THE EFFECT OF ULTRASOUND ON Na–A ZEOLITE SYNTHESIS BASED ON SODIUM ALUMINOSILICATE GELS AND SOLID MATERIALS

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To explain some aspects about the mechanism of zeolite synthesis from reagent materials, law temperature (100 °C) hydrothermal reaction was performed in alkali solutions by using sonochemically-assisted pre-treatment method. This pre-treatment method reduces the formation times of zeolites. Clear-to-the-eye sodium aluminosilicate gels and solid sodium aluminosilicate mixtures were used as raw materials. By using sodium aluminosilicate gels, it is observed that after hydrothermal treatment and sonication up to 10 minutes samples exhibit a rise in the crystallinity of Na-A zeolite up to 1.44 times, compared to a sample without sonication. When solid components as raw materials were used, the application of ultrasound irradiation and hydrothermal treatment resulted in the replacement of Na-A zeolite crystals to Na-X zeolite, which is a more stable zeolitic phase. In both cases Na-A zeolite was not detected in the synthesized products by using only sonication without the using of hydrothermal treatment. It was observed that the Na-A zeolite crystallization level is higher for samples which were obtained from the raw material of aluminosilicate gel.

Keywords: *Na-A zeolite synthesis; sonication; hydrothermal synthesis*

1. Introduction

Zeolites are crystalline, microporous, aluminosilicate [1]. They can be described as inorganic polymers consisting of tetrahedral shaped $[SiO_4]^{4-}$ and $[AlO_4]^{3-}$ monomers. These tetrahedra are connected through shared oxygen atoms and make up the so-called secondary units, which, in turn, constitute the three-dimensional framework structures of zeolites [2]. The variety of geometric configurations of zeolite frameworks is rather extensive and new structures are still being discovered. Due to their unique properties, zeolites have a very wide range of possible applications. They can be used as catalysts in the chemical and oil industries, as molecular sieves in liquid and gas filtration, as sorbents for collecting various chemical waste products and even radioactive fallout, as additives to animal and human food, as antibacterial materials or medicine delivery vehicles, as additives to structural materials in the construction industry, etc [1, 3-7]. Considering the wide range of possible applications for zeolites as well as the substantial demand across various industries, the improvement of the process of zeolite synthesis is a relevant area of research.

One of the more common synthetic zeolites is Na–A zeolite, which is often synthesized using the hydrothermal synthesis approach. It has been observed that with the use of ultrasound the hydrothermal synthesis process may become more efficient and yield better results—an effect attributed to cavitation [8 - 10].

The usage of ultrasound could influence the types and stability areas of the phases, shorten the crystallization time, crystal size and crystallinity of the zeolites, reduced the temperature of hydrothermal treatment. Andaç et al. [11] has stated that it was possible to obtain highly crystalline Na–A zeolite from a clear-to-the-eye sodium aluminosilicate solution in the presence of ultrasound. This ultrasound treatment affected the types and stability areas of the zeolitic phases that formed during metastable phase transformations. Jianmei et al. [12] has obtained MCM-49 zeolite with high crystallinity. This type of zeolite was synthesized from a silica source with a low specific surface area and ultrasound treatment was used. At the same time by using the aging method with ultrasound treatment the crystallization time of MCM-49 zeolite shortened. The decrease of hexamethylene imine/SiO_2 ratio has been observed. Khoshbinet al. [13] have synthesized a series of ZSM-5 zeolite by using the ultrasonic treatment of aluminosilicate mixtures. By changing the parameters of ultrasound treatment significant change in the morphology and porous properties was determined. The XRD analysis showed that the application of ultrasound has led to decrease in the crystal size and crystallinity of ZSM-5. The morphology of synthesized ZSM-5 zeolites became finer. It changed from micro-scale hexagonal-shaped to much smaller rough spheres according to the FESEM analysis.

One of the potentials applications of fly ash are zeolite synthesis. Bukhari et al. [14] investigated the impact of ultrasound energy at different temperatures on the zeolitization of aluminosilicate initial mixtures based on of coal fly ash. The crystallinity of zeolitic crystals produced with ultrasound treatment increased two times compared to conventional (hydrothermal) zeolite

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synthesis at 85 °C. It was determined that the synthesis at 85 °C combined with ultrasonic treatment leads to the best crystalline structure with a pure single phase of zeolite-A. Application of ultrasound dramatically reduces the synthesis duration and allows obtaining zeolitic phases with high purity and high crystallinity. Belviso et al. [9] have investigate the low-temperature (25–60 °C) hydrothermal synthesis of zeolites from fly ash by using sonication, as well. According to XRD and SEM studies, the ultrasonic treatment of initial mixtures influenced the formation of zeolites at lower temperatures, as compared to similar mixtures without sonication.

Zeolites are microporous aluminosilicate with many useful properties. Due to their widespread use in various industries it is important to find ways to improve the process of synthesis. In this paper the effect of ultrasound on Na–A zeolite hydrothermal synthesis by using two types of raw materials: sodium aluminosilicate gels and solid sodium aluminosilicate materials were investigated.

2. Material and methods

Na–A zeolite was synthesized from following reagent materials: amorphous $SiO_2 \cdot nH_2O$ (surface area S = 1301 m^2/kg; loss on ignition - 19.0%); $Al(OH)_3$, predominant strain – gibbsite (S = 104.9 m^2/kg); NaOH and water. The molar ratio of the initial reagents was $Na_2O:Al_2O_3:Si_2O:H_2O$ = 2:1:2:20. This molar ratio was chosen based on reference data found in literature [15]. In this study two different raw materials preparation methods were used: clear-to-the-eye sodium aluminosilicate solution and solid sodium aluminosilicate materials.

By using the first preparation method 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. Once the materials were fully dissolved (clear-to-the-eye solutions), the two solutions were mixed together. Gels formed immediately after mixing.

For the second raw material preparation method SiO_2 and $Al(OH)_3$ were directly placed into a NaOH solution. The mixture was then exposed to an ultrasound treatment. The power of ultrasonic radiation was chosen to be 200 W and the duration of exposure ranged from 0 to 10 minutes. Changes in temperature caused by the heating of the ultrasonic horn were not accounted for as it has been suggested that this is not enough to cause zeolite crystallization and has no significant influence on the crystallinity of the samples [9]. After sonication, a hydrothermal treatment was carried out at 100°C in the unstirred suspension at isothermal curing duration of 1 hour. The final product of synthesis was filtered, and dried at approximately 60 °C.

The mineral composition of synthesized products was examined using X-Ray Diffraction spectroscopy (XRD) and Fourier Transform Infra-Red spectroscopy (FT-IR). X-ray diffraction analysis of the materials was performed using the X-ray diffractometer Bruker D8 Advance. CuKα radiation and Ni filter were used. Powder X-ray diffraction patterns were identified with references available in the PDF-2 data base (PDF – 2 International Centre for Diffraction Data, 12 Campus Boulevard Newtown Square, PA 19073-3273 USA). 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. The spectra were registered in the range of 4000–400 cm^{-1}.

The morphology of zeolitic samples was studied by scanning electron microscope (SEM). A high-resolution scanning electron microscope FEI Quanta 200 FEG with a Schottky field emission gun (FEG) was used for the research.

Crystallinity of the samples was evaluated from XRD data using the method of comparison with a standard [10]. A formula to calculate crystallinity is as follows:

$$C = \frac{\sum I_e}{\sum I} \cdot 100, \quad (1)$$

where C—material crystallinity (%), I_e—the sum of the intensities of XRD peaks of the standard sample, I— the sum of the intensities of XRD peaks of the standard sample. For practicality, only 10 peaks of highest intensities were summed. A commercially produced Na – A zeolite was used as the standard and its crystallinity was assumed to be 100 %.

3. Results and discussion

XRD analysis of material produced from aluminosilicate gels indicate that in the samples which did not receive ultrasound treatment, only amorphous phase was present (Fig. 1a). In this case the aluminium hydroxide did not have an ordered crystal structure, so only a halo peak was observed in the XRD pattern. After 2 min and 5 min of sonication the crystallisation of aluminosilicate gels was observed. The XRD peaks which belong to gibbsite and bayerite (d: 0.483, 0.437, 0.431, 0.324 nm) could be noticed, but any zeolite was detected. After 10 min of sonication the material became X-ray amorphous again (Fig. 1a). These phenomena can be explained by ultrasound-induced cavitation [9, 10]. Initially cavitation helps to form crystallization centres and provides the energy needed for zeolite crystallization but in later stages of material decomposition destructive phenomena begin to prevail and the crystalline structure is destroyed.

After hydrothermal treatment (Fig.1, b), Na-A zeolite dominates in the samples (d: 1.231, 0.870,.

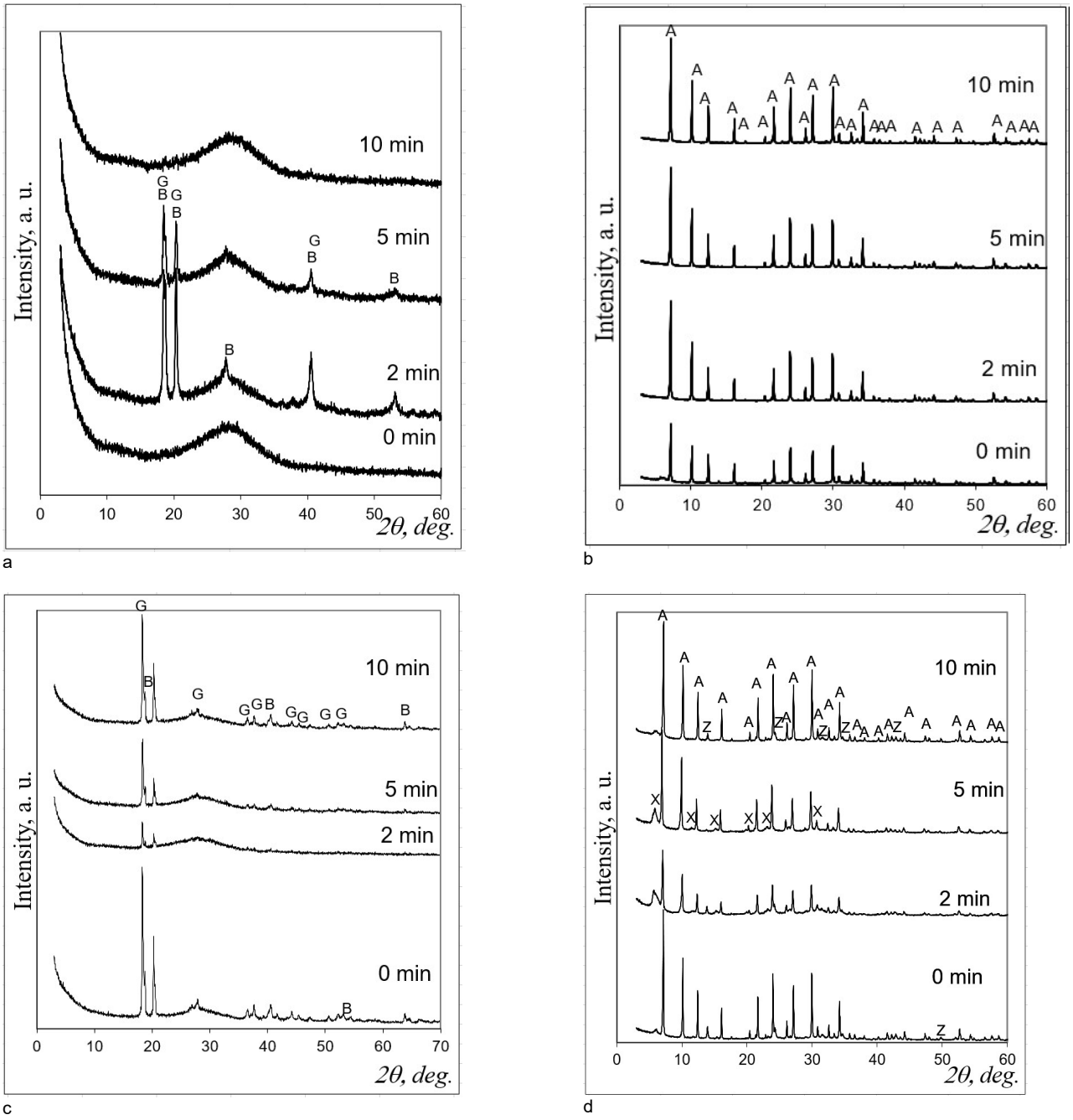


Fig. 1 - XRD spectra of samples after ultrasonic treatment (a, c) and ultrasonic with hydrothermal treatments (b, d). The duration of ultrasonic treatment was, as indicated: 0, 2, 5 and 10 min. Synthesis product obtained by using sodium aluminosilicate gels (a, b) and by using solid materials (c, d). Notes: G – gibbsite, $Al(OH)_3$ (7-324), B – bayerite $Al(OH)_3$(77-114), A – zeolite A(Na) $Na_{96}Al_{96}Si_{96}O_{384}\cdot 216H_2O$ (39-222), Z – sodium aluminium silicate hydrate, $Na_6(AlSiO_4)6\cdot 4H_2O$ (42 – 216), X – zeolite X(Na) $Na_{86}Al_{86}Si_{106}O_{384}\cdot 264H_2O$ (38-237)

0.371, 0.329, 0.298, 0.262 nm) [16, 17]. As the time of ultrasound treatment increased from 0 to 10 min, the peak of Na – A zeolite increased, too.

When solid components were used as raw materials, similarly to the previous method, zeolite was not obtained after application of ultrasound treatment (Fig. 1, c). According to some studies [18], it is possible to synthesize zeolite by using ultrasound treatment alone, but a longer treatment time is required (several hours). In our samples only the crystalline phases of gibbsite and bayerite could be seen. With increasing ultrasonic treatment duration from 2 min to 10 min the XRD peaks of gibbsite and bayerite increased, as well. According to the XRD curves (Fig. 1, a, c) the presence of the amorphous phases could be explained by the presence of a 'hump' appearing between 20 and 42° 2θ in both the samples only after ultrasonic treatment. This result was similar to that reported by Ameh [19].

From the XRD patterns presented in Fig. 1, d, it can be observed that Na-A zeolite dominated in all mixtures. The XRD peaks of Na-A zeolite were seen to decrease in intensity upon increase

of ultrasound treatment from 2 min to 5 min and it increases again after 10 min.

By developing an ultrasound-induced cavitation based hypothesis, it can be argued that destructive cavitation phenomena degrade previously formed crystals and fine particles in a hydrothermal mixture, thus the surface area of the particles involved in subsequent reactions increases. Also, cavitation can have a positive effect on the formation of new crystallization nuclei during hydrothermal treatment. In Fig. 1, b and d these factors determine a visible positive effect of ultrasound treatment on the crystallinity of the resulting zeolite.

XRD analysis showed that the application of ultrasound energy enhanced the crystallinity of the synthesized samples after hydrothermal treatment in all cases where sodium aluminosilicate gels were used (Fig. 2).

The results show that the use of ultrasound treatment together with hydrothermal synthesis allows achieving a higher degree of Na-A zeolite crystallinity without increasing the hydrothermal treatment time or temperature. In this case the use of ultrasound treatment allows for the reduction of time, energy and other resource costs. It is also seen that increase of ultrasonic treatment duration results in a higher crystallinity of zeolite (Fig. 2). After 10 min of ultrasound treatment, the crystallinity of zeolite increased 1.44 times compared with the sample which did not receive ultrasound treatment.

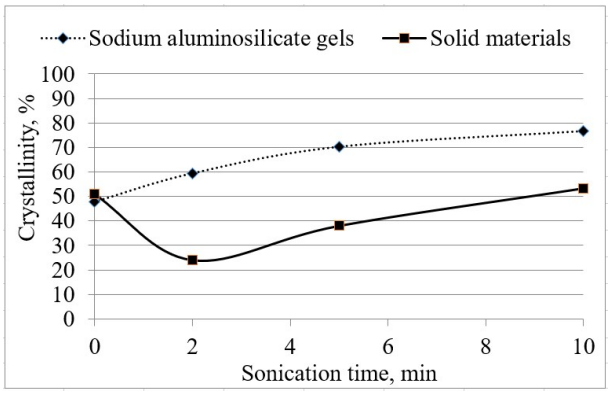


Fig. 2 -The relative crystallinity (%) of Na-A zeolite after hydrothermal treatment, as a function of the ultrasonic treatment time.

When solid materials were used as raw materials after hydrothermal treatment the crystallinity decreases after 2 min and 5 min ultrasound treatment (24 % and 38 % respectively) and then after 10 min ultrasound treatment it increase again till 53%.

In the Fig. 3 Fourier transform infrared spectroscopy (FT-IR) curves which were used to identify the synthesised products were submitted. In the case were aluminosilicate gel was used as raw material the absorption bands 3646 - 3658, 3551 - 3554, 3422 - 3484, 1007 - 1015, 722 – 731 cm^{-1} of the samples (Fig. 3, a) are assigned to gibbsite and bayerite ($Al(OH)_3$) [20, 21]. Besides above mentioned gibbsite and bayerite after ultrasound treatment a broad band of week intensity was noticed around 588-555 cm^{-1}, this band indicate the presence of Na–A zeolite. It can be assumed that ultrasound treatment had effect on small Na-A zeolite crystals formation. After hydrothermal treatment (Fig. 3, b) the FTIR spectrum bands: 992-1011 cm^{-1}, 737 - 761, 772, 667 - 672 cm^{-1}, 554 - 555 cm^{-1} and 464 - 466 cm^{-1}could be associated with presence of Na-A zeolite in the samples. These bands are corresponding to the asymmetric atomic vibrations, symmetric atomic vibrations, double frame rings and Si(Al) – O deformation vibration respectively. Ojumu et al. [22] assigned similar spectral bands to Na-A zeolite. After hydrothermal treatment crystallinity of Na–A zeolite increased because of the application of ultrasound. FT-IR analysis revealed that the small, X-ray amorphous crystals of Na-A zeolite, were obtained from the aluminosilicate gel. These crystals formed early in the samples and the process was also enhanced with the application of ultrasound.

By using solid materials as raw materials after ultrasound treatment (Fig. 3, c) the IR spectrum shows the following absorption bands: 3600 - 3642, 3527 - 3528, 3452 - 3458, 1015 - 1023, 735 - 746, 672 - 674 cm^{-1}, which confirmed the presence of $Al(OH)_3$.

It is obvious that in the spectrum of samples where Al is six coordinated, the broad band (900–1200 cm^{-1}) has a pronounced maximum in the region 1023 cm^{-1}, and it can be attributed to the vibrations Si–O–Al^{VI}–O (Fig. 3, c, the lowest curve). The main band of aluminosilicates, where Al is in the fourth coordination, has a completely different appearance [23]. There is a shift of intensities, and this band is narrower (1020-1200 cm^{-1}), has a more intense absorption maximum in the shorter-wave part (996-1019 cm^{-1}). In compounds where gradual increase of aluminium instead of silicon - in the tetrahedral position weak bands appear in the region of 850-867 cm^{-1} (Fig. 3, a and c–three upper curves).

After hydrothermal treatment (Fig. 3, d) the four bands most typical for Na-A zeolites could be clearly distinguished in the intervals of 1003–1007 cm^{-1} (asymmetrical stretching of (Si, Al)-O bond), 662–668 cm^{-1} (symmetrical stretching of (Si, Al)-O bond), 520–559 cm^{-1} (4-membered double rings D4R and the vibrations of the linkages between these rings) and 450–463 cm^{-1} (Si, Al)-O bending vibration) [24]. Moreover, in the IR spectrum of investigated samples some insignificant bands were assigned to Na-X zeolite [25] the absorption bands: 992-1003 cm^{-1} of asymmetric atomic vibration, 723 - 736, 662 - 668 cm^{-1} of symmetric atomic vibration, 460-465 cm^{-1} of Si, Al- O deformation vibration could be assigned to the Na-X zeolite.

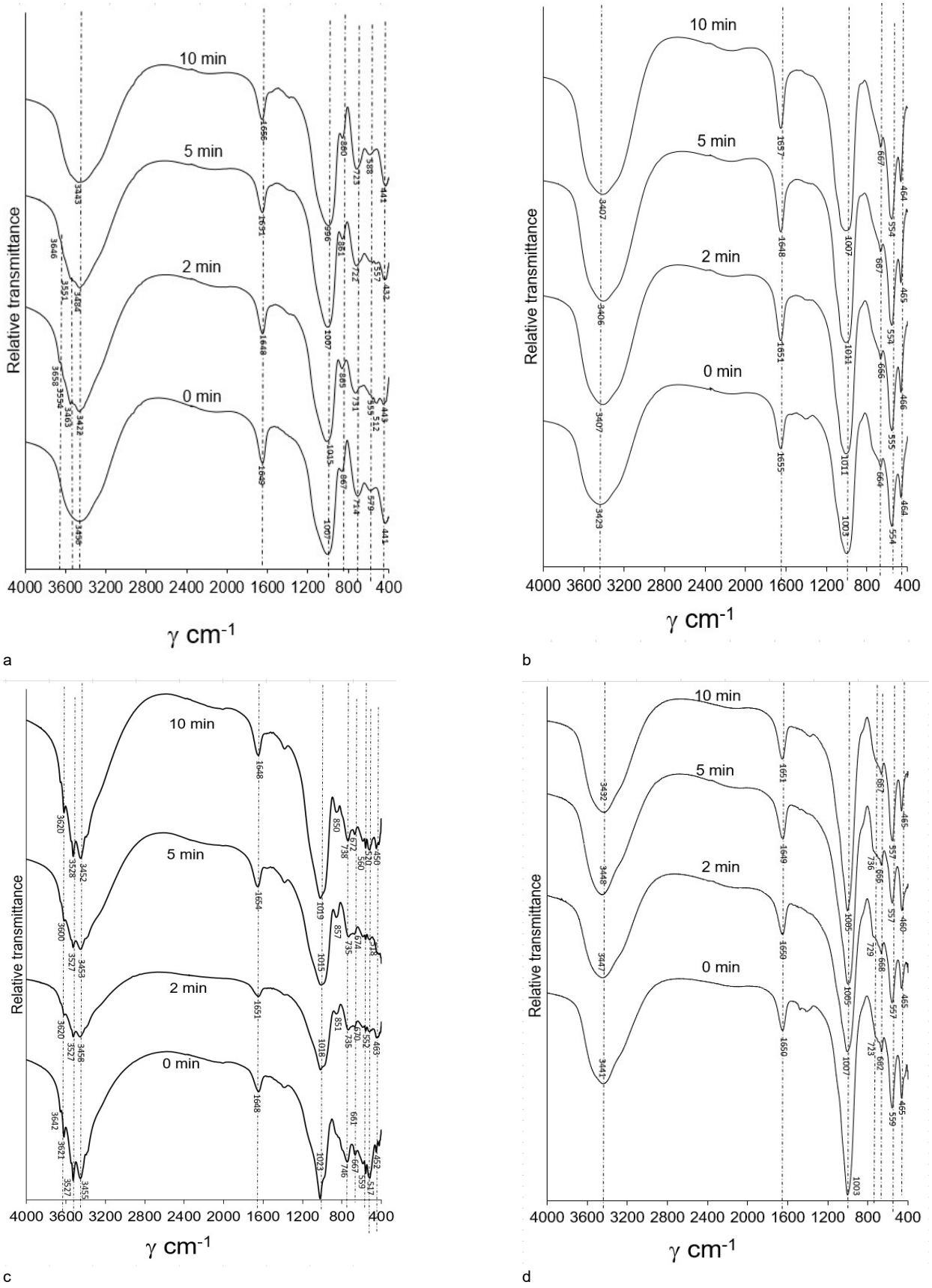
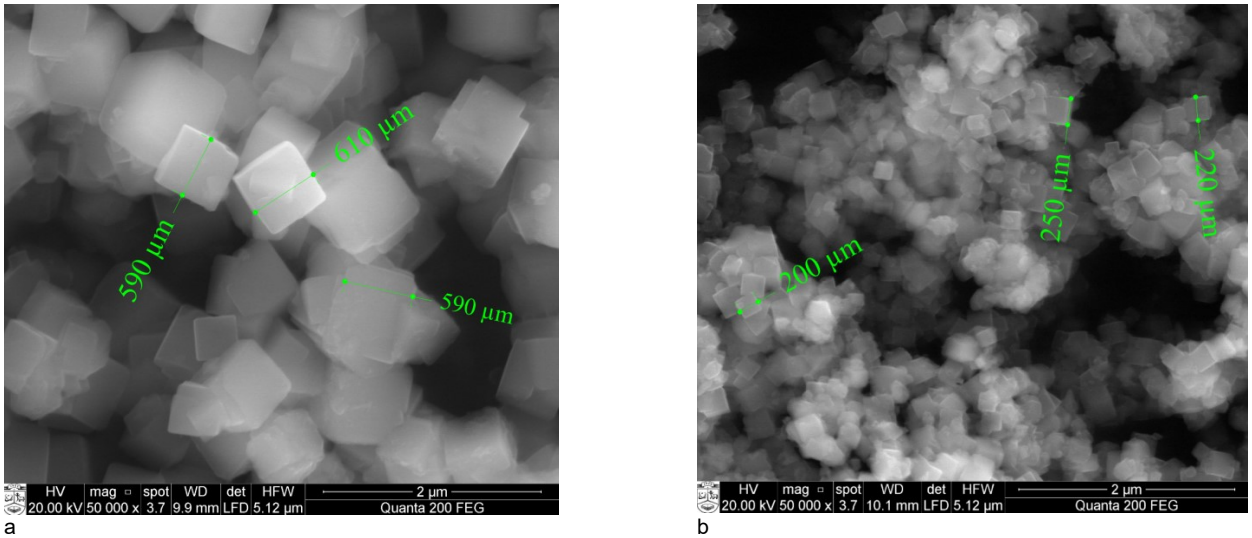


Fig 3 - FT-IR spectra of samples after ultrasonic treatment (a, c) and ultrasonic with hydrothermal treatments (b, d). The duration of treatment was, as indicated: 0, 2, 5 and 10 min. Synthesis product obtained by using sodium aluminosilicate gel (a, b) and by using solid materials (c, d).



a b

Fig 4 - SEM images of the samples after ultrasonic and hydrothermal treatment, by using a sodium aluminosilicate gels (a) and solid materials (b). The duration of ultrasonic treatment was 10 min.

In all curves (Fig. 3) the OH group of adsorbed water could be assigned to the vibration band in the range of 1632 - 1657 cm^{-1}. Absorptions at 3406 - 3458 cm^{-1} are due to the O-H stretches of water in zeolites [26].

Scanning electron microscope (SEM) was used to evaluate the morphology and crystals size of synthesized zeolites. It was found that the crystals of Na-A zeolite prepared from aluminosilicate gels and solid materials had a similar shape. The crystals were seen to be cubic in form [27]. These results obviously show the significant development in crystals size which increased by using of aluminosilicate gels as initial materials compared with zeolites made from solid materials mixtures.

According to SEM image analysis (Fig. 4, a) it was determined that the sizes of cube shaped crystals were in the ranges from 590 to 610 nm when sodium aluminosilicate gels were used as raw materials. Meanwhile when solid materials mixtures were used as initial materials, the sizes of crystals for zeolite sample (Fig. 4, b) vary from 211 to 247 nm. This means that, on average, the use of aluminosilicate gels as initial materials for synthesis of zeolite increased the crystal size about three times as compared with zeolites made from solid materials.

4. Conclusions

XRD, FT-IR and SEM investigations show that the use of sonication and hydrothermal treatment facilitates the formation of zeolitic phases from sodium aluminosilicate gels and from solid material mixtures, as well.

- By using only ultrasonic treatment without the application of hydrothermal treatment Na-A zeolite was not detected in the.
- In the case when sodium aluminosilicate gel was used, after 10 min of ultrasound treatment and 1 h of hydrothermal treatment at 100°C, zeolite crystallinity of 77% can be reached. In the case where ultrasound treatment was not used the crystallinity reached 48%.
- By using solid components as raw materials, the use of ultrasound irradiation and then hydrothermal treatment promote in the transition of Na-A zeolite phase to Na-X zeolite, because is a more thermodynamically stable zeolitic phase.

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