

ATMOSPHERIC PRESSURE SYNTHESIS ROUTE FOR UTILIZATION OF MUNICIPAL AND AGRICULTURE WASTES INTO A USEFUL ZEOLITIC PRODUCT

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Key words: rice husk, aluminum scrap, zeolite NaA, waste utilization, hydrothermal method, “atmospheric pressure” method

Abstract: A new energetically efficient method is proposed for utilization of two wastes, rice husk (RH) and aluminum scrap into a useful zeolitic product – zeolite NaA. The method possesses two main advantages over the conventional hydrothermal route for zeolite synthesis. Firstly, all synthesis procedures as the preparation of the initial Si and Al containing hydrogels as well as the nucleation, growth and ageing of zeolite NaA crystals are carried out under atmospheric pressure. In this way, the energetically unfavorable hydrothermal treatment is avoided. Secondly, the Si containing hydrogel is prepared without preliminary burning of the RH employing instead direct extraction of Si from this waste product. As shown, practically complete dissolution of Si from the RH can be achieved by its alkali treatment (with 10 wt.% NaOH for 7 h) at boiling temperature and atmospheric pressure. The initial wastes and the zeolitization products are characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and X-ray diffraction (XRD). Besides, the kinetics of zeolitization is followed to determine the optimal treatment times needed for synthesis of NaA zeolite crystals possessing high purity and perfect morphology simultaneously achieving possibly high yield. The results of “atmospheric pressure” method in respect to the quality and yield of the zeolite product are compared with those obtained employing the conventional hydrothermal synthesis path.

ОПОЛЗОТВОРЯВАНЕ НА ЗЕМЕДЕЛСКИ И ГРАДСКИ ОТПАДЪЦИ ДО ПОЛЕЗЕН ЗЕОЛИТЕН ПРОДУКТ ПОСРЕДСТВОМ СИНТЕЗ ПРИ АТМОСФЕРНО НАЛЯГАНЕ

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Ключови думи: оризови люспи, алуминиеви опаковки, зеолит NaA, оползотворяване на отпадъци, хидротермален метод, метод при атмосферно налягане

Резюме: Предложен е нов енергетично ефективен метод за оползотворяване на два отпадни продукта, оризови люспи (RH) и алуминиеви опаковки, до полезен зеолитен продукт – зеолит NaA. Методът има две основни предимства пред конвенционалния хидротермален способ за зеолитен синтез. Първо, всички синтезни процедури като изготвяне на съдържащите Si и Al хидрогелове, както и зародишообразуването, растежът и стареенето на зеолитните NaA кристали се провеждат при атмосферно налягане. По този начин се избягва енергетично неблагоприятната хидротермална преработка. Второ, хидрогелът, съдържащ Si, се приготвя без обичайното предварително изгаряне на RH, а Si се извлича директно от този отпаден продукт. Както е показано, практически пълно извличане на Si от RH може да се постигне чрез алкално третиране (с 10 wt.% NaOH за 7 часа) при температура на кипене и атмосферно налягане. Използваните отпадъци и зеолитните продукти са характеризирани с помощта на сканираща електронна микроскопия (SEM), рентгенов енерго-дисперсионен анализ (EDX) и рентгенова дифракция (XRD). Освен това е проследена кинетиката на зеолитизация, за да се определи оптималното време на третиране, необходимо за синтез на NaA зеолитни кристали, притежаващи висока чистота и перфектна морфология, постигайки

същевременно възможно най-висок добив. Направено е сравнение между двата метода на синтез по отношение на качеството и добива на зеолитния продукт.

Introduction

Rice husk (RH) is one of the major agricultural wastes with annual world production of about 120-130 million tons [1-3]. That is why the ecological problems connected with the rice husk disposal as well as with the possibilities for utilization of this high tonnage by-product are object of intensive investigations (see for e.g. [4-8]). Due to its high silica content (about 9 wt.%), the rice husk (RH) should not be considered as a waste but as a raw material, e.g. for the cement, ceramic, steel and construction industries [2,4,7]. Moreover, since silica exists in the rice husk in the form of nanoparticles [9], this waste is suitable for low cost production of nanosilicate structures which can find application as adsorbents [10,11], for effective gene delivery [9] or in the high performance Li-ion batteries [3,9]. Another possibility for the RH utilization is to use this by-product as a source of Si for synthesis of zeolites [12-16]. Usually, high quality zeolites are produced under hydrothermal conditions [1,17-21]. However, this way of synthesis is energetically inefficient and it is connected with the usage of autoclaves, i.e. of expensive and complex equipments. Moreover, in the conventional methods, the Si containing gel is prepared not by direct extraction from the rice husk but by alkali treatment of rice husk ash (RHA). This requires preliminary burning of the husk, which is also an energetically ineffective process. That is why the aim of the present study is to develop a method for zeolite production at atmospheric pressure and direct extraction of Si from rice husk. Moreover, this route of synthesis will be environmentally more friendly since it avoids the preliminary rice husk burning causing substantial atmospheric pollution. As shown further, the atmospheric pressure method enables the synthesis of a valuable zeolite product - zeolite NaA ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 20\text{H}_2\text{O}$) simultaneously achieving high quality and yield. Zeolite NaA discovered by Milton in the middle of the 20-th century [22] is presently the most commercially important zeolite. It finds application as a water softening component in laundry detergents, in different (waste)water treatment and purification procedures and its annual consumption amounts more than one million tons [23]. Moreover, environmental risk assessments of zeolite NaA have established that its use in detergent products does not pose a risk for any of the environmental compartments, i.e. water, sediment, soil and sewage treatment plant [24]. That is why the development of methods for its possibly low cost production is of enormous practical interest.

Materials

Two waste products, rice husk and aluminum cans, were used as sources of Si and Al, respectively. The rice husk (sort "Halil B") was supplied by "Rice company" Ltd., Stara Zagora, while the waste aluminum cans were taken from the system for separate municipal solid waste collection in Sofia. The cans were cut off, their printed decoration was removed by putting in 50 % H_2SO_4 , and after that they were washed and dried. Technical grade NaOH and distilled water were used to prepare 10% NaOH solution needed for the alkali treatment of the rice husk and the Al scrap. Rice husk ash was also used for preparation of Si containing gel in order to resemble the conventional hydrothermal methods for synthesis of zeolite NaA. For this purpose, rice husk was burnt in an electrical muffle furnace at 800°C for 2 h. This regime was chosen to obtain rice husk ash containing highly reactive amorphous SiO_2 [25]. Under these conditions, it was found that 6 g rice husk yielded 1 g rice husk ash containing about 92.1 wt.% SiO_2 [26]. The ash also contains traces of other components such as K_2O , CaO, MgO, and MnO. Besides, the rice husk ash analysis confirmed the complete burning of carbon.

Synthesis procedures

For preparing the Si containing gel, 6 g RH was mixed with 60 ml 10 wt.% NaOH and heated 7 h at 105°C under continuous intensive stirring in a vapor refluxing system. The Si-gel thus obtained was filtered through a cellulose filter and the indissoluble precipitate was washed by 100 ml hot water, dried and weighted. The Al containing gel was obtained by treating 1 g Al scrap with 60 ml 10% NaOH for 12 h at room temperature and without stirring. After that the Si and Al gels were mixed at room temperature and the gel mixture was heated for 5 h at 85°C in a reflux system under atmospheric pressure. The preparations of the Si – Al gel mixture, and the following heat treatment were carried out under regime of intensive stirring. All these procedures (similar to those used in [26]) are schematically presented on Fig.1. After completing the heating, the gel mixture was left for further 19 h aging at room temperature without stirring.

For comparison, zeolite NaA was also synthesized using Si containing gel prepared under hydrothermal conditions from rice husk ash. For this aim, 1 g rice husk ash obtained by combustion of

6 g rice husk was treated with 60 ml 10% NaOH in a Teflon-lined stainless steel autoclave at 145°C for 7h under autogenous pressure without stirring. The obtained gel was also filtered and the separated indissoluble precipitate was dried and weighted. The Si-gel prepared in this way was further used for synthesis of zeolite NaA repeating the same steps as in the case of “atmospheric pressure” method (see Fig.1).

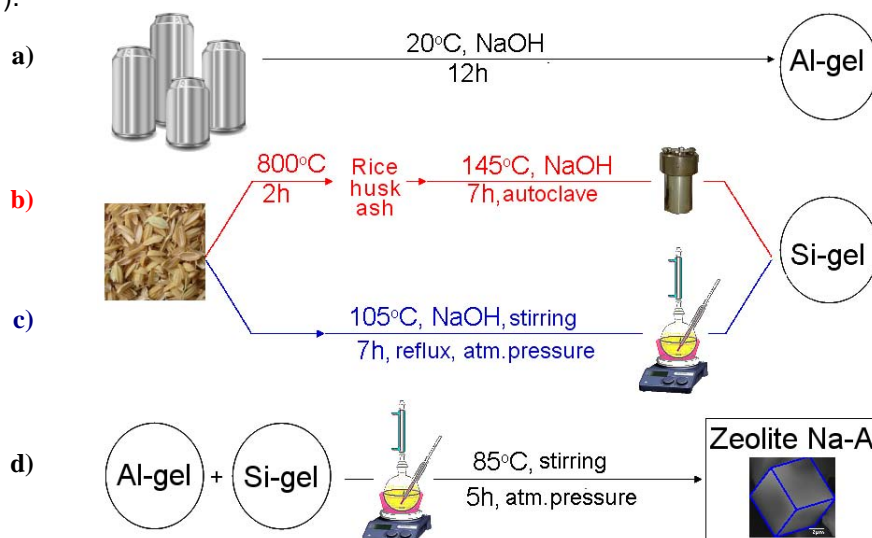


Fig. 1. Schematic illustration of the hydrothermal and “atmospheric pressure” methods for synthesis of zeolite NaA. (a) Preparation of the Al gel. (b) and (c): The two ways for preparing the Si gel under hydrothermal conditions and at the atmospheric pressure, respectively. (d) Heat treatment regime used in both synthesis methods.

Methods for analysis

For characterization of the reaction products, small aliquots from the reacting suspensions were taken during all synthesis stages. Before examination, every suspension probe was filtered, washed up to neutral pH, dried and weighted.

Morphology and elemental composition of initial materials, intermediate and final products were investigated by scanning electron microscope (JEOL JSM6390) equipped with energy-dispersive X-ray (EDX) analyzer (Oxford Instruments). Average sample composition was determined employing the so-called “integral spectra” taken at low magnification. Moreover, the particle size distribution of the zeolite NaA crystallites was investigated during different synthesis stages using SEM micrographs. For this purpose, the size of about 300 individual particles was determined for every sample.

Phase identification of the reaction products was performed by powder X-ray diffraction. Powdered samples with equal masses and identical sample holders were used in all measurements. X-ray diffraction data were collected by Philips PW 1050 automatic diffractometer, using $\text{CuK}\alpha$ filtered radiation and Bragg-Brentano geometry in 2θ interval from 5 to 85 degrees.

The mass (in g) of the dry zeolitic product, obtained from 6 g RH was used as a measure for the synthesis yield. This way of yield definition was introduced accounting for that all synthesis procedures were carried out with one and same quantity of 6 g rice husk or with the ash (approximately 1g) obtained after its burning.

Results and discussion

Table 1 summarizes some important characteristics of the two methods for preparing the Si containing gels: at atmospheric pressure and under hydrothermal conditions. These include the percentage content of the indissoluble precipitates, their SiO_2 content as well as the total amount of SiO_2 remaining in these precipitates. As seen from the table, SiO_2 can be almost fully extracted from the rice husk at atmospheric pressure and what is more important the extraction degree is comparable to that obtained under hydrothermal conditions. The high degree of Si extraction at atmospheric pressure is most probably due to the more intensive mixing resulting from the intensive stirring in the reflux system.

Table 1. Data for the indissoluble precipitates obtained after the alkali treatment of RH and RHA.

Method of Si-gel preparation	Initial material	Content of the precipitate, wt. %	SiO ₂ content in the precipitate, wt. %	Amount of SiO ₂ in the precipitate, g
Atmospheric pressure method	RH, 6 g	30	0.19	0.057
Hydrothermal method	RHA, 1 g	6.8	0.95	0.065

Figure 2 presents the X-ray diffraction patterns of the zeolite samples synthesized by the two methods described. Both diffractograms were recorded with samples obtained after completing the whole synthesis cycle, i.e. after the room temperature ageing. As visible, the diffractograms are very similar and in both samples the presence of zeolite NaA (PDF 00-039-02222) is detected, only.

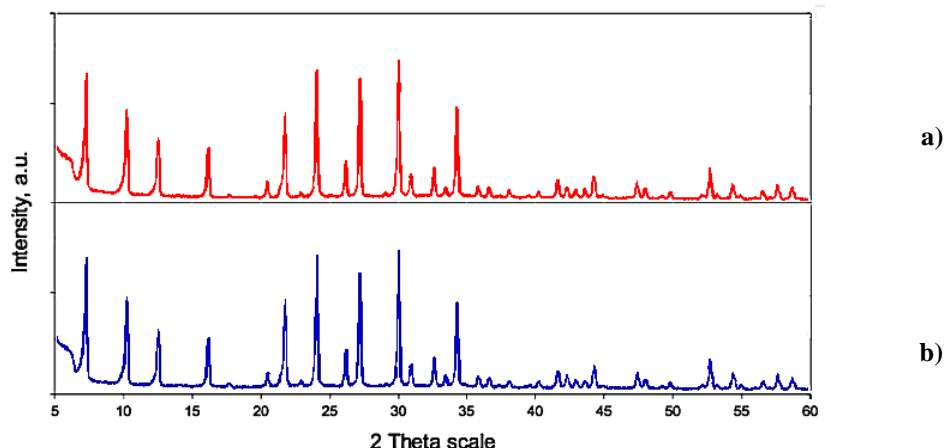


Fig. 2. X-ray diffractograms of two zeolitic samples synthesized by the hydrothermal method (a) and by the atmospheric pressure method (b). For the synthesis conditions used by the two methods see Fig. 1.

SEM micrographs of these two samples, together with the data for the respective yields, are shown on Fig.3. Both samples consist predominantly of crystals with the typical for zeolite NaA cubic morphology. The size distribution histograms of the zeolitic crystals are given under the respective SEM images.

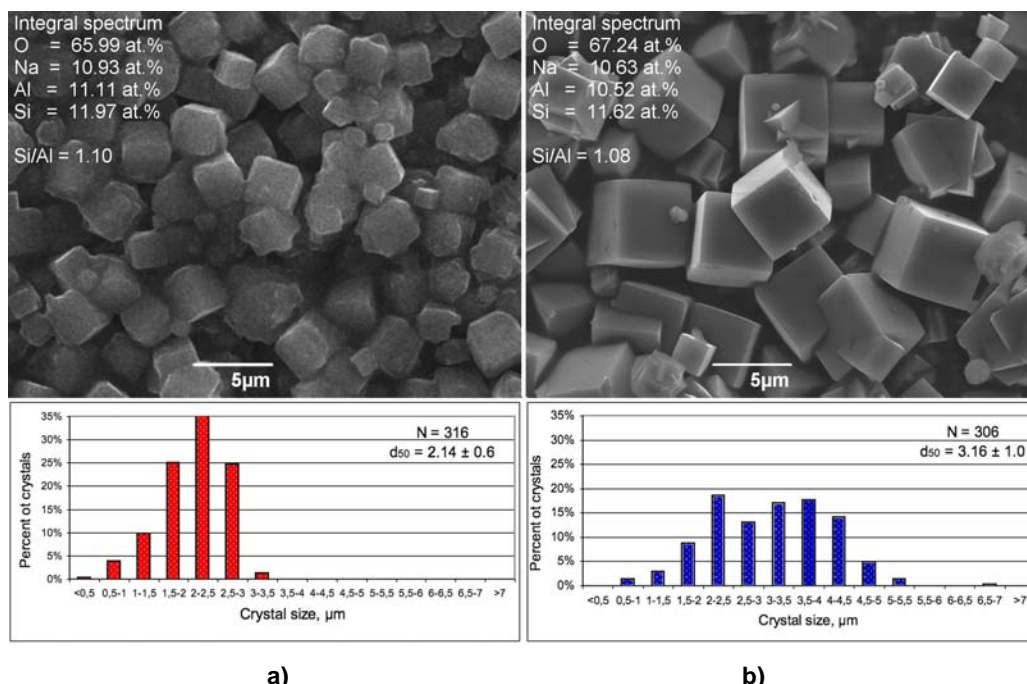


Fig. 3. SEM micrographs of the zeolitic samples synthesized by the hydrothermal (a) and the “atmospheric pressure” (b) methods. The synthesis conditions are the same as for the samples in Fig. 2. The average elemental composition of the zeolitic products are given on the left up corner of the SEM images, while below them the final size distribution of the zeolitic crystals in the respective samples are presented.

The crystals obtained by the “atmospheric pressure” method possess predominantly regular shapes with smooth faces and sharp edges (Fig.3b). In the case of hydrothermal synthesis, the larger part of crystals has not so well developed cubic forms (Fig.3a).

The zeolite crystals obtained by the “atmospheric pressure” method are characterized with broader size distribution and larger mean size ($d_{\text{mean}} \sim 3.16 \mu\text{m}$, Fig.3b) as compared with those obtained under hydrothermal conditions ($d_{\text{mean}} \sim 2.14 \mu\text{m}$, Fig.3a).

The zeolite crystals synthesized by the hydrothermal method, i.e. using rice husk ash as a source of Si, possess yellowish coloring. In contrast, the crystals obtained by the atmospheric pressure method, directly from rice husk, are white which makes them suitable for different detergent applications.

As seen from the data given on Fig.3, the elemental composition of the two zeolitic products differs insignificantly from that of the stoichiometric zeolite NaA ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 20\text{H}_2\text{O}$).

Another important advantage of the “atmospheric pressure” method is that the yield is substantially higher than that under hydrothermal conditions from RHA (4.06 g compared to 2.63 g, respectively).

Accounting for the advantages of the “atmospheric pressure” method, we thoroughly investigated the evolution of morphology, yield and size distribution with the time of alkali treatment.

On the next figure (Fig.4), a series of SEM micrographs are presented taken at different stages of the “atmospheric pressure” synthesis. Up to about 60 minutes from the beginning of the synthesis amorphous precipitates are visible only, and they disappear after 210 min. The first zeolite crystals can be detected after about 80 minutes. As seen, these crystals are initially not well faceted, while with the progress of time they grow and their shape becomes more and more perfect.

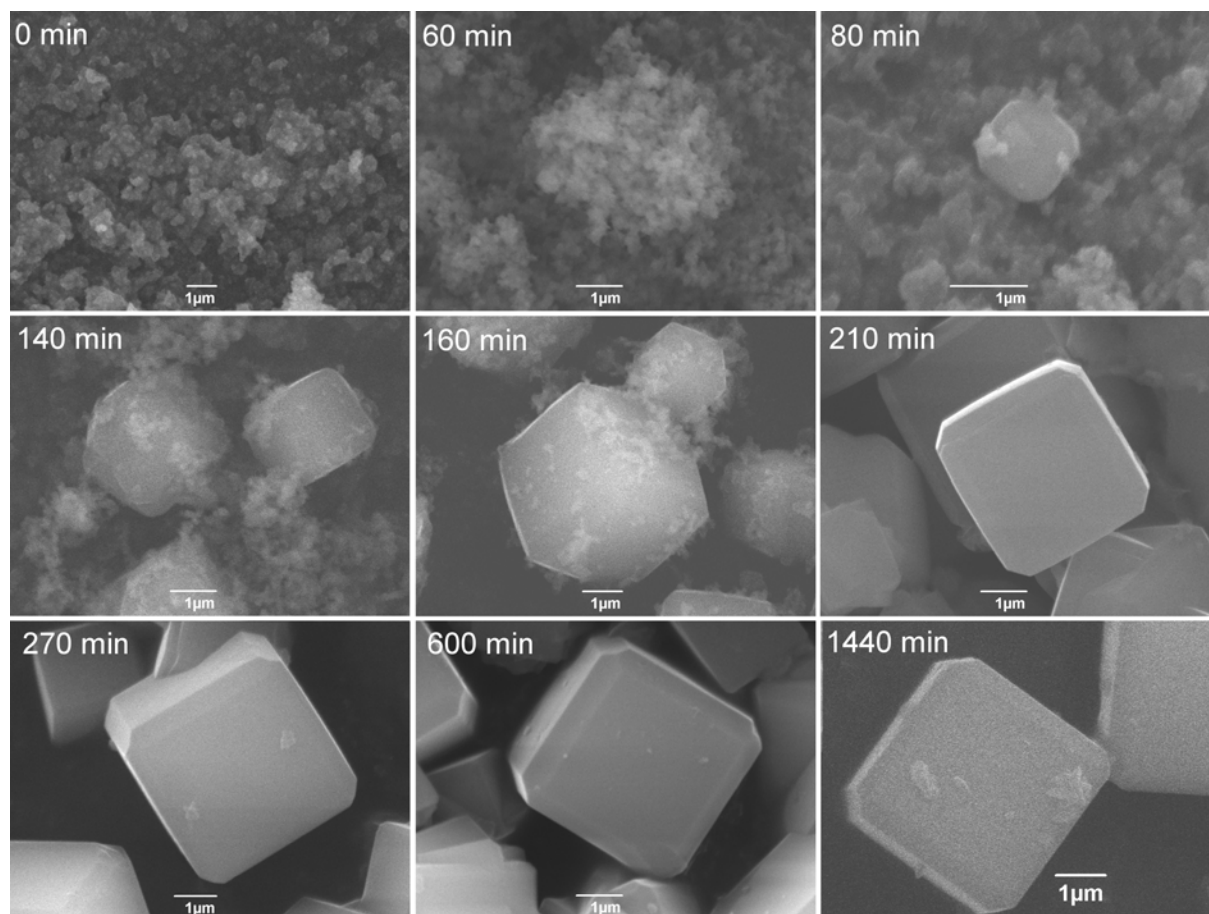


Fig. 4. SEM images of zeolitic samples obtained after different times of alkali treatment by the atmospheric pressure method. The treatment time is given in the left upper corner of each micrograph.

The respective size distributions of the above zeolite crystals are shown on Fig.5. As seen, the initial narrow and similar to “delta” type distribution becomes broader with the treatment time.

On the next figures (Fig.6), the maximum crystal size, D_{max} , is presented in coordinates $D_{max}^3(t)$ vs t , t being the time of alkali treatment. The time dependence of the yield Y was also investigated and the results are shown on Fig.7.

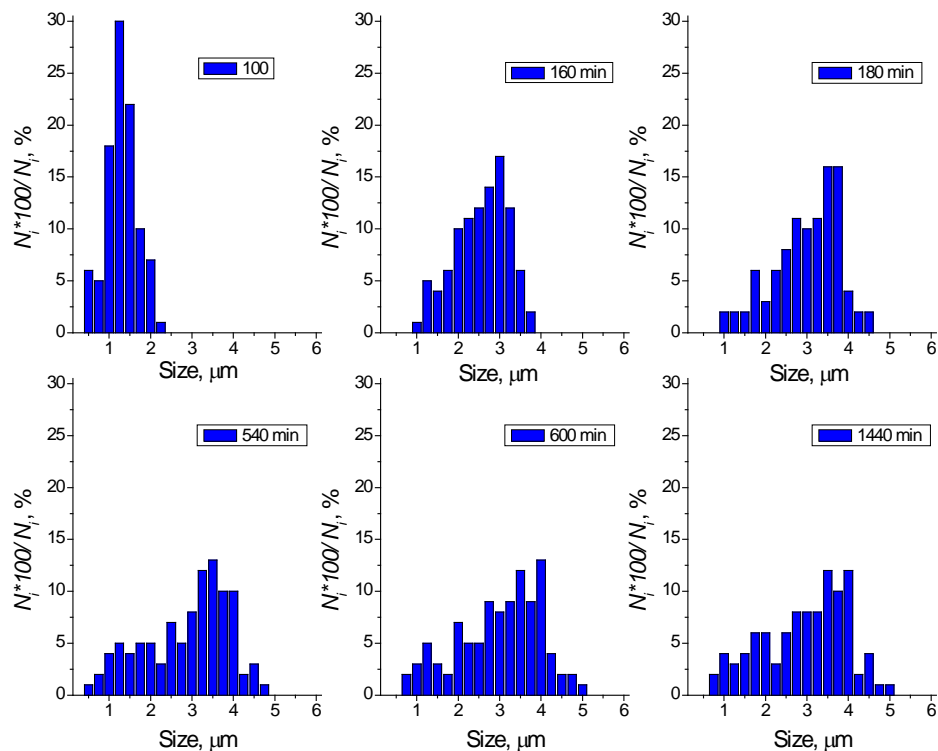


Fig. 5. The evolution of size distribution of NaA zeolite crystals with the time of alkali treatment. The respective treatment time is given in the right upper corner of each histogram. Here, N_i and the ratio $N_i*100/\sum N_i$ denote the number of crystals of a given size and their relative content in %, respectively.

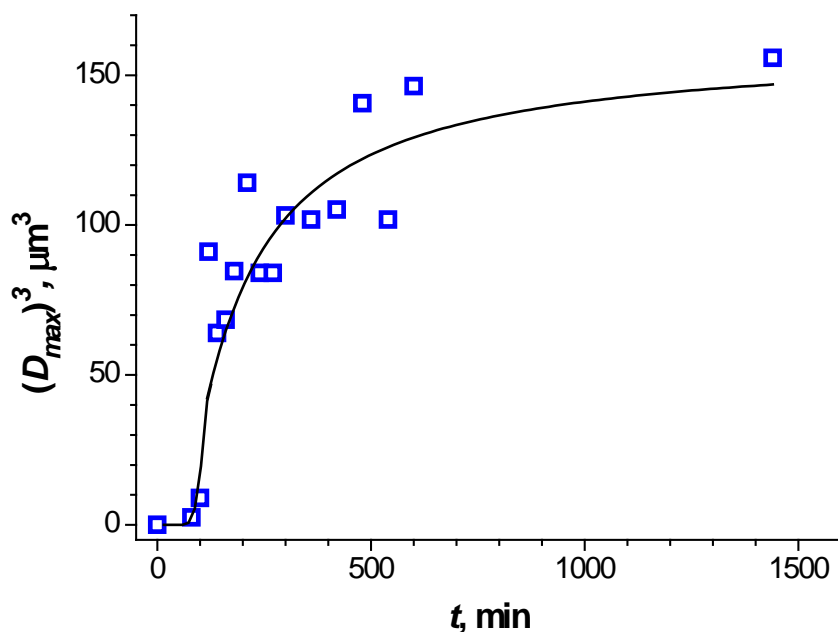


Fig. 6. The maximum size D_{max} of zeolite NaA crystallites in coordinates D_{max}^3 vs. the time t of alkali treatment.

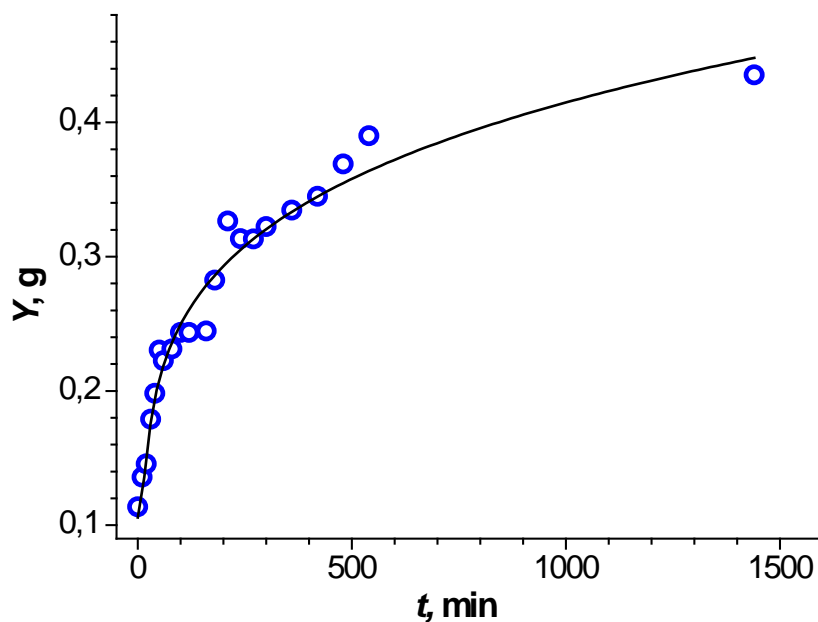


Fig. 7. The yield Y of zeolite NaA crystals synthesized by the “atmospheric pressure” method vs. the time t of alkali treatment.

As seen from Figs. 6 and 7, the $D_{max}^3(t)$ - and $Y(t)$ - dependences have a similar course. During the first 400 minutes of alkali treatment, both curves steeply rise. After that, $D_{max}^3(t)$ as well as $Y(t)$ begin to increase more slowly. Nevertheless, the growth rate of both quantities remains high enough as to insure about 24% higher yield and also about 22% larger in size crystals after finishing the aging. The above results, i.e. that the yield and size of zeolite crystals substantially increase during the ageing are very important from practical point of view accounting for that this synthesis stage is taking place at room temperature and without stirring, i.e. without additional energy consumption.

Conclusions

A new energetically efficient and environmentally friendly method for synthesis of high quality zeolite NaA is proposed using as sources of Si and Al two waste products - rice husk and aluminum scrap. The results of present investigation show that zeolite NaA can successfully be synthesized using Si containing gel prepared by direct alkali treatment of rice husk at atmospheric pressure. This way of Si-gel preparation ensures almost full extraction of Si from the rice husk simultaneously avoiding the ecologically unfriendly husk burning traditionally applied in the conventional methods of zeolite synthesis. Moreover, the degree of Si extraction at atmospheric pressure is comparable to that obtained under hydrothermal conditions. This effect is explained by the more intensive mass and heat exchange in the reflux system. It is of decisive importance for the further development of our “atmospheric pressure” method for synthesis of zeolite NaA. Besides, the zeolite crystals synthesized at substantially milder conditions of the “atmospheric pressure” method, i.e. at substantially lower energy consumption are characterized by perfect morphology, larger mean size and substantially higher yield as compared with the zeolite product of the high energy consuming hydrothermal route. Due to their high purity these white colored zeolite crystals synthesized at atmospheric pressure could be used not only as detergents, but also to find many other applications, e.g. in medicine, biology, etc.

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