Scientific paper

Relation of the Aged Gels Microstructure on the Zeolite A Particulate Properties

Ana Palčić,[1,2,*] Sanja Bosnar,[1] Damir Bosnar,[3] Jasminka Kontrec[1] and Josip Bronić[1,*]

[1] *Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*

[2] *Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen Basse-Normandie, CNRS, 6 Boulevard Maréchal Juin, 14050 Caen, France*

[3] *Department of Physics, Faculty of Science, University of Zagreb, Bijenička 32, 10000 Zagreb, Croatia*

* *Corresponding author: E-mail: josip.bronic@irb.hr, ana.palcic@irb.hr*

Abstract

The microstructure of the starting hydrogel has extremely important role in the synthesis of the microporous materials. Due to the fact that very limited number of experimental methods (techniques) can be used for gel analysis, there are still a lot of missing information about the processes on molecular level, which occur before and during the nuclei formation. In this paper, various methods were used in characterization of pretreated (aged) hydrogel before the process of its hydrothermal transformation to zeolite A. The results obtained from different techniques (FTIR, PALS, BET, DTG) show the changes in chemical composition and in microstructure of the solid phase, indicating that the structure of the ordered phase (potential nuclei) within gel matrix (completely amorphous according to PXRD patterns) is rather of different structural units typical for FAU and SOD (or their mixture) than the final product (LTA) only!

Keywords: Zeolite A, gel microstructure, FTIR, PALS, DTG

1. Introduction

Zeolites are aluminosilicate materials (powders) of microporous structure. The size and shape of the crystal voids (pore openings, channels and caves) depend on zeolite type. The size of the zeolite crystals can vary from nanocrystals (30–50 nm) to sizeable powder (over 100 μm), while the morphology can be from regular crystals with sharp edges to irregular shape within agglomerated twins or even their assemblies. Physico-chemical properties of the zeolites (especially structural and particulate properties) have crucial role in their applications as catalysts, adsorbent, molecular sieve and/or ion exchangers.

Many studies have shown that gel aging has significant influence on the zeolite formation (quickening of the crystallization process) as well as on the properties of the final product(s) (decreasing the crystals' size).[1,2] However, the change of the linear crystal growth rate was not observed. Sometimes, gel aging can affect the crystal morphology as well as the phase and chemical composition of the final product.[3–5] These results indicate that many processes occur during gel aging and the most important of them is the nuclei formation. Recently, Palčić *et al.* have found that the crystal nuclei are formed during gel aging at the surface and subsurface regions of the gel particles.[6] As the aging time gets longer, more nuclei are formed at the peripheral parts of the gel particles.

Phenomena of low-silica zeolite synthesis from hydrogels (colloidal precursors) were studied from many different aspects, including events occurring during precursors preparation,[7–10] via gel's microstructure characteristics,[11,12] and mechanisms of nucleation and crystal growth,[13–17] to the characteristics of the final product (zeolite crystals).[18–20]

The gels of different chemical composition, and prepared in different ways showed different structural features. The aim of this work is to investigate the microstructure of the gels, prepared by the same procedure but aged

for different times, especially to see if some ordered (structured) parts are present.

2. Experimental

2. 1. Precursors Preparation and Hydrothermal Synthesis of Zeolite A

Aluminosilicate hydrogels studied in this paper were prepared as described in our previous paper.[6] Dissolving the needed amounts of fumed silica (SiO_2–99.8 wt%, Sigma), sodium hydroxide (NaOH reagent grade, >98 wt%, Kemika) and sodium aluminate ($NaAlO_2$–41 wt% Na_2O, 54 wt% Al_2O_3, Riedel de Haën) in demineralised water, alkaline sodium silicate and alkaline sodium aluminate solutions were prepared. The sodium aluminate solution was centrifuged to remove the impurities and only supernatant was used for further experiments. After mixing the alkaline sodium aluminate and alkaline sodium silicate solutions, obtained hydrogels have following molar oxide composition:

$$3.2 \, Na_2O \times 1.05 \, Al_2O_3 \times 2 \, SiO_2 \times 250 \, H_2O.$$

The precipitated hydrogels were homogenised by mechanical disperser. The hydrogels were transferred in HDPE bottles and aged for t_a = 0 h (the freshly precipitated hydrogel), 10 h, 38 h, 66 h, 113 h, 158 h and 209 h at 25 °C. After given aging times, the hydrogels were washed by repeated cetrifugation until the pH value of the supernatant was 9, to avoid preconcentration of NaOH and its possible influence to the gel microstructure. Before characterization, the washed solid was dried at 105 °C in the convection oven and cooled to the room temperature in desiccator over silicagel. Hydrothermal transformation of the prepared gels was conducted under static (convection oven) and dynamic conditions (magnetic stirrer in steel reactor) at 80 °C. Prior to characterization, the final products were treated in the same way as the aged gels.

2. 2. Methods of Samples Characterization (PXRD, DTG, FTIR, PALS, SEM, BET)

Powder X-ray diffraction was used for the phase analysis. Diffraction patterns were recorded at the Philips PW 1820 diffractometer using Bragg-Brentano optics in the range of 2θ = 5-50°, and copper K_α monochromatized radiation.

Thermal analysis of the dried gels was performed at Mettler D50 TG-DTG system. The measurements were conducted in the air atmosphere, with heating rate of 10 K/min.

Fourier transformed infrared (FTIR) spectra of the samples were measured by PerkinElmer 2000 spectrometer using the KBr pellets method.

For positron annihilation lifetime spectroscopy (PALS) measurements, two times of 0.3 g of each sample was pressed into two self-supported pellets of diameter 13 mm, and around 2 mm thick. Before mounting into the PALS apparatus, the pellets were dried for two hours at 200 °C. PALS measurements were conducted with modified version of digitized positron annihilation lifetime spectrometer.[21] In the present setup conical BaF_2 scintillators (bases of 2.5 cm and 5 cm, and height of 2.5cm) coupled to XP2020 URQ photomultiplier tubes were used and with the same signal processing and data acquisition chain as in ref. [21]. The time window in the measurements was 100 ns, the source activity was approx. 1 MBq, achieved time resolution was about 220 ps, and for each sample, approx. 10^6 annihilations were recorded. Obtained lifetime spectra have been analyzed using LT v.9 fitting program[22] and corresponding lifetimes and intensities (related to the void concentration) have been extracted.

Using the Tao-Eldrup model,[23,24] it is possible to correlate positronium lifetimes to the sizes of voids in which they annihilate:

$$\frac{1}{\tau} = \lambda_b \left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi} \sin(2\pi \frac{R}{R+\Delta R}) \right] \qquad (1)$$

where t is positronium lifetime in ns, R is void radius in nm, ΔR = 0.166 nm, is empirical parameter, and $\lambda_b = 2$ ns^{-1}, is the positronium decay rate in the bulk.

Scanning electron microscope (SEM) images of the samples were taken by Philips XL 30 microscope.

Nitrogen adsorption on the samples was measured by Micromeritics instrument model Gemini 2380. The specific surface areas were calculated using the software Gemini V2.00.[25] The samples of the precipitated gels were previously dried and outgassed at 200 °C for 2 h. The method includes measurements of nitrogen isotherm at –196 °C with data evaluation according to the BET (Brunauer–Emmett–Teller) theory in the relative pressure range, p/p_0, from 0.005 to 0.3.

After aging for the given time, systems were put at 80 °C for crystallization under static and dynamic conditions. Transformation of the all systems ends with pure zeolite A phase,[6] but of different crystal's size distributions (consequently, specific number of crystals is also different).

3. Results And Discussion

According to the PXRD patterns (Fig. 1), all aged systems (gels) have only very wide maxima in the 2Θ region from 17 to 40 degrees, typical for amorphous silica-type materials. This means that there is not sufficient quantity or size (or both) of the crystalline material (crystals) in the systems (if they exist), to be detected by PXRD method.
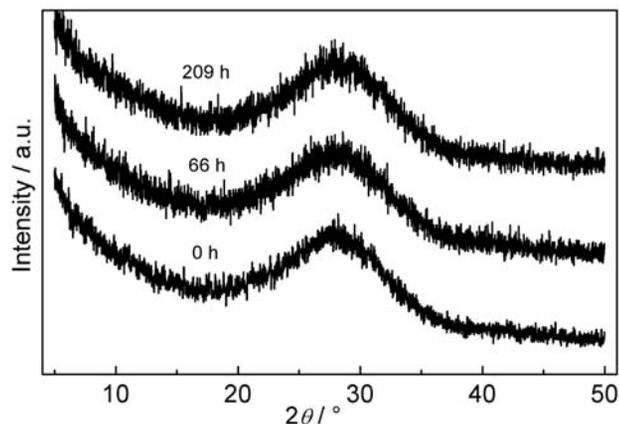
Figure 1. Powder XRD patterns of the solid phase of the systems aged for 0, 66 and 209 h. All patterns were very similar and only 3 representatives (shortest, middle and longest time of aging) were shown.

On the other hand, FTIR spectra of the gels (Fig. 2A) in all aged systems show presence of the T-O vibrations of the framework elements (structural elements assigned to 4R, 6R, D4R and D6R secondary building units in the region 800–450 cm^{-1}), while T-O vibrations of the gel are in region 520–380 cm^{-1}. Generally, IR bands at 805–640 cm^{-1} are slightly stronger with aging time, but there is no significant difference in intensity of the peaks in mentioned region of the aged gels samples (Fig. 2A). The IR bands, characteristic for the relevant low-silica

zeolites are shown at Fig. 2B. It is interesting that almost all bands of zeolites, lie at the same regions (512–640 cm^{-1} and 640–805 cm^{-1}) as two wide bands present in spectra of fresh and aged gels.

It is evident that zeolite A has only weak peak in region 800–630 cm^{-1}, (assigned to 6R unit at 655 cm^{-1}) while wide and much stronger peak is present in gel. Taking into account this and the fact that crystallizing fields of several zeolites overlap each other (e.g. ZA, ZX, HS, EMT)[26,27] and often crystallize alongside (usually mixture of two types of crystals), it seems that structured material present within matrix of gel is rather building units (or very small particles) of zeolite X (FAU) or mixture (ZX, HS, and maybe traces of ZA) than zeolite A, in spite of the fact that all aged systems transform to pure zeolite A! This is an indication of solution mediated transformation.

All zeolites for comparison of IR spectra (mentioned in Fig. 2B) were synthesized using procedures described in according references: hydroxysodalite (SOD),[26] EMC-2 (EMT),[27] chabazite (CHA),[28] zeolite A (LTA),[6] zeolite L (LTL),[29] and zeolite X (FAU).[30]

From dTG curves (Fig. 3), one can see wide minima of water desorption, which peaks are slightly shifted towards higher temperature with ageing time. Fresh gel has minimum at 132 °C, while the most aged gel (209 h) at 146 °C. The corresponding minimum for pure zeolite A is found at 170 °C. This means that more water molecules are strongly bonded to matrix, indicating that the amount of the ordered phase (still amorphous – according to
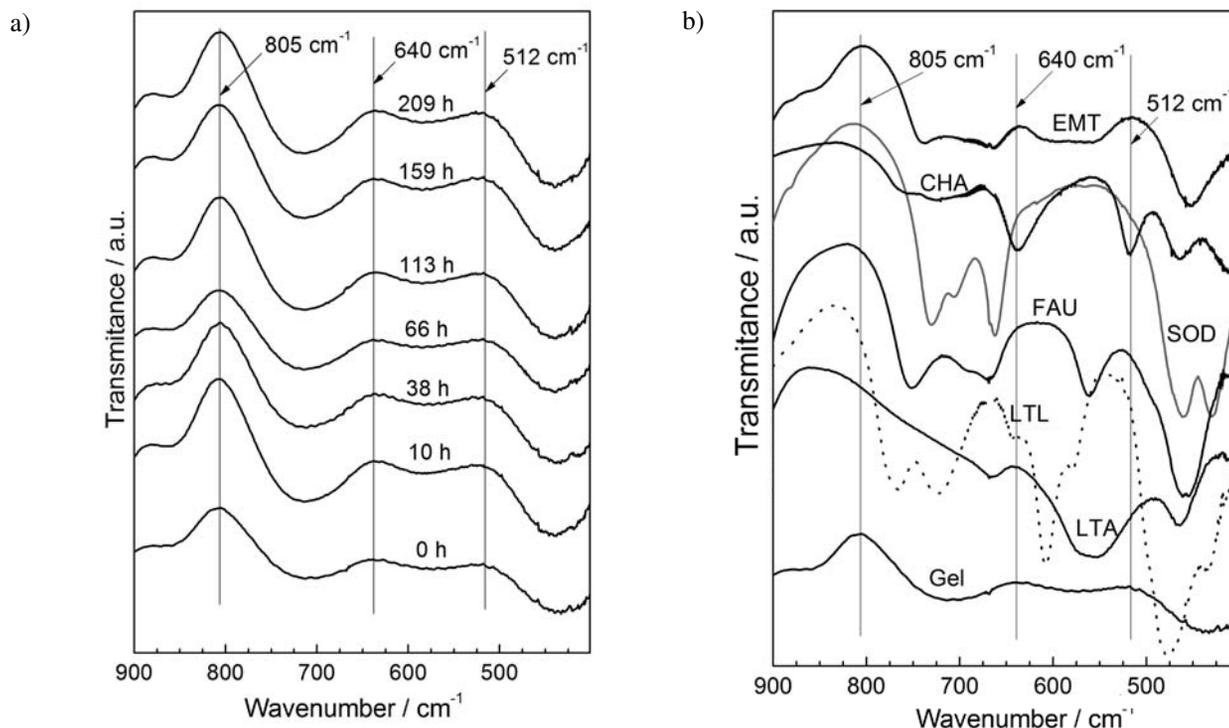

Figure 2. FTIR spectra of: a) the starting gels aged for certain time (0–209 h), and b) the typical low-silicate zeolite types: SOD (grey), CHA, EMT, LTA, LTL (dots), and FAU, recorded at 25 °C.
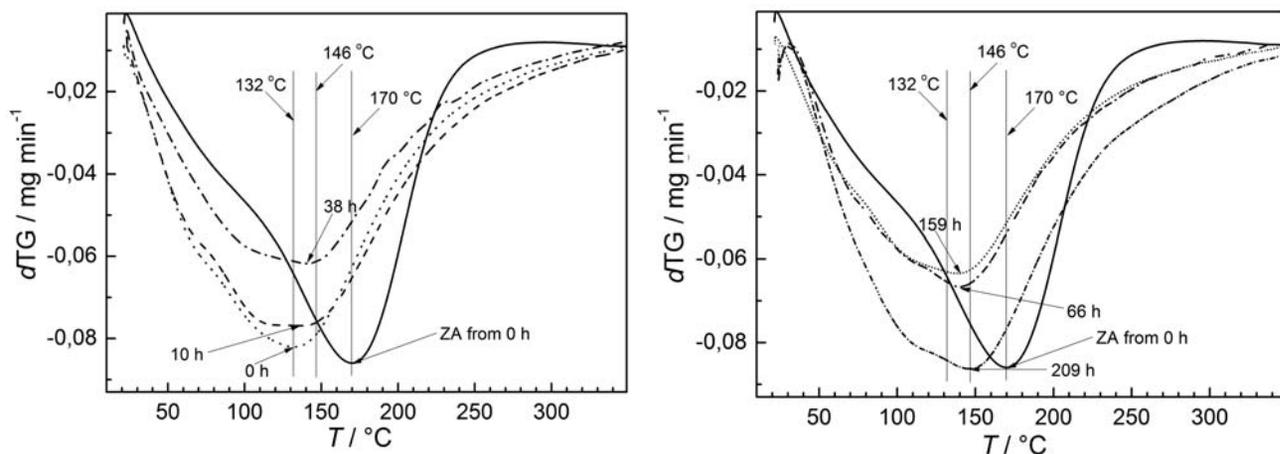
Figure 3. The dTG curves of the gels aged for 0 (dots), 10 (dash), 38 (dash-dot), 66 (dash-dash-dot), 159 (short-dot), 209 h (short-dash-dash-dot) and zeolite A (solid curve) crystals (curve for gel aged 113 h was not shown due to technical problem). Arrows show the minimum at dTG curves.

PXRD patterns, and undefined zeolite type(s) but the structure elements are clearly present) increases with the aging time.

Positron annihilation lifetime spectroscopy data show (Fig. 4) almost linear (except for smaller voids in fresh and 10 h aged samples) increase in the number of voids (corresponding to the intensity of the annihilated introduced positrons) present within gel matrix with the time of the gel aging. The diameter of the sodalite (or β) cage which is the building unit of SOD, LTA, FAU and EMT framework types is around 0.7 nm, while the diameters of the α-cage in the LTA zeolite and supercage in the FAU are 1.1 and 1.2 nm, respectively. The dimension of the D6R, which is building unit of FAU type of zeolites, is 0.31 nm for the length of the hexagonal face and 0.69 nm for the length of the space diagonal of the hexagonal prism. The length of the space diagonal of the D4R in LTA
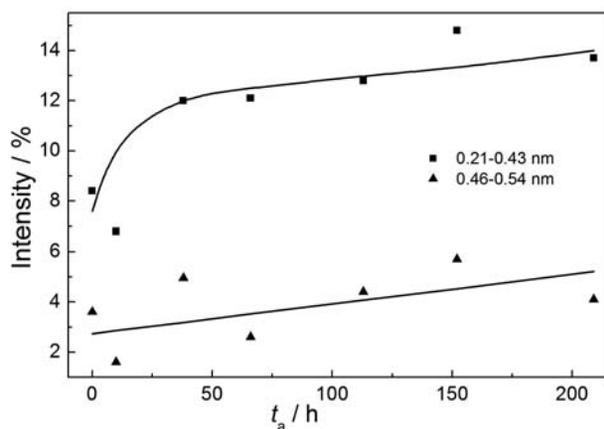

Figure 5. The specific Brunauer–Emmett–Teller (BET) surface area of the samples aged for 0, 10, 38, 66, 113, 159, and 209 h.

framework is 0.53 nm (a = 0.31 nm). When these data are compared with the size of the voids determined from the PALS results, almost all of the structural elements of the smaller SBU (4R, 6R, D4R, D6R) can be placed to the two voids groups found by PALS, but there are no voids of the corresponding larger SBU (< 0.7 nm) within mentioned zeolites (α cage and supercages, even β cages)! For this reason, we cannot make the conclusions regarding the type of the building units present in the gels. However, we have unambiguously observed the rising of the quantity of the cavities having the radius in the ranges of 0.21–0.43 and 0.46–0.54 nm which is a strong indication that the number of short-range ordered units in the gels is becoming higher with gel aging. These »islands« of ordered material (possible nuclei) still not have all elements of the crystals unit cell of the final product (supercages are missing).

Similarly, specific surface area (Fig. 5), calculated from adsorption of N_2 (BET method) show significant decrease from 68 to 57 m^2g^{-1} (trend line was calculated from

Figure 4. Positron annihilation lifetime spectroscopy (PALS) data of gels aged for 0, 10, 38, 66, 113, 159, and 209 h. Squares represent values calculated from experimental τ_3 values, while triangles represent values calculated from τ_4, both using Tao-Eldrup model in corresponding ranges of voids sizes. Intensity represents a proportional number of the voids in each of the measured samples.
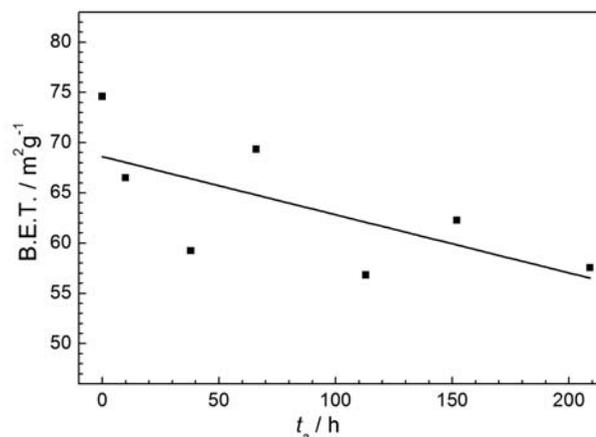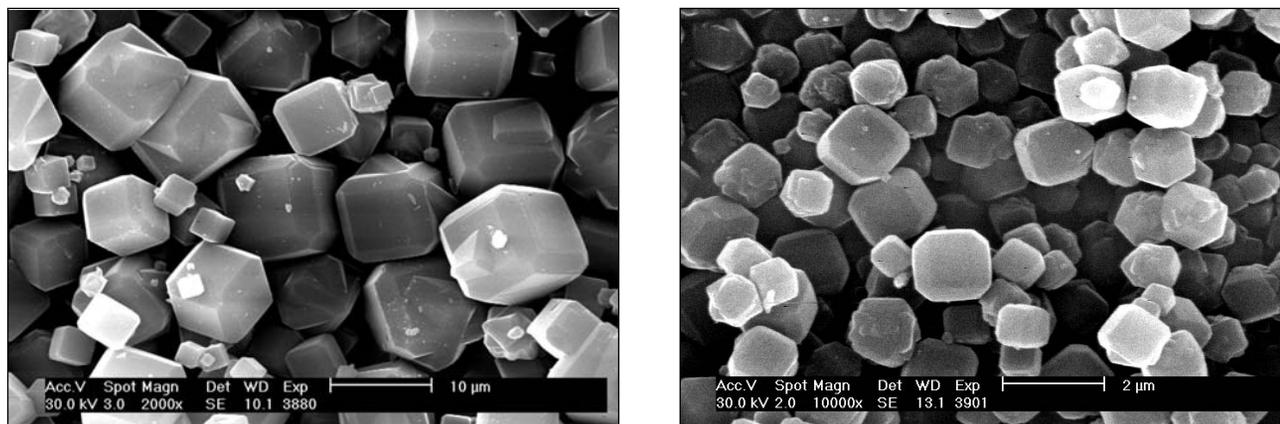
Figure 6. SEM micrographs of the zeolite A crystals obtained after transformation of the fresh gel (A) and gel aged for 209 h (B).

measured points using least square method), representing increase in the amount of structured material with time of gel ageing (generally, structured particles of the porous materials have lower external surface area than the amorphous particles of the same size).

Another direct evidence of the changes within the gel matrix during ageing time is increase of the Al content; Si/Al ratio drops from 1.306 for fresh gel, via 1.148 for system aged for 66 h, to 1.067 for system aged for 209 h (data adopted from the Table 1 of ref. [6]). Consequence of the reaction of Al species from liquid phase with terminal OH groups at gel's surface during »induction period« is the generation of the new nuclei at surface and subsurface volume of the gel particles, and the fact that average size of the crystals at the end of crystallization decreases. It also can be seen at SEM micrographs (Fig. 6), where the size of the largest crystals, obtained after crystallization from fresh gel (A), are several times larger than crystals obtained from gel aged for 209 h.

4. Conclusions

According to the FTIR spectra, wide IR bands (which correspond with some structured units) exist within gel matrix of fresh gel as well as in all aged gels. In spite of the fact that all systems transform to pure zeolite A, it seems that the structural elements present in gels are rather some building elements of zeolite X (FAU) or a mixture (ZX, HS, and maybe traces of ZA) than zeolite A only.

PALS data show trend of increased number of the smaller (0.21–0.43 nm) and also larger (0.46–0.54 nm) structured voids with gels' aging time. These results also confirm main hypothesis (observation) that there is an increase in the number of the structured units within gel matrix with gel aging, and the structured units belongs to simple SBU (4R, D4R, 6R, D6R), while large (complex) units such as sodalite cage (α cage, supercage) were not detected.

The minimums of the dTG curves are shifted towards larger temperature in accordance with time of gels'

aging. Since the »crystalline« water in zeolite A is strongly bonded to framework (minimum at 170 °C) than the water to amorphous aluminosilicate network of the same chemical composition (maximum at 132–146 °C, due to the time of gel aging) our conclusion is that the amount of the »crystalline material« (ordered parts within gel matrix) increases with time of aging.

Indirect evidence of the increase in the number of nuclei (amount of structured material within gel matrix) during hydrogel aging are SEM photos of the crystals after transformation of the fresh gel and gel aged for 209 h (Fig. 6), where average crystals size significantly decreases with time of aging of the starting hydrogels.

The main conclusion here is that the structured units within gel matrix are simple SBU (4R, D4R, 6R, D6R), which represent possible nuclei, but does not contain whole unit cells of the end product (zeolite A), nor the whole unit cells of any of the mentioned high aluminum zeolites.

These results are in accordance with the literature data, which are based on chemical composition of the solid and liquid phases, several kinetic parameters (crystallinity, chemical composition of liquid phase, the size of the largest crystals) during hydrothermal transformation of the aged hydrogels to zeolite A, and on analysis of the final product (crystal size distribution, curves of nuclei formation).

5. Acknowledgements

6. References

1. S. P. Zhdanov, N. N. Samulevich, In: L. V. Rees (Ed.), Proceedings of the Fifth International Conference on Zeolites,

Naples, Italy, 1980, Heyden, London-Philadelphia-Rheine, **1980**, 75–84.

2. J. Bronić, B. Subotić, I. Šmit, LJ. A. Despotović, *Stud. Surf. Sci. Catal.*, **1988**, *37*, 107–114.
http://dx.doi.org/10.1016/S0167-2991(09)60587-5

3. O. Larlus, V.P. Valthev, *Chem Mater.* **2004**, *16*, 3381–3389.
http://dx.doi.org/10.1021/cm0498741

4. S. Ferchiche, J. Warzywoda, A. Sacco, Jr., *Int. J. Inorg. Mater.* **2001**, *3*, 773–780.
http://dx.doi.org/10.1016/S1466-6049(01)00046-0

5. M. Ogura, Y. Kawazu, H. Takahashi, T. Okuba, *Chem. Mater.* **2003**, *15*, 2661–2667.
http://dx.doi.org/10.1021/cm0218209

6. A. Palčić, J. Bronić, Đ. Brlek, B. Subotić, *Cryst. Eng. Comm.* **2011**, *13*, 1215–1220.
http://dx.doi.org/10.1039/C0CE00102C

7. S. Mintova, N. Petkov, K. Karaghiosoff, T. Bein, *Mater. Sci. Engin. C* **2002**, *19*, 111–114

8. S. Yang, A. Navrotsky, *Micropor. Mesopor. Mater.* **2002**, *52*, 93–103.
http://dx.doi.org/10.1016/S1387-1811(02)00276-7

9. T. Antonić. B. Subotić. N. Stubičar, *Zeolites* **1997**, *18*, 291–300.

10. C. S. Cundy, P. A. Cox, *Micropor. Mesopor. Mater.* **2005**, *82*, 1–78.
http://dx.doi.org/10.1016/j.micromeso.2005.02.016

11. V. Valtchev, S. Rigolet, K. N. Bozhilov, *Micropor. Mesopor. Mater.* **2007**, *101*, 73–82.
http://dx.doi.org/10.1016/j.micromeso.2006.10.016

12. G. Bonilla, D. G. Vlachos, M. Tsapatsis, *Micropor. Mesopor. Mater.* **2001**, *42*, 191–203.
http://dx.doi.org/10.1016/S1387-1811(00)00317-6

13. S. M. Auerbach, M. H. Ford, P. A. Monson, *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 220–225.
http://dx.doi.org/10.1016/j.cocis.2005.09.012

14. R. Grizzetti, G. Artioli, *Micropor. Mesopor. Mater.* **2002**, *54*, 105–112.
http://dx.doi.org/10.1016/S1387-1811(02)00357-8

15. S. Bosnar, B. Subotic, *Micropor. Mesopor. Mater.* **1999**, *28*, 483–493.
http://dx.doi.org/10.1016/S1387-1811(98)00338-2

16. N. D. Hould, A. Foster, R. F. Lobo, *Micropor. Mesopor. Mater.* **2011**, *142*, 104–115.
http://dx.doi.org/10.1016/j.micromeso.2010.11.024

17. B. Subotić, **J. Bronić**, T. Antonić Jelić, Chapter 6 *»Theoretical and Practical Aspects of Zeolite Nucleation«* in *»Ordered Porous Solids: Recent, Advances and Prospects«*, Svetlana Mintova, Valentin Valtchev, Michael Tsapatsis, (Eds.), Elsevier, Amsterdam, **2009**, 127–185.
http://dx.doi.org/10.1016/B978-0-444-53189-6.00006-8

18. M. Haouas, L. Lakiss, C. Martineau, J. El Fallah, V. Valtchev, F. Taulelle, *Micropor. Mesopor. Mater.* **2014**, *198*, 35–44.
http://dx.doi.org/10.1016/j.micromeso.2014.07.011

19. H. Julide Koroglu, A. Sarýoglan, M. Tatlýer, A. Erdem-Senatalar, O. T. Savasci, *J. Cryst Growth* **2002**, *241*, 481–488.
http://dx.doi.org/10.1016/S0022-0248(02)01321-0

20. S. Dumrul, S. Bazzana, J. Warzywoda, R. R. Biederman, A. Sacco Jr., *Micropor. Mesopor. Mater.* **2002**, *54*, 105–112.
http://dx.doi.org/10.1016/S1387-1811(02)00354-2

21. D. Bosnar, Zs. Kajcsos, L. Liszkay, L. Lohonyai, P. Major, S. Bosnar, C. Kosanović, B. Subotić, *Nucl. Instrum. Meth. A* **2007**, *581*, 91–93.
http://dx.doi.org/10.1016/j.nima.2007.07.035

22. J. Kansy, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **1996**, *374*, 235–244.

23. S. J. Tao, *J. Chem. Phys.* **1972**, *56*, 5499–5510.
http://dx.doi.org/10.1063/1.1677067

24. M. Eldrup, D. Lightbody, J.N. Sherwood, *J. Chem. Phys.* **1981**, *63*, 51–58.

25. StarDriver V2.03, from Micromeritics, upgraded for Gemini v 2380, **1997–2000**.

26. S. Bosnar, J. Bronić, I. Krznarić, B. Subotić, Croat. Chem. Acta **2005**, 78, 1–8.

27. E.-P. Ng, J.-M. Goupil, A. Vicente, C. Fernandez, R. Retoux, V. Valtchev, S. Mintova, *Chem. Mater.* **2012**, *24*, 4758–4765.
http://dx.doi.org/10.1021/cm3035455

28. H. Robson, Verified Synthesis of Zeolitic Materials, 2nd revised edition, Elsevier, **2001**, pp123.

29. L. Itani, K. N. Bozhilov, G. Clet, L. Delmotte, V. Valtchev, *Chem. Eur. J.* **2011**, *17*, 2199–2210.
http://dx.doi.org/10.1002/chem.201002622

30. P. K. Dutta, J. Bronić, *Zeolites* **1994**, *14*, 250–255.
http://dx.doi.org/10.1016/0144-2449(94)90092-2

Povzetek

Mikrostruktura izhodnih hidrogelov ima zelo pomembno vlogo pri sintezi mikroporoznih materialov. Za analizo gelov je primernih le zelo omejeno število eksperimentalnih metod. Zaradi tega je kar nekaj mankajočih informacij o procesih, ki se dogajajo na molekularnem nivoju, pred nastakom (formiranjem) jeder. V članku poročamo o različnih metodah, ki smo jih uporabili za karakterizacijo predhodno obdelanih (staranih) hidrogelov pred procesom njihove hidrotermalne transformacije v zeolit A. Rezultati, pridobljeni z različnimi tehnikami (FTIR, PALS, BET, DTG), kažejo na spremembe v kemijski sestavi in mikrostrukturi trdne faze. Struktura urejene faze (potencialna jedra) znotraj matrice gela (popolnoma amorfen glede na XRD) ima drugačne zeolitne strukturne enote, ki so značilne za FAU in SOD strukturi (ali njune mešanice), od končnega produkta (strukturna koda LTA).