

Synthesis and physico-chemical properties of extra-large-pore zeolite-like germanate IPC-3

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Zeolite IPC-3 isostructural with extra-large-pore germanate zeolite ASU-16 and its Si-, Al- and Ti-forms were synthesized using template 1,6-diaminohexane. It was established that Si occupies the tetrahedral positions in the IPC-3 framework, Al occupies octahedral or tetrahedral ones and Ti - octahedral ones. Germanate zeolite IPC-3 and Si-, Al-, Ti-IPC-3 are stable up to 200–300 °C. Despite the presence of template, which stabilizes the framework of IPC-3, adsorption capacity of previously degassed at 200 °C samples is up to 0.13 sm³/g.

1. INTRODUCTION

The search for new oxide materials with the extra-large-pore open structures, unique framework topologies and novel polyhedral connectivity is extremely intensive currently. The interest in novel microporous germanates results from the fact that germanium is the closest analogue of silicon, and its ability to form polyhedra different from those of silicon—trigonal bipyramids (square pyramids rarely) and octahedra. High coordination numbers offer the possibility to form germanate frameworks with high charge densities in comparison with those of silicate zeolites, which may result in multidimensional channel systems and novel structures with extra large pores [1].

Recently one of the extra-large-pore zeolites ASU-16 with 24-MR and low FD (8.6 Ge atoms nm⁻³) was synthesized with diaminobutane [2]. The secondary building unit (SBU) Ge₇(O,OH,F)₁₉ contains 7 germanium atoms with mixed coordination: 4 tetrahedral GeO₄, 2 trigonal bipyramidal GeO₄F and 1 octahedral GeO₅F. The variety of Ge coordination numbers in microporous germanate

ASU-16 may influence a course and limits of isomorphous substitution of elements with proper coordination numbers.

Herein we make an attempt to study the peculiarities of silicon, aluminium and titanium isomorphous substitution in the framework of IPC-3 isostructural with ASU-16 and study physico-chemical properties of Si-, Al- and Ti-IPC-3 zeolites.

2. EXPERIMENTAL.

Synthesis. Germanate zeolite IPC-3 was synthesized [3] using template 1,6-diaminohexane (DAG, 99%, Aldrich). A reaction mixture contains GeO_2 , water, pyridine and HF (48 wt. %) with the molar ratio: 1 GeO_2 : 12 DAG: 70 H_2O : 40 Py: 2 HF. Si-IPC-3, Al-IPC-3 and Ti-IPC-3 were obtained from a mixture containing tetraethylorthosilicate ($\geq 98.0\%$, Fluka), aluminum isopropoxide ($\geq 98\%$, Aldrich) or titanium (IV) isopropoxide (97%, Aldrich) in the calculated quantities. The reaction mixture was prepared as follows: GeO_2 was dissolved in a solution containing Py, H_2O and DAG, HF and the source of heteroelement was then added. The final solutions were heated in a Teflon-lined autoclaves at 150–180 °C for 3–5 days. The obtained crystals were washed with water and dried at 40 °C.

Characterizations. X-ray powder diffraction was performed on a DRON-3M, $\text{CuK}\alpha$. FTIR spectra (KBr pellets) were recorded on a Perkin Elmer Spectrum One spectrometer. FTIR spectroscopy was applied to monitor the element incorporation into the IPC-3 framework by Ge-O intensity changes. Si and Ge contents were determined by a gravimetric method with the relative error < 2%, Al content – by reverse complexometric titration with Trilon B with relative error < 2%. Thermogravimetric analysis was carried out in air in the temperature range of 200–1000 °C with a heating rate of 10°/min on Q-1000. To characterize the porous structure we used a gravimetric adsorption method (adsorbates: methanol and water), the data obtained were treated using the Dubinin–Radushkevich equation of micropore volume filling theory [4]. The sample was degassed at 473 K for 2 h.

3. RESULTS AND DISCUSSION

Using XRD, FTIR spectroscopy and chemical analysis we make an attempt to investigate the peculiarities of silicon, aluminium and titanium isomorphous substitution in the framework of IPC-3 and to determine limit of their inclusion in the structure.

It is well known than Si occupies exceptionally tetrahedral positions, therefore incorporation of Si in the IPC-3 framework obviously takes place with

substitution of Ge in the tetrahedral coordination. Since SBU of zeolite ASU-16 contains 4 tetrahedrons, the Si content equivalent to 4/7 of SBU polyhedra is limited. We observe only redistribution of some reflex intensities in the XRD patterns of samples, which contain fewer than 0.4 mol fractions (m.f.) of Si in the reaction mixture, that evidences Si inclusion in the structure without significant deformation (Figure 1a). Increasing of Si content up to 0.57 m.f., which corresponds to infilling of all structure tetrahedra by Si, results in significant intensity decreasing and reflex broadening in the XRD patterns of samples, that obviously cause structure deformation and changing of some atoms crystallographic localization with retaining of IPC-3 structure. Zeolite ZSM-5 was obtained from solutions, which contain considerable Si quantities up to 0.6–0.8 m.f.

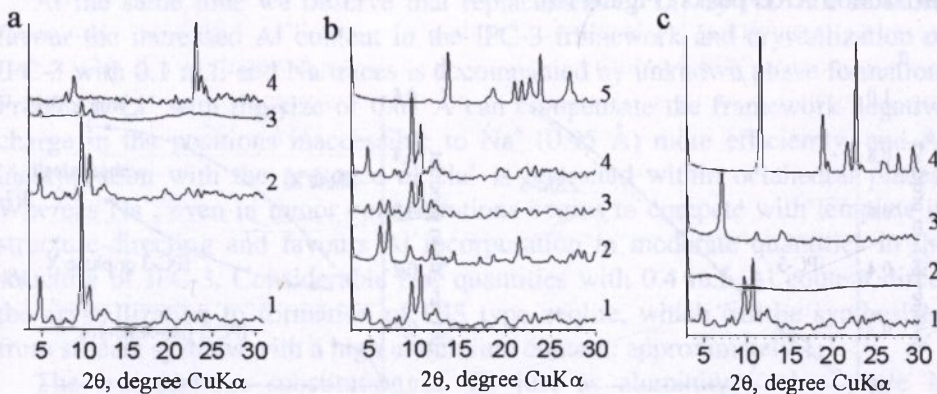


Fig. 1. XRD patterns of as-synthesized germanate IPC-3 (1a) и zeolites IPC-3 with the following element content in the reaction mixture: 2a – Si-IPC-3 (0,40 m.f.), 3a – Si-IPC-3 (0.57 m.f.), 4a – Si-IPC-3 (0.80 m.f.); 1b – Al-IPC-3 (0.07 m.f.), 2b – Al-IPC-3 (0.10 m.f.), 3b – Al-IPC-3 (0.10 m.f.) + Na, 4b – Al-IPC-3 (0.10 m.f.) + Li, 5b – Al-IPC-3 (0.40 m.f.); 1c – Ti-IPC-3 (0.10 m.f.), 2c – Ti-IPC-3 (0.20 m.f.), 3c – Ti-IPC-3 (0.40 m.f.), 4c – Ti-IPC-3 (0.60 m.f.).

A chemical analysis of crystalline Si-IPC-3 zeolite (Figure 2a) proves that inclusion of Si in the IPC-3 samples occurs. The results of chemical analysis show that up to the limit 4/7 (or about 0.57 m.f. Si) of Si content in the mixture samples contain smaller quantities of Si than the reaction solution has and in the case of reaction mixtures with the Si content higher than 0.57 m.f., the product (with MFI structure) was enriched with Si.

The incorporation of Si in the zeolite framework was monitored by the IR-spectra. With the Si content increase up to 0.4 m.f. which corresponds to infilling of less than 3/4 tetrahedra by Si, the view of spectra almost does not

change. Only after substitution of all Ge atoms in the tetrahedral positions by Si stretching and banding bands assigned to Si-O at 1208, 1085 and 473 cm^{-1} appear that may result in formation of uninterrupted siloxane chains in the IPC-3 structure. Similar to this in the IR-spectra of Ti-silicate zeolites with sufficiently large Ti content, the absorption bands assigned to Ti-O do not appear. One may observe only a shoulder near 970 cm^{-1} , attributed to the Si-O vibrations in the Si-O-Ti fragments. ZSM-5 formation from large Si (above 0.6 m.f.) reaction gel causes the appearance of its structure-sensitive bands at 400–500 cm^{-1} .

Isomorphous substitution of Al takes place in tetrahedral or octahedral positions and mainly in octahedral positions in the absence of compensative cations or charged templates. The introduction of fewer than 1 polyhedron out of 7 (under 0.07 m.f.) into the reaction gel results in step-by-step lowering of some diffraction XRD peaks (Figure 1b).

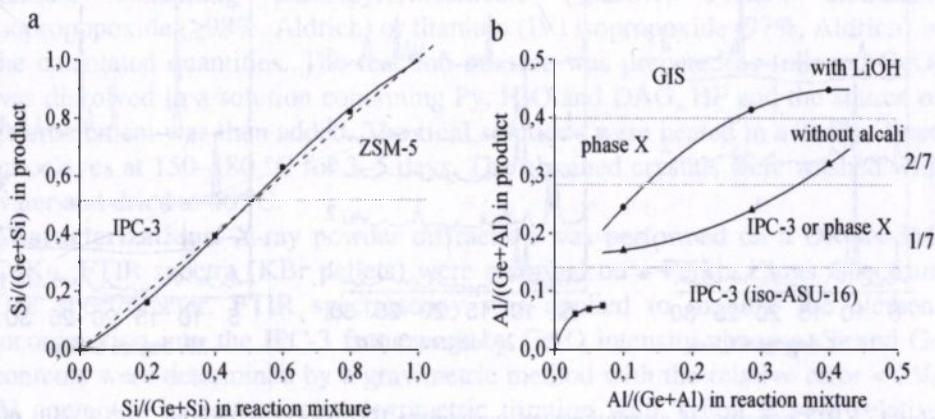


Fig. 2. The dependence of Si (a) and Al (b) contents in the zeolite product on their contents in the reaction mixture.

This phenomenon may be connected with decreased occupation of some reflection planes as well as different electronic structures of Ge^{4+} and Al^{3+} ions. At the same time the intensity of absorption band at 984 cm^{-1} assigned to Ge-O in the octahedral coordination [5] in the FTIR spectra decreases step-by-step with the growth of Al content.

A comparison of chemical analysis of the product and reaction gel composition (Figure 2b) shows that Al-IPC-3 obtained from the reaction mixture with 0.03–0.07 m.f. Al contains 0.065–0.071 m.f. Al which is below 1/7 limit. The next Al content increase from 0.1 m.f. to 0.4 m.f. leads to crystallization region change to an unknown phase X.

By means of alkali cations one may obtain zeolites with a high aluminium content of the product IPC-3. For example, from the reaction gel with 0.1 m.f. Al and Li traces the zeolite Al-IPC-3 with 0.24 m.f. Al (that corresponds to Al framework incorporation fewer than 2/7 polyhedrons of SBU) can be crystallized. With consideration of Loewenstein rule, which forbids the Al-O-Al linkages in the zeolite frameworks the only possibility to realize a theoretically possible limit 2/7 is Al occupation of two opposite tetrahedra.

A comparison of IR-spectra of samples with different Al content also shows that Li traces favour the increased Al content in the IPC-3 framework. The intensity of absorption band at 984 cm^{-1} assigned to Ge-O in the octahedron coordination [5] decreases for IPC-3 with 0.07 m.f. Al and remains invariable for IPC-3 with 0.1 m.f. Al and Li traces.

At the same time we observe that replacement of Li^+ by Na^+ not so much favour the increased Al content in the IPC-3 framework and crystallization of IPC-3 with 0.1 m.f. and Na traces is accompanied by unknown phase formation. Probably, Li^+ with the size of 0.61 \AA can compensate the framework negative charge in the positions inaccessible to Na^+ (0.95 \AA) more efficiently, and Al incorporation with the presence of Na^+ is restricted within octahedral places. Whereas Na^+ , even in minor concentrations begins to compete with template in structure-directing and favours Al incorporation in moderate quantities in the structure of IPC-3. Considerable Na^+ quantities with 0.4 m.f. Al content direct the crystallization to formation of GIS type zeolite, which can be synthesized from silicate systems with a high aluminium content: approximately 1:1.

The isomorphous substitution of Ti, just as aluminium, takes place in tetrahedral or octahedral positions with the incorporation limit of 4/7 or 1/7 polyhedron of SBU, respectively. The introduction of fewer than 0.1 m.f. Ti into the reaction gel results in lowering and broadening of diffraction XRD peaks of the product with retaining the general topology of IPC-3 (Figure 1c). Such changes in the XRD patterns are caused by incorporation of Ti atoms with a larger ionic radius (0.64 \AA) compared to Ge atoms (0.44 \AA) into the zeolite framework and consequently local disordering. An intensity of a IR-band at 984 cm^{-1} assigned to Ge-O in octahedral coordination [5] decreases with the increase of Ti content to 0.1 m.f. that may evidence for Ti incorporation in octahedral positions. Crystallization of GIS type zeolite takes place in the Ti-containing systems with 0.6 m.f. Ti.

The TG and DTA curves of as-synthesized sample IPC-3 and Si-IPC-3 are given in Figure 3. Three steps of weight loss are observed: from $20\text{ }^\circ\text{C}$ up to $310\text{ }^\circ\text{C}$ and between $310\text{--}650\text{ }^\circ\text{C}$, which corresponds to the removal of water and decomposition of template; the third step near $900\text{ }^\circ\text{C}$ corresponds to dehydroxylation of the amorphous germanium dioxide and removal of carbonaceous

residues. The calcinations of the samples at 550 °C lead to X-ray amorphous gray powder, that confirms the incomplete removal of template from zeolite.

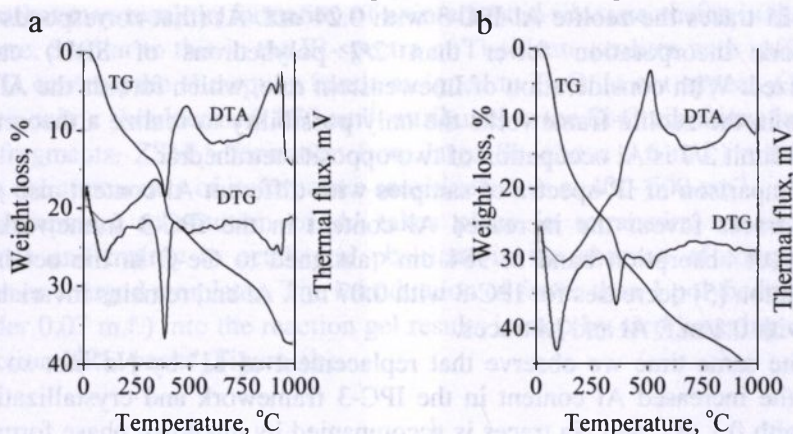


Fig. 3. The TG, DTA and DTG curves of sample 1 (a) and sample 3 (b).

Thermogravimetric analyses show a dramatic weight loss due to the 3D channel system of IPC-3, filled with water and template, and which depends on the chemical composition of samples: 38, 47, 24, 30 wt % for IPC-3 and Si-IPC-3, Al-IPC-3, Ti-IPC-3 respectively. The higher values of weight loss of Si-IPC-3 in comparison with germanate IPC-3 may be due to the substitution of considerable quantities of tetrahedral Ge on Si with lower atomic weight.

The results of TG analyses and XRPD of samples, calcined at different temperatures, showed that germanate IPC-3 and Si-, Al-, Ti-IPC-3 is stable up to 200–300 °C. It is necessary to note that the frameworks of isostructural zeolites ASU-16 [2] and SU-12 [6] are stable to 150 and 200 °C respectively.

Despite the presence of template, which stabilizes the framework of IPC-3, adsorption capacity of previously degassed at 200 °C samples is up to 0.13 cm³/g (Table 1). For the sample 3 (Si-IPC-3) we calculate theoretical pore volume of zeolite without template in the pores – 0.66 cm³/g.

It is worth noting that characteristic adsorption energies are very low – 3.1–4.6 kJ/mole (Figure 4), which may be due to the chemical nature of germanium and zeolite pore size. The diameter r of channels is close to that, as the isostructural zeolite ASU-16 has – 15 Å. This is a transition region between micropores, where adsorption is described by the theory of volume filling of micropore equations, and mesopores with multi-layer adsorption, calculated from the BET theory of adsorption. For zeolites with such a pore size the characteristic features of micropores disappear gradually and features of mesopores arise. Therefore the values of characteristic adsorption energies E_0 for

zeolite IPC-3 are lower than those typical of silicate zeolites. Similarly, the authors [7] observed low characteristic adsorption energies (8.7–10.3 kJ/mole) for zeolites Ti-VPI-8 and explained the significant increase of VPI-8 unit cell parameters.

Tab. 1. Adsorption properties of zeolite IPC-3 with Si, Al, Ti.

Sample	Element content in reaction mixture	Weight loss, wt %	Methanol		Water	
			V_o , cm ³ /g	E_o , kJ/mole	V_o , cm ³ /g	E_o , kJ/mole
1	–	38	0.05	3.6	0.03	4.2
2	0.2 Si	–	0.08	3.6	0.05	3.8
3	0.4 Si	47	0.05	4.6	0.04	4.4
4	0.1 Al	24	0.11	3.8	0.13	3.3
5	0.1 Ti	30	0.07	3.1	0.06	3.2

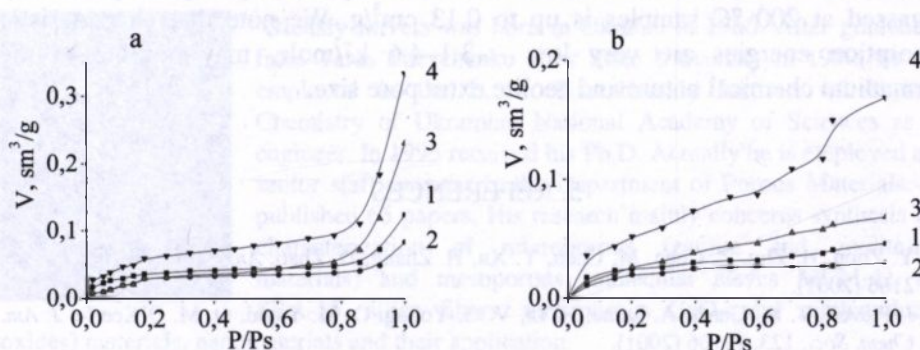


Fig. 4. The isotherms of methanol (a) and water sorption on samples 1, 3, 4 and 5.

The values of V_o , calculated from methanol sorption are higher than those of water sorption in 25–35% for germanate IPC-3 and Si-, Ti-IPC-3. Such affinity of the samples with methanol may be due to “dissolving” of methanol in template, which is in the pores, and the increase of pore volume is observed. Besides we note an impetuous growth of methanol isotherm near $P/P_s > 0.85$, which is not characteristic of isotherms of water sorption, and may be connected with the additional “dissolving” of methanol. For the samples containing Al the opposite results in V_o calculated from methanol and water sorption are observed. The values of V_o calculated from water sorption are slightly larger, probably because of significant hydrophilicity of Al-IPC-3 with 0.25 m.f. Al content.

The lower pore volume for sample 3 compared with sample 2 was explained by diffusion difficulties caused by sample partial amorphisation with the increasing Si content in the structure.

4. CONCLUSIONS

Thus we have obtained isostructural zeolite IPC-3 with germanate zeolite ASU-16 with 1,6-diaminohexane. The silicon, aluminium and titanium analogs of IPC-3 have been synthesized. It is shown that silicon occupies tetrahedral positions with the limit 4/7 polyhedron of SBU, aluminium may occupy tetrahedral and octahedral positions with the limit 2/7 polyhedron and titanium-octahedral positions with the limit 1/7 polyhedron of SBU in IPC-3 framework. We have noted that Li^+ traces favored Al octahedral coordination in Al-IPC-3 and increased Al content in the structure. Thermogravimetric analyses shows dramatic weight loss up to 47 wt %, which depends on the chemical composition of samples, due to very open structure of IPC-3. Germanate zeolite IPC-3 and Si-, Al-, Ti-IPC-3 are stable up to 200–300 °C. Despite the presence of template, which stabilizes the framework of IPC-3, adsorption capacity of previously degassed at 200 °C samples is up to 0.13 cm³/g. We note that characteristic adsorption energies are very low – 3.1–4.6 kJ/mole, may be due to the germanium chemical nature and zeolite extra pore size.

5. REFERENCES

- [1] Y. Zhou, H. Zhu, Z. Chen, M. Chen, Y. Xu, H. Zhang, D. Zhao, *Angew. Chem. Int. Ed.*, 40, 2166 (2001).
- [2] J. Plevert, T. M. Gentz, A. Laine, H. Li, V. G. Young, O. M. Yaghi, O. M. O'Keeffe, *J. Am. Chem. Soc.*, 123, 12706 (2001).
- [3] N. V. Kasian, A. V. Shvets, S. A. Sergienko, V. G. Ilyin, *Theoretical and Experimental Chemistry*, 42, 255 (2006).
- [4] M. M. Dubinin, *Zh. Fiz. Khim.*, 30, 1652 (1965).
- [5] T. Conradsson, Z. Xiaodong, M. S. Dadashov, *Inorg. Chem.*, 39, 1716 (2000)
- [6] L. Tang, M. Dadachov, X. Zou, *Chem. Mater.*, 17, 2530 (2005).
- [7] A. V. Shvets, N. V. Kasian, G. M. Tel'biz, V. G. Ilyin, *Theoretical and Experimental Chemistry*, 38, 324 (2002).

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