Influence of suspension heating rate on properties of zeolite 13X

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Abstract

It is known that the temperature of crystallization during the synthesis of zeolite is one of the most important process parameters. However, during the research work on the synthesis of zeolite 13X and the introduction of this material into regular industrial production, it was noticed that the heating rate of the starting reaction suspension can have an equally important influence. This influence can be so pronounced that a difference of just a few minutes in reaching the crystallization temperature can make a significant difference in product quality, affect the presence of other phases in the crystal, or even determine the direction of zeolite crystallization. Therefore, the aim of this work was to show the influence of the heating rate on the quality of the obtained 13X zeolite powders. The obtained samples were analysed in terms of crystallinity (by X-ray diffraction), chemical composition, granulometry and specific surface area (by Brunauer-Emmett-Teller analysis), and regarding water and CO_2 adsorption capacities. Additionally, scanning electron microscopy analysis of the samples showed the morphological characteristics of different 13X zeolite powders. The analysis results of the obtained powders confirmed the influence of the heating rate and helped to define the optimal synthesis parameters *i.e.* the initial temperature and heating time, that resulted in stable product quality.

Keywords: Heating rate, Linde type A zeolites, suspension, synthesis

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1. INTRODUCTION

Zeolite 13X is one of the most commercially popular synthetic zeolites thanks to the characteristics of its crystal structure. This type of zeolite stands out primarily for its adsorption characteristics, so it has found application in a large number of adsorption processes. Some of the most important of these processes are oxygen production [1], processing of natural and liquid petroleum gas [2], industrial production and purification of hydrogen (H_2) [3], refining of biofuels [4], industrial production and purification of alcohol [5], refining of petroleum compounds [2], *etc*.

Based on the great possibilities for the application of zeolite 13X and the potential growth in demand due to the development of new adsorption processes, especially those related to the reduction of greenhouse gas emissions (GHG) [6], it was of particular interest to find optimal parameters for the synthesis of this type of zeolite for wider commercial use.

During hydrothermal synthesis of zeolite powders, including zeolite 13X, several factors affect the quality of the synthesized product. The crystallization temperature, the duration of crystallization, the molar ratio of Si/Al in the system and the alkalinity of the synthesis system are among the most important process parameters, whose influence on synthesis is most often investigated [7-9].

However, in order to obtain a pure phase of zeolite 13X with satisfactory quality, in specific industrial conditions a number of other influences occur that are less mentioned in literature most likely because this type of zeolite is a commercial product.

The initial reaction suspension for the synthesis of zeolites 13X, as well as the hydrothermal conditions of synthesis, can easily lead to the formation of other forms of zeolites, which would by their presence violate the purity of the phase

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of zeolite 13X and thus other quality characteristics of the product. During heating, conditions are suitable for the formation of other crystalline zeolite forms, especially those corresponding to a lower crystallization temperature, such as Linde type A (LTA) zeolites or Sodalite [10]. Therefore, the focus of this paper is research on the influence of the heating rate of the reaction suspension (reaching the crystallization temperature in the targeted time) on the quality of zeolite 13X the synthesized powders.

To determine the quality and characterization of synthesized powders, the degree of crystallinity of the obtained powders, the mean diameter of the particle, the specific surface area, and the adsorption capacity for water and CO_2 were determined. In addition, samples of the obtained powders were analyzed regarding the morphology and structure by scanning electron microscopy, to correlate these properties with the other quality parameters.

2. EXPERIMENTAL

2. 1. Synthesis

Experimental syntheses of zeolite 13X were carried out in a reactor (V = 1 m^3) with a vertical stirrer (P = 3 kW, 10-120 rpm) of the Pilot zeolite production plant, company Alumina Ltd. Zvornik, (Bosnia and Herzegovina) as part of a wider research work on determining optimal technological parameters to produce this zeolite type.

The starting raw materials for zeolite synthesis were: NaOH solution (50 %) procured for industrial production in the factory (BorsodChem, Hungary); $NaAlO_2$ solution obtained by dissolving aluminium hydrate ($Al(OH)_3$, approximately 65 % Al_2O_3) in NaOH solution; waterglass produced in the factory by dissolving quartz sand (SiO_2) in NaOH solution, which is otherwise used for zeolite production purposes and demineralized water, which is also used in the factory in a number of processes.

Heating of the reaction suspension as well as maintaining the crystallization temperature is carried out by heating using water vapor. The reactor was a closed vessel with indirect heating through the jacket equipped with the previously described type of stirrer. The temperature in the reactor was set and maintained automatically through a system (Schneider Electric, France) that regulates the flow of steam indirectly with the possibility of setting the heating rate of ~0.8 °C min^{-1}, Temperature measurement was performed using a measuring probe inserted directly into the reaction space.

A total of nine (9) experimental syntheses are performed at different heating times between 60 and 120 min. Relevant experimental process conditions are shown in Table 1.

Table 1. *Experimental process conditions of obtained zeolite samples S1-S9 at a crystallization temperature of 85 °C*

Sample unit	Molar ratio $M(SiO_2)/M(Al_2O_3)$	Initial suspension temperature, °C	τ_{heat} / min	Concentration of (Na_2O) in filtrate, g dm^{-3}
S1	2.49	35	120	44.32
S2	2.39	34	120	43.28
S3	2.41	35	120	44.94
S4	2.42	36	90	45.33
S5	2.29	36	90	43.87
S6	2.38	35	90	42.76
S7	2.32	35	60	44.99
S8	2.42	34	60	42.28
S9	2.35	35	60	44.81

Apart from the difference in the heating time of the reaction suspension, all syntheses were performed under industrial conditions, with almost equal controlled process parameters at 85 °C based on previous industrial experiments for optimal crystallization temperature for the FAU (Faujasite) form of zeolite 13X.

During the experimental synthesis, demineralized water, and waterglass (sodium-silicate) as well as a part of NaOH solution are first added to the reactor, while the second part of the solution during this time is used to dissolve aluminium hydrates, *i.e.* to obtain sodium aluminate solution. After dissolving the hydrate, the resulting sodium aluminate solution is dosed into the reactor and mixed with other raw materials, considering the constant speed of mixing, the dosage rate of the aluminate solution and the temperature. The resulting reaction suspension is then homogenized for a certain period before it begins to be heated from the homogenization temperature to the crystallization temperature. The difference between these temperatures was ~50 °C and the time of reaching this temperature difference is a parameter whose influence was further examined in the work.

2..2. Characterization

The degree of crystallinity of zeolites (%) obtained in the syntheses was determined in the Central Laboratory of Alumina Ltd. Zvornik, by X-ray diffraction (XRD) analysis using the reference sample method (Bruker Discover) XRD was performed on the X-ray diffractometer Bruker D8 ENDEAVOR (Bruker Corporation, USA) with an X-ray tube with a cobalt anode, using CoKα wavelength radiation λ = 0.178897 nm, in the range of diffraction angles 2θ from 25.0 to 29.0° with an angle step of 0.02° and an exposure of 0.50 s per step.

Particle size distribution and $D_{s50\%}$ diameter determination were performed on the CILAS 1090 liquid device (CPS, USA) ranging from 0.02 to 500 µm, with 30 s of sonication, according to the internal method for determining particle size distribution, MA. GX 032a.

The specific surface area was analysed according to the Brunauer–Emmett–Teller (BET) method in gaseous nitrogen (N_2) current on the Device GEMINI VII (Micromeritics Instrument Corporation, USA) with the preparation of a sample of 13X zeolite by thermal activation in ceramic pots in the furnace for a period of 4 h (520 °C) and 1 h (400 °C) by degassing in the nitrogen stream in the Flow-Prep block of the same device. Determination of the adsorption capacity of CO_2 was also performed by using the same device. The sample is prepared by degassing in a stream of nitrogen for 4 h at 520 °C and 1 h at 400°C. Determination of water adsorption capacity was performed in the Cambic KK-105-CH air chamber (CiK Solutions GmbH, Germany) under conditions of 20 °C, relative humidity rH = 50±2, 24 h. The method also prescribes pre-preparation of the sample by thermal activation in the furnace at t = 350-550 °C.

Imaging of zeolite crystals to characterize the morphology of the powders was performed by using a scanning electron microscope MIRA3 TESCAN device (TESCAN Group a.s., Czech Republic), with magnifications up to 10,000 times, operating at 20 kV. Before the examination, all samples were sputter-coated with gold using a sputter coater to avoid the electrostatic charge.

3. RESULTS AND DISCUSSION

The data obtained from the analyses of synthesized zeolite powders $D_{s50\%}$ and specific area are shown in Table 2 as well as relative crystallinity (%) in the diagrams shown in Figure 1 and H_2O and CO_2 adsorption in Figure 2. As can be seen, the heating time of the initial reaction suspension shows a significant impact on the analysed properties of the powders. The heating time affects both the degree of crystallinity of zeolite powders in terms of the desired Faujasite form of zeolite 13X (FAU), as well as the presence of other crystalline zeolite structures.

In addition to the FAU form, the presence of LTA form zeolite (4A), is also quantified and evident, and these values are listed among the results of the analysis (Figure 1).

A very high presence of LTA crystal structure crystals is evident in powder samples synthesized after 120 min of heating the suspension, up to almost 40 % of the relative crystallinity. By shortening the heating time*, i.e.* increasing the rate of heating, the presence of LTA form is reduced, so this phase is practically not recorded in powder samples synthesized after 60 min of heating (Figure 1).

On the other hand, reducing the heating time to 60 min before the period of crystallization itself, resulted in a high degree of relative crystallinity of FAU zeolites 13X crystal structure, so that all three samples (S7-S9) synthesized under these suspension heating conditions have satisfactory relative crystallinity of over 95 %, or even over 100 % (relatively), measured against the standard FAU sample or 0 % to the standard LTA sample of zeolite S8-S9, Figure 1.

However, powders synthesized after 90 min of heating of the reaction suspension did not have a satisfactory degree of relative FAU crystallinity form.

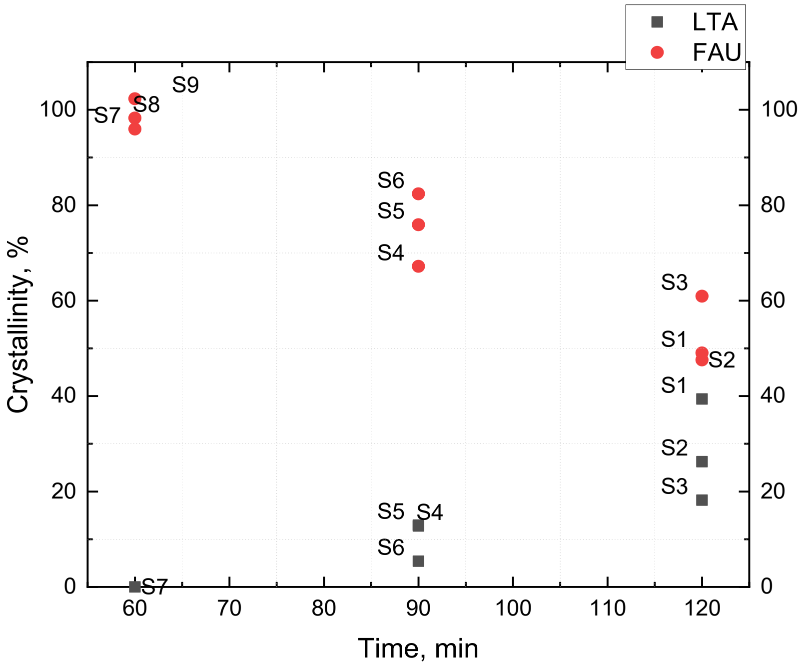

Figure 1. *Correlation of the degree of crystallinity of synthesized powders in relation to the heating time*

Table 2. *Specific surface area and particle size distribution values of 13X zeolite powders*

Sample	S1	S2	S3	S4	S5	S6	S7	S8	S9	SD[c]
$D_{s50\%}$ / µm[a]	3.92	4.31	3.68	4.28	3.98	4.15	3.39	3.08	2.99	0.66
Specific area, m^2 g^{-1} [b]	384.19	383.43	401.32	412.58	449.39	474.85	542.51	550.66	560.29	124.52

[a] he $D_{s50\%}$ is the medium value of the particle size distribution.
[b] Specific area is a specific particle surface area determined by the BET method.
[c] Standard deviation

The observed mean diameter of the prticles (Table 2), does not show a constant correlation with the degree of relative crystallinity of the zeolite 13X phase (compared with Figure 1), but it is noticeable that three samples that have high and satisfactory crystallinity (S7-S9) have the smallest mean particle diameter. However, it is possible to correlate the measured values of the mean diameters to the degree of crystallinity of all the phases present in one sample, or with the presence of agglomerates that are noticeable in the SEM images of individual samples (Figure 4). The specific surface area of the analysed powders increases with the increase in the purity of the crystal phase of 13X zeolite, which indicates that this parameter corresponds to a more regular and uniform crystal structure and lower values of the mean particle size.

The values of water and carbon dioxide adsorption capacities (mass %) are presented graphically, as functions of the degree of relative crystallinity (Figure 2). As with crystallinity itself, it is noticeable that satisfactory values of adsorption capacities were obtained only in samples with high degrees of crystallinity of the 13X zeolite phase (S7-S9), without the presence of other crystallinity forms. That is, the satisfactory values of these two key parameters for the commercial application of 13X zeolite were achieved only with the highest heating rate of the reaction suspension*, i.e.* at a heating time of 60 min.

The results of relative crystallinity and the presence of phases are graphically shown by diffractograms in Figure 3. The presence of the LTA crystal line is clearly visible in samples of S1-S6 synthesized after 120 and 90 min (Figure 3a and b), while the pure phase of 13X zeolite can be observed in Figure 3c. In addition, the diffractograms in Figures 3a and 3b also show the presence of other crystalline forms that do not correspond to FAU or LTA crystal structures. These peaks are not fully qualitatively or quantitatively determined but, according to the positions of the peaks, could correspond to the sodalite form (SOD) or zeolite NaP (GIS crystallographic form) [11].

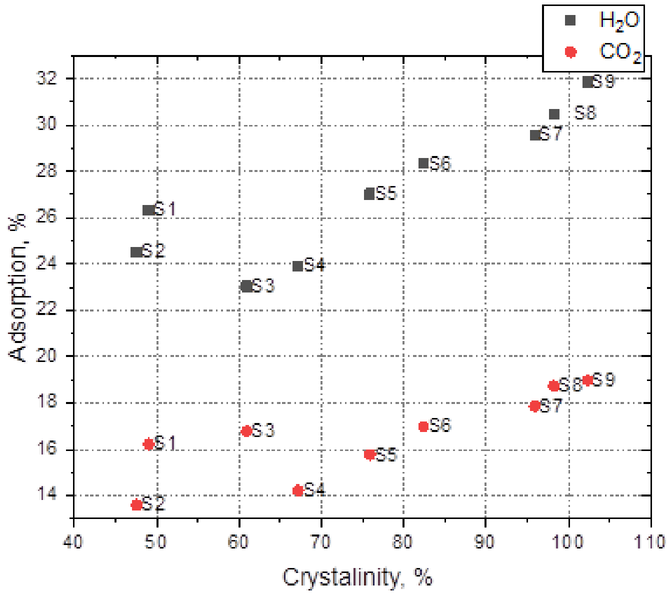

Figure 2. *Correlation of the adsorption capacity (mass %) of synthesized in relation to crystallinity (%) of 13X crystallographic form*

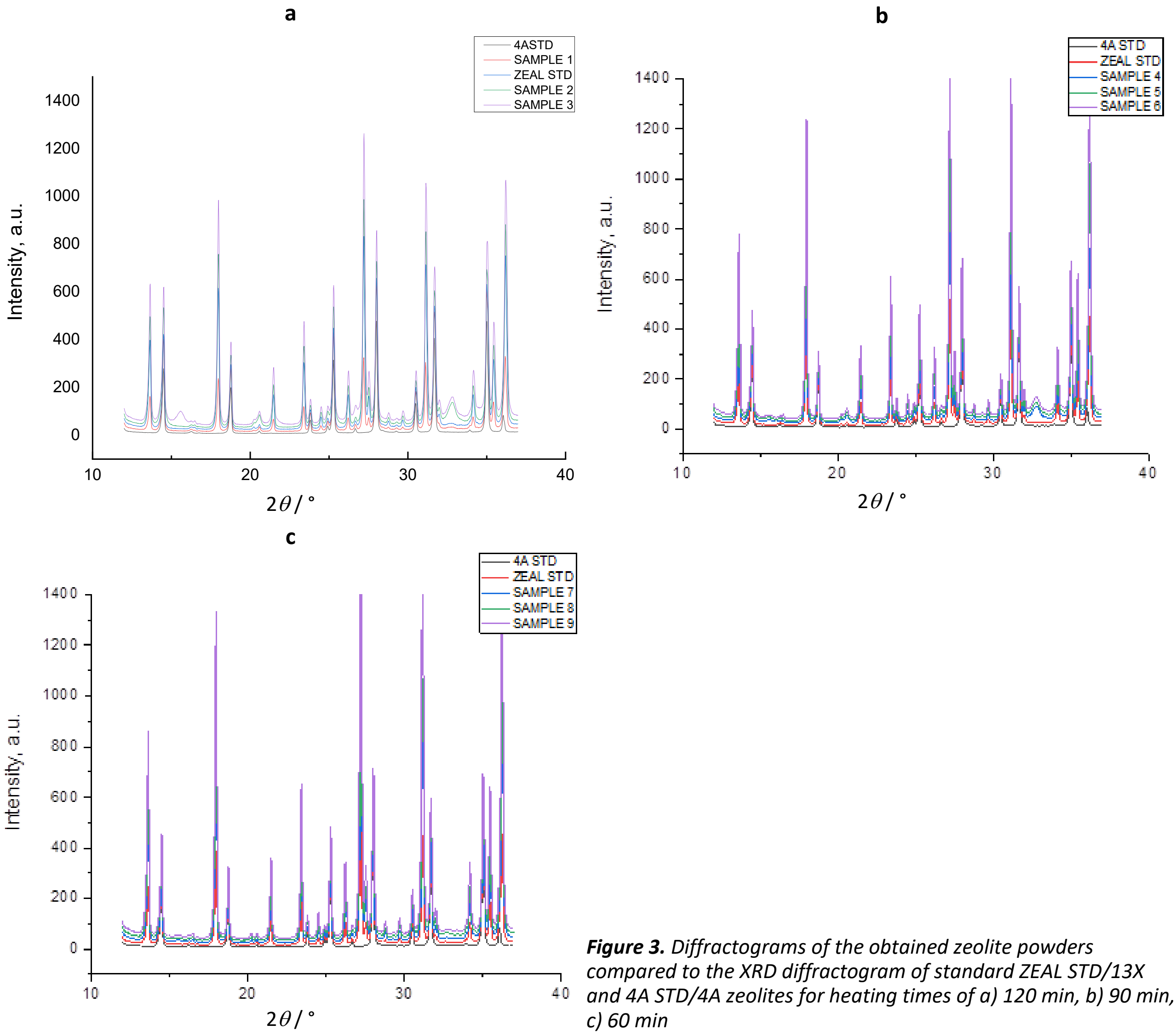

Figure 3. *Diffractograms of the obtained zeolite powders compared to the XRD diffractogram of standard ZEAL STD/13X and 4A STD/4A zeolites for heating times of a) 120 min, b) 90 min, c) 60 min*

In the SEM images (Figure 4), the presence of different shapes of particles and morphology can be noticed, expressed by crystallites of non-uniform size and morphology, which is especially pronounced in the samples (S1-S4), that according to the results of XRD analysis, had the greatest presence of unwanted phases.

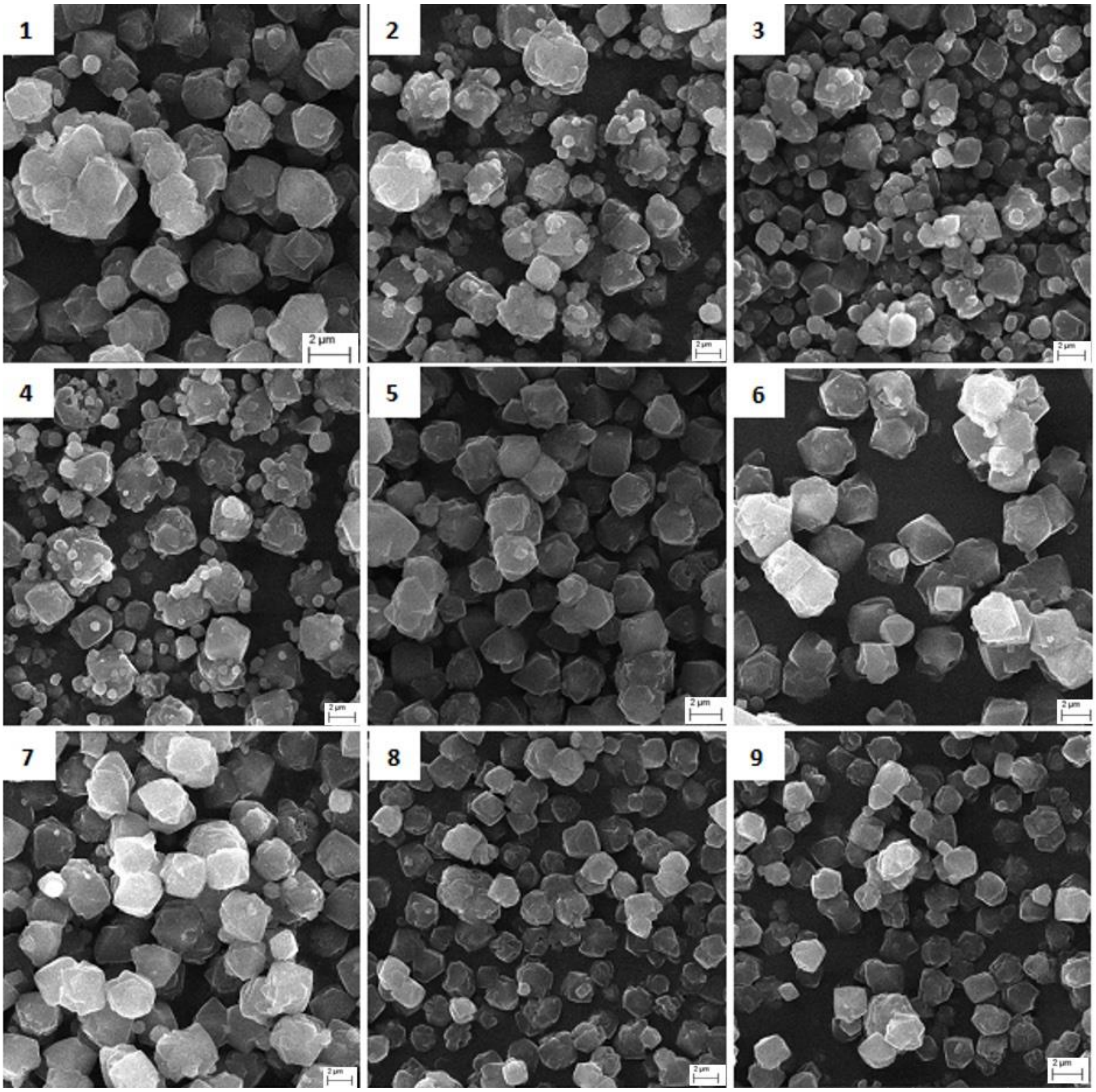

Figure 4. *SEM of the synthesized zeolite powders of samples S1 to S9, scale bar = 2 µm*

The presence of agglomerates is also evident in these samples. In samples S5 and S6, uniformity in the size and morphology of crystallites is greater, but the significant presence of agglomerates is still noticeable. SEM images of samples S7-S9 show uniform crystallite size and morphology, and the absence of agglomerates.

Experimental results follow data from the literature that lower or higher temperatures support the formation of other crystalline forms.

4. CONCLUSION

Based on the obtained results, it can be concluded that faster heating of the reaction suspension, results in a cleaner phase of zeolite 13X, a higher degree of crystallinity and a larger specific surface area of the material. Consequently, with a higher degree of crystallinity, the adsorption capacity of the obtained powders is higher, both in terms of water (H_2O) and CO_2 adsorption, as the two most important parameters that determine the quality of the product obtained and the possibility for its final application.

The results, especially those of XRD and SEM analyses, confirm the assumption that during the heating time, the crystallization system passes through different ranges that enables the formation of other zeolite phases, primarily LTA crystallographic form (zeolite type NaA) but also other forms of zeolite (SOD or NaP), and their presence is greater if the heating is slower, due to the longer retention of crystallization systems in unfavourable temperature ranges. This indicates that crystallization nucleation of different zeolite phases can occur already during the heating period, and later in the process of crystallization can continue to grow, although the final conditions have been achieved to correspond to crystallization of the targeted zeolite form.

Finally, heating of the suspension for 60 min resulted in a very satisfactory quality of the zeolite 13X product in the given process conditions and can be taken as the optimal value of this parameter in the tested crystallization system.

The presented study demonstrates the importance of considering the reaction preparatory conditions in zeolite 13X synthesis such as the heating rate of the reaction mixture, which is particularly important for specific industrial applications.

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Uticaj brzine zagrejavanja suspenzije na osobine zeolita 13X

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(Naučni rad)

Izvod

Poznato je da temperatura kristalizacije tokom sinteze zeolita predstavlja jedan od najznačajnijih procesnih parametara. Međutim, tokom istraživačkog rada na sintezi zeolita 13X i uvođenju ovog materijala u redovnu industrijsku proizvodnju, primećeno je da i brzina zagrejavanja polazne reakcione smeše može da ima jednako bitan uticaj. Ovaj uticaj može biti do te mere izražen, da razlika od samo nekoliko minuta u postizanju temperature kristalizacije može da napravi značajnu razliku u kvalitetu proizvoda ili utiče na prisustvo drugih faza u kristalu, odnosno čak da odredi i pravac kristalizacije zeolita. Stoga, cilj ovog rada bio je da se prikaže uticaj brzine zagrejavanja na kvalitet dobijenih prahova zeolita 13X. Dobijeni uzorci analizirani su u pogledu kristaličnosti, hemijskog sastava, granulometrije i specifične površine, te su određivani kapaciteti adsorpcije vode i CO_2. Dodatno, snimci uzoraka pomoću skenirajuće elektronske mikroskopije prikazali su i morfološke karakteristike različitih prahova zeolita 13X. Rezultati analiza dobijenih prahova potvrdili su uticaj brzine zagrejavanja i pomogli da se definišu optimalni parametri sinteze koji su rezultovali stabilnim kvalitetom proizvoda zeolita 13X..

Ključne reči: Brzina zagrejavanja, LTA, sinteza, suspenzija, 13X