The Influence of Alumosilicate Gel Aging on the Synthesis of NaX Zeolite

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Abstract: **Zeolites are among the least-known products for environmental pollution control, separation science and technology. The work studies synthesis of gel aging and duration of Na-X zeolite crystallization in studied conditions. To obtain the maximum crystallinity (40%) zeolite, gel aged for 24 h at room temperature and it lead to reduction of zeolite synthesis' (95 °C) duration from 3 to 0.5 hours. The longer duration of aging time had been, the smaller zeolite crystals were obtained. An obtained IR spectrum showed that all samples of the absorption bands at the positions of maximum were as follows: 983-1012 cm^{-1}, 717-756 cm^{-1}, 564-590 cm^{-1} and 450-465 cm^{-1} were practically identical. This allowed ascribing tested samples to one type of zeolites Na-X. An obtained DSC curves for all samples were practically similar and have a wide endothermic peak with maximum 135 – 169 ^{o}C and a small exothermic peak about 853 – 956^{o}C. Thermal analysis like IR spectra allowed ascribing the tested samples to one type of zeolites Na-X. The zeolite gel aging can be effectively used not only for shortening the duration of hydrothermal crystallization, but also for controlling size of zeolite crystals.**

Keywords: **aging, aluminosilicate gel, hydrothermal synthesis, scanning electron microscopy SEM, X-ray diffraction, zeolite NaX**

I. Introduction

The zeolites are framework aluminosilicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4 with a structural formula $Me_{x/n}[(Al_2O_3)_x(SiO_2)_y]\cdot wH_2O$; where Me – represents the exchangeable cation of valence n, x and y - numbers from 1 to 5 depending on the zeolite structure, w - number of water molecules. The zeolites are wide spread in the nature, but there is not interest of working with them in technological process because it is complex and expensive. As the result of that, a need to obtain the synthetic zeolite exists.

Zeolites are among the least-known products for environmental pollution control, separation science and technology. Due to their unique porous properties, they are used in various applications in petrochemical cracking, ion-exchange and separation and removal of gases and solvents.

According to the classic scheme, technologic production of synthetic zeolites is carried out in 3 stages: getting alumosilicate gel, its aging and zeolite synthesis, which are carried out by heating the aged gel from 25 to 200 ºC [1]. One of the main zeolite productions - zeolite aging gel, on which the synthetic zeolite properties depend.

By investigating effect of the gel aging temperature on the crystallization of RHO zeolite [2], it was found that gel aging temperature increases from room temperature to 55 °C, greatly affecting the crystal purity, size, and the formed crystalline phases during the synthesis of RHO zeolite.

Zeolite gel aging influences not only the induction period, the crystallization process and purity of final product, but also types and sizes of zeolites formed [3-9]. Increasing time of gel aging leads to shortening the induction period, acceleration of the crystallization process, increases final product's purity and leads to a decrease in size final product's crystals.

Katovic et al. [4] reported that the induction periods of zeolites X and Na-Pc are shortened and the X zeolite yield increases by increasing the gel aging time. It is generally known that gel aging leads to shortening the induction period and acceleration of the crystallization process. The authors suggested these phenomena would rearrange zeolite's structure during the gel aging.

By investigating influence of zeolite gel aging at room temperature on the zeolite properties, it was found that optimal aging time was 18 h [5]. Of which, maximum crystallinity degree of the zeolite with the highest SiO_2/Al_2O_3 ratio of 1.72 was synthesized.

The aging influence on the NaY zeolite properties attracted particular attention. In the research work [6] synthetic Y-zeolite crystal size, their distribution, crystallinity and Si/Al ratio dependence of gel aging, time and temperature were established. With decreasing gel aging temperature of Y-zeolite crystals decreased and the Si/Al ratio increased.

As well as gel aging affects the synthesis of zeolite [7-10], synthesis of zeolites depends on the composition of the products generated during the aging gel composition.

In this paper, synthesis of gel aging and the duration of the Na-X zeolite crystallization are studied, by assessment review of the literature mentioned in the scientific experience section.

II. Materials and methods

Zeolite Na-X was synthesized from reagents: amorphous $SiO_2\cdot nH_2O$ (surface area S = 1301 m^2/kg; loss on ignition - 19.0%); $Al(OH)_3$, predominant strain - gibsite (S = 104,9 m^2/kg); NaOH and water.

Simultaneous thermal analysis (STA: differential scanning calorimetry-DSC and thermogravimetry-TG) were also employed for measuring thermal stability and phase transformation of products at a heating rate of 15 ^{o}C/min, temperature ranged from 30 ^{o}C up to 1000 ^{o}C under the air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used.

IR spectra were recorded with Perkin Elmer FT-IR System spectrometer. For the IR analysis, 1 mg of the substance was mixed with 200 mg of KBr and compressed in a forming press under vacuum. Studies have been conducted in the basic infra-red spectrum ranges from 400 to 4000 cm^{-1}.

The structure of zeolite was studied by scanning with an electronic microscope. FEI Quanta 200 FEG high-resolution scanning electron microscope with the Zener-type electron equipment was used.

The X-ray powder diffraction data was collected with DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu Kα radiation and graphite monochromator, operating with 30 kV voltage and emission current of 20 mA. The step-scan covered the angular range 2-70° (2θ) in steps of 2θ = 0.02°.

III RESULTS AND DISCUSSIONS

A sodium silicate solution was obtained by dissolving amorphous SiO_2 in NaOH solution, and solution of sodium aluminate was obtained by dissolving $Al(OH)_3$ in NaOH solution. These solutions were mixed at room temperature in proportions that the molar ratios of initial materials were Na_2O/SiO_2 = 1.2; SiO_2/Al_2O_3 = 10; H_2O/Na_2O = 23 (in accordance with literature source [1]). The gel formed immediately after solutions had been mixed.

Gels were aged at room temperature for 0, 24, 48, and 72 hours. X-rayed diffraction patterns of the aged gels showed that all gels were in amorphous state. The formed crystalline nuclei had not been observed by this analysis method thus the spectroscopic analysis was carried out.

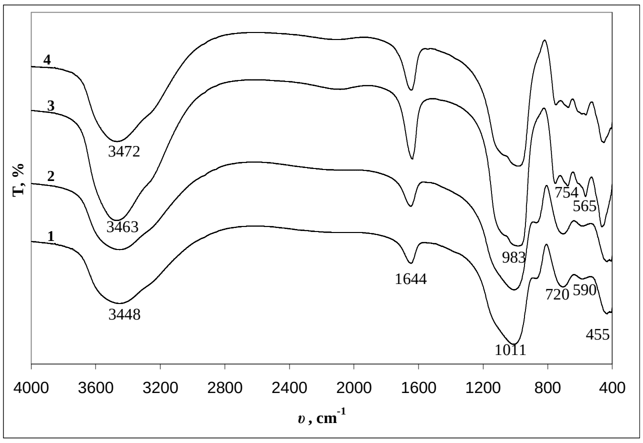


Fig. 1. The IR - spectra of the product of synthesis, gel aging: 1 – 0 h; 2 – 72 h; 3* – 0 h and 4* – 72 h. *- Zeolite synthesized for 4 h at 95 °C. *Notes*: X – zeolite Na-X, $Na_2Al_2Si_{2,4}O_{8,8} \cdot 6{,}7H_2O$.

The IR - spectra of gel (Fig. 1, 1 and 2 cr.) consisted of several main absorption bands that were characteristic for Na-X zeolite: in the 983 – 1012 cm^{-1} of asymmetric atomic vibration; in the 717 – 756, 564 – 590, 450 – 465 cm^{-1} – symmetrical atomic vibration and in the 450 – 465 cm-1 – Si (Al) deformation vibration were not found.

When aged gels were compared to not-aged gels, it was found that aged gels in 72 h absorption bands in the 724, 590, and 450 cm^{-1} were more intense than not aged gels (Fig. 1, 1 and 2 cr.). This indicates that in the gel aging process at the room temperature the zeolite crystal nucleus had grown.

After being aged the gels were crystallized at 95 °C for 4 h isothermal duration. When gel that had been aged from 0 to 72 hours was used, Na-X zeolite (Fig. 2) formed in all studied cases.

In the IR spectrum of synthesized zeolite (Fig. 1, 3 and 4 cr.), an intense shift of absorption band joined by hydrogen bands in the region of 3448-3472 cm^{-1}, which is specific to the hydroxyl groups, was observed. The absorption band at 1644 cm^{-1} was attributed to deformation variation of water molecules.

According to the data of IR spectra, zeolite structure was obtained. The middle spectrum area is particularly interesting, since the vibrations of the external SiO_4 and AlO_4 tetrahedral bonds, which are sensitive to the changes in the structure, were noticed. An obtained spectrum showed that all samples of absorption bands at the positions of maximum were the following: 983-1012 cm^{-1}, 717-756 cm^{-1}, 564-590 cm^{-1} and 450-465 cm^{-1} were practically identical. This allowed ascribing the tested samples to one type of zeolites X [1].

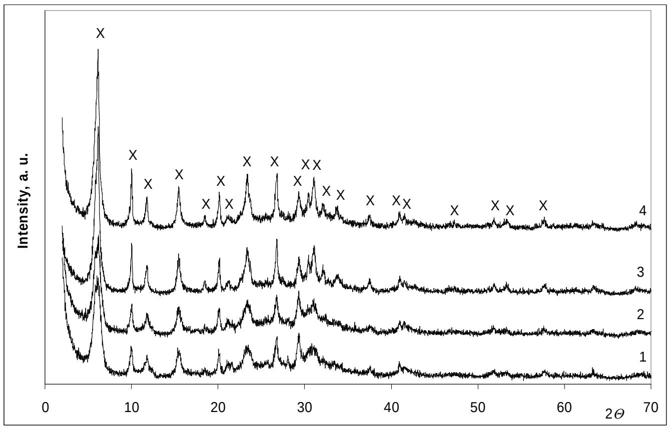


Fig. 2. The X-ray diffraction patterns of the product of synthesis, gel aging: 1– 72 h; 2 – 48 h; 3 – 24 h and 4–0 h. Zeolite synthesized for 4 h at 95 °C. *Notes*: X – zeolite Na-X, $Na_2Al_2Si_{2,4}O_{8,8} \cdot 6{,}7H_2O$.

At all spectra, bands of the maximum intensity with maximum curves of IR spectra in the region of 1011-983 cm^{-1} existed. It is important to note that such wave number of this kind of absorption band and the Si/Al ratio in alumosilicate frame of little shell interrelated. These absorption bands were attributed to frequencies of (Si, Al)-O bond in tetrahedron along the lines that bind $[(Si, Al)\,O_4]^{4-}$ tetrahedron oxygen atoms with central Si or Al atom. Other literature source [11] states, that the position of the most intensive band in the gap of 950–1200 cm^{-1} that arises from the Si(Al)–O stretching vibrations, depends on the Al:Si ratio in zeolites. It shifts to the lower wave numbers with the increase of Al contents (Fig. 1).

Valence vibrations, involving mainly (Si, Al)-O_4 tetrahedron, are in the gap of 717-756 cm^{-1} absorption band. These absorption bands are affected with Si/Al ratio of zeolite frame: when the silicon atoms in tetrahedron were increased, wave numbers became of higher band frequency range (Fig.1). In the situation of deformation absorption, bands in the gap of 450-465 cm^{-1} of Si/Al ratio had little influence.

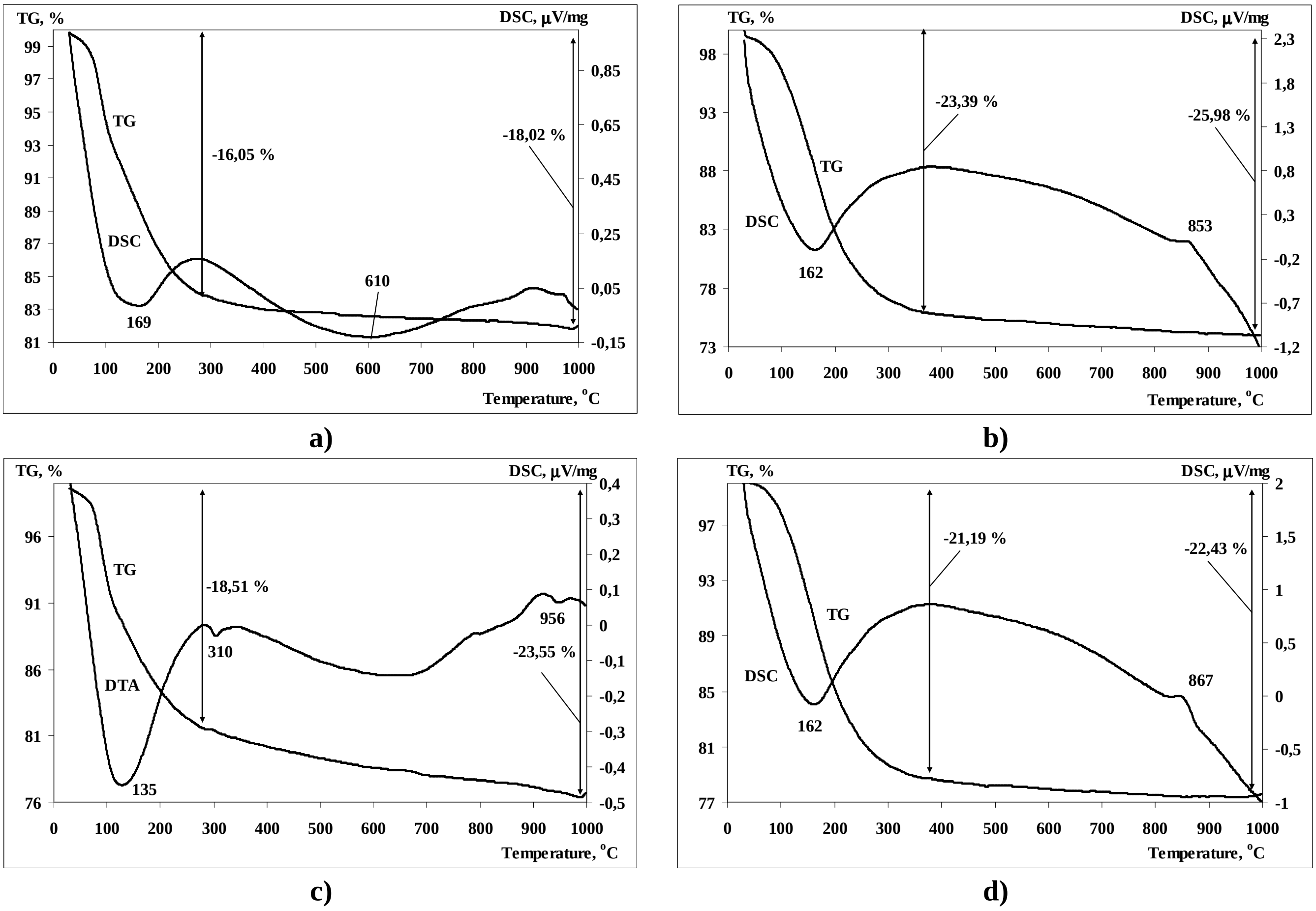


Fig. 3 The DTA curves of the product of synthesis, gel aging: a – 0 h; b – 72 h; c* – 0 h and d* – 72 h. *- Zeolite synthesized during 4 h at 95 °C.

Second type of vibrations between the tetrahedron absorption bands belong to 564-590 and 450-465 cm^{-1}. The absorption bands within gaps of 564-590 cm-1 are resulted by double rings in the frame. They are often in zeolites with twin four-membered and six-membered ring structure. The basic first type of asymmetric vibrations, i.e. vibrations inside (Si, Al)O_4 tetrahedron, and the intensity of an absorption band depend on the composition of crystalline alumosilicate framework expressed in tetrahedral oriented part of Al atoms. This band's intensity decreased with increasing of number of atoms in the Al frame. If compared with amorphous zeolites, crystalline Na-X zeolites have the most intense peaks at 566, 564 cm^{-1}.

Thermal analysis is shown in Fig. 3. The loss of water started above room temperature to about 280 ^{o}C for amorphous NaX zeolites (Fig. 3, a, b) and for crystalline NaX zeolites (Fig. 3, c, d) to about 350 ^{o}C. The exothermic peaks at 853 – 956 ^{o}C indicate decomposition of the lattice followed by recrystallization and above 900 ^{o}C the zeolite becomes amorphous. Obtained DTA curves for all samples were practically similar and have wide endothermic peak with maximum 135 – 169 ^{o}C and a small exothermic peak about 853 – 956 ^{o}C. Thermal analysis like IR spectra allowed ascribing the tested samples to one type of zeolites X [1].

In order to identify the crystalline phase and crystallinity (%) setting, the X-ray analysis data was used. Crystallinity (%) was calculated according to (1) equation [12]. Commercial zeolite X was used as a standard.

$$\%\,Crystallinity = \left(\frac{\sum \text{intensity of XRD peaks of product}}{\sum \text{intensity of XRD peaks of standard}} \right) \times 100 \quad (1)$$

Crystallinity percentage was taken as the sum of the unknown materials divided by the sum of the peak heights of a standard material that had been assumed to be 100 % crystalline.

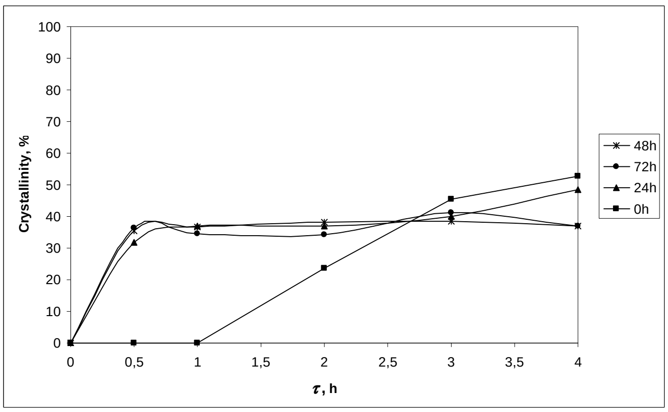
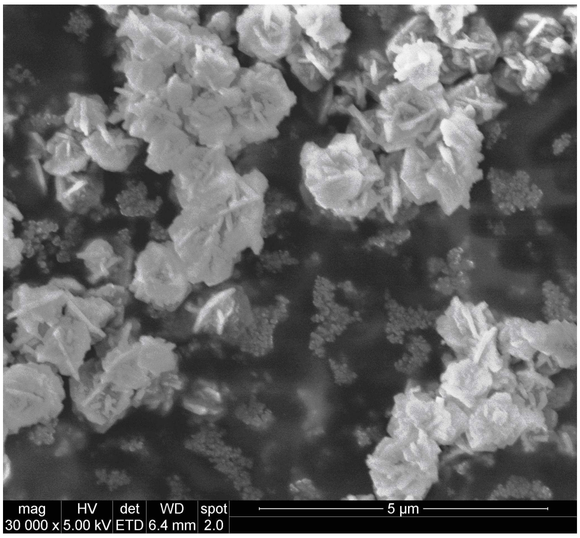


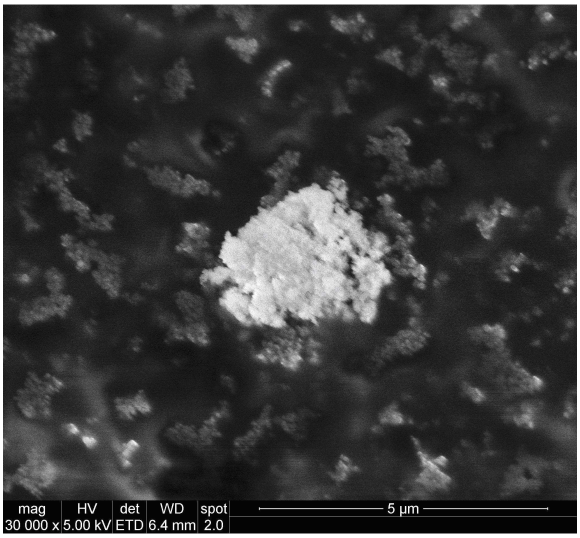
Fig. 4. Na-X zeolite crystallinity dependence from synthesis duration. Gel aging at room temperature for 0; 24; 48 and 72 h. Zeolite synthesized for 0.5 - 4 h at 95 °C.

After 0.5 or 1 h long synthesis using the not-aging gel technique, crystalline zeolite did not form, though when aged from 24 to 72 h gel was used after 0.5 h of synthesis the crystalline zeolite formed (Fig. 4 and 5). Alumosilicate gels that have been aged for 24, 48 and 72 h at room temperature and were used for Na-X zeolite synthesis, crystallized faster than the mixtures, which have not been maintained under such conditions.

Seeds of crystalline zeolites form inside the gels during the process of aging. This process accelerates gel crystallization. After 3 hours of synthesis, when both aged and not aged gels were used, zeolite crystallinity degree was in the range of 35-45%. Changes in colloidal structure proceed after alumosilicate gel is aged. These changes may be related to the rearrangement process: small particles which have dissolved during the gel aging process, due to their high solubility according with the Ostvald - Thomson dependence and mass, transfer on the surface of larger particles and the spacing between them [13].



a)



b)

Fig. 5. The SEM images of Na-X zeolite. Gel aging for: a) 0 h; b) 72 h. Zeolite synthesized for 4 h at 95 °C.

The formation phases of X zeolite crystal are as follows: dissolution of raw materials → formation of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedron → the formation of many- member rings and cage β crystal structures → crystal nucleus and nano-particle → aggregation growth of nano-particles in a crystal → coalescence growth of crystallite. The crystal habits of X zeolite are intimately related with crystallization orientation of β cage in crystal and with its coupling stability on every crystal family [9].

Zeolite gel aging can be effectively used not only to shorten the duration of hydrothermal crystallization, but also to control the crystal size of zeolites (Fig. 5).

IV. Conclusion

1. During the investigation, it was established that the crystallinity of synthetic NaX zeolites depends on the duration and on the aged gels of the synthesis. The maximum crystallinity (40%) zeolite was obtained when the gel aged for 24 h at room temperature was used; furthermore, the duration of the zeolite synthesis (95 °C) was reduced from 3 to 0.5 hours.
2. The gel aging can be effectively used for controlling the crystal size of zeolites. The longer the duration of aging time had been, the smaller zeolite crystals were obtained.

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Jolanta Doneliene, Danute Vančukiniene, Aras Kantautas. Alumosilikātu gēla vecošanas ietekme uz Na-X ceolīta sintēzi.
Ceolītus plaši izmanto apkārtējās vides piesārņojuma samazināšanai, sadalīšanas procesu zinātniskos un tehnoloģiskos pētījumos. Dabā plaši izplatītos ceolītus sadalīšanas tehnoloģiskos procesos izmanto jau sen. Vienlaicīgi ir liels pieprasījums pēc sintētiskiem ceolītiem, kas no dabas ceolītiem atšķiras ar lielu viendabību un tīrības pakāpi. Darbā tika pētīts sintētiskā ceolīta NaX kristāliskums atkarībā no gēla vecošanas un gēla sintēzes laika. Silikāta un nātrija alumināta šķīdumi tika samaisīti istabas temperatūrā, atbilstoši literatūras [1] datiem, saglabājot izejmateriālu attiecības: Na_2O/SiO_2 = 1,2; SiO_2/Al_2O_3 = 10 un H_2O/Na_2O = 23. Nātrija hidroalumosilikātu gēls izveidojās tūlīt pēc silikāta un nātrija alumināta šķīdumu sajaukšanas. Gēla vecošana tika veikta istabas temperatūrā 0, 24, 48 un 72 stundas. Tika noskaidrots, ka lai minētajos apstākļos iegūtu ceolītu ar maksimālo kristāliskumu (40%), gēlam pirms sintēzes ir jāļauj novecot istabas temperatūrā 24 stundas. Šādos nosacījumos ceolīta sintēzes laiks (95 ^{o}C) samazinās no 3 stundām līdz 0,5 stundām. No gēla, kura vecošanas laiks bija lielāks, tika iegūts ceolīts ar mazākiem kristāliem. Visu paraugu IS spektri parādīja, ka absorbcijas joslu maksimumi faktiski ir identiski un atrodas robežās no 983-1012 cm^{-1}, 717-756 cm^{-1}, 564-590 cm^{-1} un 450-465 cm^{-1}. Visu paraugu uzņemtās termogrammas arī bija līdzīgas – ar platu endotermisko efektu, kura maksimums atradās robežās no 135-169 ^{o}C (dehidratācija) un mazu eksotrmisko efektu robežās no 853-956 ^{o}C (amorfizācija). Iegūtās termogrammas un IS spektri ļauj secināt, ka iegūtie savienojumi ir attiecināmi pie viena ceolīta tipa - Na-X. Ceolīta gēla vecošanu var efektīvi izmantot ne tikai lai samazinātu Na-X ceolītu hidrotermisko kristalizāciju, bet arī lai regulētu kristālu izmērus.

Иоланта Донелене, Дануте Ваичюкинене, Арас Кантаутас. Влияние старения алюмосиликатного геля на синтез цеолита Na-X.
Цеолиты широко используются в экологической борьбе с загрязнением окружающей среды, в науке и технологии процессов разделения. Широко распространенные в природе цеолиты в технологических процессах используются давно. Также имеется большой спрос и синтетических цеолитов, которые от природных различаются большой степенью чистоты и однородности. В данной работе была исследована зависимость кристалличности синтетического цеолита NaX от старения геля и продолжительности его синтеза. Растворы силиката и алюмината натрия были смешаны при комнатной температуре в пропорциях, чтобы мольные соотношения начальных материалов в соответствии с литературными данными [1] были Na_2O/SiO_2 = 1,2; SiO_2/Al_2O_3 = 10; H_2O/Na_2O = 23. Гидроалюмосиликатный гель натрия образовался сразу после смешивания растворов силиката и алюмината натрия. Гели подвергались старению при комнатной температуре 0, 24, 48, и 72 часа. Установлено, чтобы в исследуемых условиях получить максимальную кристалличность (40 %) цеолита, гель нужно перед синтезом подвергать старению при комнатной температуре в течение 24 ч. При этом сокращается продолжительность синтеза цеолита (95 °C) от 3 часов до 0,5 часа. Из гелей, подвергавшихся старению дольше, был получен цеолит с меньшими кристаллами. ИК спектры всех образцов показали, что положения максимумов полос поглощения были фактически идентичны: 983-1012 $см^{-1}$, 717-756$см^{-1}$, 564-590 $см^{-1}$ и 450-465 $см^{-1}$. Полученные термограммы для всех образцов были также фактически подобны: широкий эндотермический пик с максимумом при 135 – 169 ^{o}C (дегидратация) и маленький экзотермический пик при 853 – 956 ^{o}C (аморфизация). Термический анализ, как и ИК спектры, позволяют приписывать проверенные образцы одному типу цеолитов Na-X. Старение геля цеолита можно эффективно использовать не только для сокращения продолжительности гидротермальной кристаллизации цеолитов Na-X, но и для управления размеров их кристаллов.