si(Al)

tetrahedra at 540, 602 cm^{-1} , and valence vibrations at 875, 1203 cm^{-1} . In the spectrum we also have intra-tetrahedral deformation vibrations at 466 cm^{-1} and valence vibrations at 1052 cm^{-1} (Table 2).

Table 2. Vibrational assignment of the IR-spectrum of studied samples

Vibrational assignment	Initial Clinoptilolite	Nanoporous material prepared under boiling conditions in a sand bath of sodium phosphate and clinoptilolite	Nanoporous material prepared under boiling conditions in a sand bath of sodium hydrophosphate and clinoptilolite	Nanoporous material prepared under boiling conditions in a sand bath of sodium dihydrogen phosphate and clinoptilolite
V_{def} – deformational vibration	466	447	466	465
$V_{\text{inter-def}}$ – Deformation vibration between tetrahedra	602	567 603	604	601
$V_{\text{intra-sim}}$ – Internal tetrahedral symmetric valence vibration	712	786	712	712
$V_{\text{intra-as}}$ – Inner tetrahedral asymmetric valence vibration	1052	1074	1048	1068
$V_{\text{inter-as}}$ – Asymmetric valence vibration between tetrahedra	1203	1139	1203	1126

Nanomodification between trisubstituted phosphate and clinoptilolite in conditions of boiling on a sand bath is weakly expressed. This is indicated by IR spectrum of the prepared nanomaterial (Table 2). The inter-tetrahedral and intra-tetrahedral deformational vibrations bands of Si–O–Si(Al) bonds characteristic of the zeolite structure at 466, 540, 602, 712 and 880 cm^{-1} , respectively, which are the most sensitive to structural changes, are unchanged

here [17]. There are insignificant changes in the case of the inner tetrahedral valence vibrational bands. Here the frequencies change from 1052 to 1046 cm^{-1} and from 1203 to 1215 cm^{-1} , respectively. The change in these frequencies is due to the coincidence of the frequency of the high-intensity band of the PO_4^{3-} tetrahedra at 1025 cm^{-1} with the aforementioned bands of zeolite vibrational frequencies.

In the IR spectrum of the material prepared after the introduction of disubstituted sodium hydrogen phosphate into the zeolite structure at the nanolevel, under boiling conditions, when compared with the spectrum of the original zeolite, it can be seen the frequencies of almost all bands change, which indicates the deformation of the zeolite structure. However, the number of anions included in the zeolite structure is small, and the bands characteristic of its IR spectrum are not fixed or are overlapped with the bands of the infrared spectrum of zeolite.

In the IR spectrum of the nanomaterial prepared by introducing sodium dihydrogen phosphate into the clinoptilolite structure at the nanolevel, by the same method, the frequencies of vibration bands at 466, 540, 712, 875, 1052 and 1203 cm^{-1} , typical for the zeolite structure, are changed, and new bands at 580, 786, 1014, 1081, 1139, 1225 and 1449 cm^{-1} , typical for sodium dihydrophosphate, are observed. This indicates the introduction of sodium

dihydrophosphate into the zeolite structure at the nanolevel.

The study of IR spectra of nanomaterials prepared by melting zeolite-clinoptilolite and all three salts of sodium phosphate separately, showed that there is a certain difference between the IR spectrum of the material prepared by melting of tri-substituted sodium phosphate with clinoptilolite and the spectrum of the original clinoptilolite. This is due primarily to a sharp increase in the intensity of the low-intensity band at 540 cm^{-1} in the zeolite structure and, as a consequence, with a complete overlap of the band at 602 cm^{-1} . This band is due to a sharp increase in the band of deformation vibrations of P–O–P. The formation of shoulders at 955 and 1140 cm^{-1} near the band of Si–O–Si(Al) valence vibrations at 1052 cm^{-1} , which are also bands of symmetric and asymmetric P–O bond vibrations, is also noticeable. All this indicates that phosphate ions enter the clinoptilolite structure in a certain amount.

Table 3. IR-spectra of samples and assignment of frequencies under cooling conditions

Vibrational assignment	Initial Clinoptilolite	Nanoporous material prepared under freezing conditions: sodium phosphate and clinoptilolite	Nanoporous material prepared under freezing conditions: sodium hydrophosphate and clinoptilolite.	Nanoporous material prepared under freezing conditions: sodium dihydrogen phosphate and clinoptilolite.	Nanoporous material after repeated washing
1	2	3	4	5	6
V_{def} – deformational oscillation	466	468	463	474	466
$V_{\text{inter-def}}$ – Deformation oscillation between tetrahedra	602	524	524	541	602
$v_4[\text{PO}_4]^{3-}$	–	572	–	594	–
$V_{\text{intra-sim}}$ – Internal tetrahedral symmetric valence vibration	712	734–1061	735	724	712
$v_3[\text{PO}_4]^{3-}$	–	–	1029	923	–
$V_{\text{intra-as}}$ – Inner tetrahedral asymmetric valence vibration	1052	–	1062	1067	1052
$\delta\text{PO}_2, \text{PO}_3$	–	–	1134; 1149	1172	–
$V_{\text{inter-as}}$ – Asymmetric valence vibration between tetrahedra	1203	–	–	–	1203

In the IR spectrum of the material prepared as a result of the melting of sodium hydrogen phosphate and clinoptilolite, the characteristic oscillation bands of the IR spectrum of both zeolite and sodium hydrogen phosphate are fixed (Table 3). This indicates that almost the entire amount of salt was included in the zeolite structure during the experiment.

In the IR spectrum of the nanomaterial prepared by melting of sodium dihydrogen phosphate with clinoptilolite (Table 3), it is also clearly seen that the salt is included in the zeolite structure in a significant amount, as indicated by the change in the frequencies of individual bands at 540,602, 712, 875, 1052 cm^{-1} , and characteristic vibration bands for the IR spectrum of sodium dihydrogen phosphate at 542, 575, 923, 1067, 1087, 1113 and 1300 cm^{-1} .

CONCLUSION

Thus, it is possible to prepare zeolite anionic nanomaterials by both of the proposed methods. The difference is that under boiling conditions on a sand bath of a zeolite and an aqueous solution of sodium phosphate salts with different substitutions, relatively fewer anions enter the zeolite structure than by melting method. This is due to the fact that the concentration of anions in the second case is much higher than the concentration of anions used under boiling conditions on a sand bath. However, during the second method, the temperature is much higher than that in the first method, which causes the kinetic energy of the ions to increase, and the

anions relatively easily occupy the space of the zeolite structure, both in the main structure and in the mesopores.

As the experiment showed, trisubstituted sodium phosphate anions enter the zeolite structure more difficultly than di- and monosubstituted salts. This is probably due to the fact that the melting point of sodium phosphate is much higher than that of its mono- and disubstituted forms. The radius of the PO_4^{3-} -anion is also large compared to the radii of H_2PO_4^- or HPO_4^{2-} [21]. The charges of the anions are also different. All this gives us a different picture of the introduction of these salts into the zeolite structure at the nanolevel. It should be noted that during the experiment the zeolite structure is preserved and only slight deformation is observed. This makes it possible to use all positive properties of zeolite structure (adsorption, ion-exchange, molecular-sieve, etc.) after preparing such materials.

If the prepared nanomaterials are washed with plenty of water, the salts are almost completely washed out of the sample, and after taking the IR spectrum of such a sample we have only a pattern characteristic of the IR spectrum of zeolite-clinoptilolite (Table 3).

The field of application of the prepared anionic nanoporous materials is quite large. These are agriculture [22, 23], medicine [9], ecology – non-polar, and treatment of water contaminated with radioactive elements [24].

Дослідження структури фосфорвмісних цеолітних аніонних нанопористих матеріалів

Г.П. Цинцкаладзе, Т.М. Шарашенідзе, Л.Г. Епрікашвілі, М.Г. Заугашвілі,
Т.Н. Кордзахія, М.А. Дзаганія

*Інститут фізичної та органічної хімії ім. П. Мелікішвілі Тбіліського державного університету ім. І. Джавахішвілі
вул. Г. Політковської, 31, Тбілісі, 0186, Грузія, giorgi.tsintskaladze@tsu.ge*

Фосфати – це специфічні сполуки складу живих організмів, які відіграють особливу роль у житті рослин і тварин. Скелет більшості живих організмів складається в основному з кальцію, натрію, магнію та інших фосфатів. Оскільки фосфор відіграє важливу роль у забезпеченні поживними речовинами навколишнього середовища, він є центральним для всіх форм життя. Тому інтерес до цього виду матеріалу великий, а сфера застосування величезна, від сільськогосподарства до медицини.

На основі кліноптилоліту, природного цеоліту, що знаходиться в Грузії, двома різними методами були отримані цеолітові наноматеріали, що містять фосфати. Перший спосіб – введення в структуру цеоліту моно-, дво- і тризаміщених фосфатів натрію в умовах кип'ятіння на піщаній бані, де утруднене введення

фосфат-іонів. При другому способі фосфат-іони практично повністю займають внутрішню структурну ділянку цеоліту.

Цеолітні нанопористі матеріали однозаміщених, двозаміщених та тризаміщених фосфатів, отримані цими методами та згодом досліджені методом Фур'є-спектроскопії.

Отримані матеріали зберегли цеолітну структуру, хоча їхні ІЧ-спектри різко відрізняються один від одного, що можна пояснити тим, що різні аніони займають різні позиції в цеолітній структурі.

Слід зазначити, що після промивання водою отриманого матеріалу фосфат-іони майже повністю вимиваються зі структури цеоліту. Наведено важливість отриманих матеріалів та перспективність їх використання.

Ключові слова: природні цеоліти, фосфати, ІЧ-спектроскопія, аніонні нанопористі матеріали, структура цеоліту

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