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Synthesis of zeolites NaA and analcime using rice husk ash as silica source without using organic template

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Abstract Silica was extracted from Fajr rice husk ash (RHA) with approximately 97% purity, converted to sodium and potassium silicate solutions and used as silica source for the synthesis of NaA and analcime zeolites. NaOH and KOH without organic templates were used in the synthesis of NaA and analcime zeolite, respectively. Conventional heating and microwave-assisted hydrothermal were used in zeolite synthesis. Zeolites were characterized with XRD, SEM and IR spectroscopy. Heating time and Si/Al ratio were optimized for the synthesis of zeolites.

Introduction

Rice husk ash (RHA) is a solid waste product from the power generating industry which is suitable for recycling. The silica in rice husk is amorphous and transforms to crystalline silica when it is heated at high temperatures [1]. The burning of rice husk in air results in the formation of RHA with a content in SiO_2 that varies from 85% to 98% depending on the burning conditions, the furnace type, the rice variety, the rice husk moisture content, the climate and the geographic area [2]. Therefore, industrial waste RHA is a potentially attractive source for the large scale production of aluminosilicate zeolites.

Synthesis of NaA and analcime zeolites has been reported in several papers and patents [3–5]. Commercial zeolites are produced from commercial silica sources in the form of sol gels and amorphous fumed silica. Yusof et al. [6] synthesized the faujasite-type of zeolites (NaX and NaY) and NaA-type of zeolite from RHA with high purity and absence of impurities via the hydrothermal conditions. They produced more than 90% amorphous silica from RHA. Also, Wittayakun et al. [7] used effectively Rice husk silica (RHS) as a silica source for the synthesis of zeolite Y in sodium form. However, waste material with high silica content such as RHA and fly ash are potential silica sources for zeolite synthesis. Zeolite crystallizes normally during heating of aluminosilicate solution. There is the conventional hydrothermal method as a batch or in oven operations in the synthesis of zeolites. Several reports about synthesis of zeolite using the other sources of heating such as microwave heating have been presented [8, 9]. The use of microwave irradiation in the synthesis of zeolite offers advantages over the conventional synthesis including: short crystallization time, fast dissolution of precipitated gels, uniform heating [10], more reproducible and more accurate. Since the discovery of the zeolite, a lot of research have been carried out to improve the synthetic methods and the quality of the products as well as to reduce the cost of production and the time of crystallization [11, 12].

Previous studies have shown that it was possible to use crystalline ash to produce pure zeolite NaA, KA [6, 13] and ZSM-5 [14–16] using organic template. In this study, both RHA and extracted silica from RHA with high purity were applied for synthesis of zeolites NaA and analcime without organic template. Attempt was made to use RHA produced the uncontrolled burning of the rice husk as a biological source of silicate in the synthesis of zeolites. The other aim was the optimization of heating time, Si/Al ratio and the effect of microwave irradiation in the synthesis and crystallinity of zeolites. The crystallinity of the synthesized zeolites was investigated using X-ray diffraction spectroscopy. The morphology and size of the prepared zeolites in

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this investigation was examined by scanning electron microscopy.

Experimental

Preparation of silica from rice husk

Fajr Rice Husk (RH) was collected from the area in the north of Iran (Babolsar, Mazandaran). The rice husk was washed with water and dried at 105 °C for 24 h to eliminate undesirable compounds or substances in rice husk sample prior burning it. RHA was prepared from the burning of RH in furnace at 600 °C. The obtained RHA was analyzed with XRF to determine concentration of components. Then Kalapathy et al. method [17] was used for extraction of silica from RHA. RHS and RHA were used as silica source for the synthesis of NaA and analcime zeolites. The synthesis of zeolites normally involves the formation of aluminosilicate gel. Successful synthesis depends strongly on the gel microstructure, which is determined by the reaction of soluble silicate and aluminate anions [18]. The following steps were used for preparation of zeolite.

Preparation of silicate and aluminate solution

Aqueous silicate solution was prepared in a plastic bottle by dissolving an appropriate quantity of RHS or RH in 2 M NaOH or KOH solutions. The dissolution of the silica was very slow at room temperature, so it was assisted by heating the sample in an oven at 70 °C for 1 week and then was filtered.

Aqueous aluminate solutions were made by dissolving suitable amounts of sodium aluminate, $NaAlO_2$ (61.3 wt% of Al_2O_3. Fisons plc), in doubly distilled water.

Aluminosilicate solutions or gels

Aluminosilicate solutions or sol gels were then obtained by mixing the freshly prepared sodium aluminate and aged alkali silicate solutions in the correct proportions for our investigations. After mixing, the solutions or sol gels were usually allowed to equilibrate for 2 days at room temperature (25 °C). The solutions were made with the initial composition of $2SiO_2$:Al_2O_3:2NaOH and $2SiO_2$:Al_2O_3:2KOH for the synthesis NaA and analcime zeolite, respectively.

Zeolitization and analysis

Crystallization of zeolite was carried out by the two methods: (1) conventional hydrothermal method and (2) microwave-assisted method, i.e. 2 h irradiation with a kitchen microwave (Panasonic NN-K543WF 1000 W) and then heating with hydrothermal method. In due to the later method, the resulting gel or solution of aluminosilicate was placed in a Teflon vessel inside the stainless steel reactor and heated in air oven at different desired temperatures after irradiation with microwave for 2 h (which is an optimum time obtained in our investigation). At the end of this period, the reactor was cooled at room temperature to stop the crystallization. The product was removed, filtered and washed with distilled water before drying at 105 °C overnight. The procedure was repeated by changing the molar ratio of Si/Al in the range of 1–50.

Apparatus

The zeolite samples and the extracted silica were evaluated by XRD spectrometry (GBC MMA). It was scanned for 2θ ranging from 5° to 60° with CuKα radiation and an acceleration voltage of 35.4 kV and current of 45 mA at a rate of 5°/min. Supplementary information concerning the structure of the prepared zeolites was obtained by further research using IR spectroscopy and the crystallinity was calculated. The percentage of crystallinity of each synthesized zeolite was calculated from the XRD patterns by using Eq. 1:

$$\text{Crystallinity}\ \% = ([I_{\text{cx}} - I_{\text{a}}]/[I_{\text{c100}} - I_{\text{a}}]) \times 100 \qquad (1)$$

where I_{c100} is the intensity for fully crystallized zeolite at 2θ 27° and I_{a} is the intensity when we have completely amorphous nature at 2θ 26.65° and I_{cx} is the intensity of each desired sample at 2θ 27°.

Supplementary information concerning the structure of the prepared zeolites was obtained by further research using IR spectroscopy. IR spectra of the samples were recorded on a Bruker-Vector 22, in the range between 400 and 4000 cm^{-1}. For this purpose, approximately 15 mg of the zeolite and 1 g of KBr were mixed, milled and grounded until a fine smooth powder was obtained.

A Philips PW2404 XRF Wavelength Dispersive Spectrometer equipped with an array of six analyzing crystals and fitted with a Rh X-ray tube target was used. A vacuum was used as the medium of analyses to avoid interaction of X-rays with air particles. Approximately 1 g of the sample was heated for 5 h at 110 °C. It was again weighed after heating to determine any adhesive water present. The sample was then heated for 5 h at 1000 °C with 1.5 gr of Norrish spectoflux.

Moreover, a JEOL-JXA-840 Scanning Electron Micro analyzer was used to take the micrographs of the samples. Samples were mounted on aluminium stubs and were then coated with a thin layer of silver.

Results

The chemical composition of RHA obtained from Fajr rice husk in the form of oxides using XRF are shown in Table 1.

The cation effect on synthesis of zeolite was examined by NaOH and KOH. Figure 1 shows the XRD pattern of NaA and analcime synthesized using NaOH and KOH with RHA silica, respectively.

To support the XRD analysis, the infrared (IR) spectroscopy was used. The FT-IR spectra of NaA and analcime were shown in Fig. 2 in the range of 400–4000 cm^{-1}.

To investigate the effect of temperature on zeolite crystallization, the heating time was fixed at 16 h after 2 h microwave treatment and the temperature was changed from 120 to 180 °C, at a 10 °C intervals. Figure 3 shows the effect of temperature on the crystallization of NaA and analcime zeolites, respectively.

The SEM micrograph of NaA and analcime synthesized from RHS at optimum conditions are displayed in Figs. 4 and 5, respectively.

As well known the SiO_2/Al_2O_3 ratio is very important in the synthesis of zeolite. In order to obtain optimum of this ratio, the effect of Si/Al ratio (in the range of 1–50) on the crystallinity of zeolite NaA was investigated and shown in Fig. 6.

The effect of heating method in synthesis of zeolite NaA was also tested by XRD and SEM (Figs. 7, 8). One of the advantages of microwave following hydrothermal method is fast preparation of zeolite or decreasing the zeolite precipitation time. Figure 7 shows the plots of percent of crystallinity against time of heating for the synthesized zeolites using both the improved and the conventional hydrothermal methods as discussed in details in the "Experimental" section.

Discussion

Table 1 shows that the major component of RHA was SiO_2 along with small amounts of Al_2O_3, Fe_2O_3, CaO, Na_2O, K_2O, MnO, TiO_2, MgO and P_2O_5. It has been found that sample of the Fajr rice husk contains higher concentration of silica in comparison to the other variety of rice samples in north of Iran (e.g. Hashemi and Benam with 94% and 94.6% SiO_2, respectively) and the direct synthesis of NaA zeolite from RH gives lower yield of NaA with respect to the RHA or RHS as silica source. Therefore, the extracted silica from Fajr RHA was used for the synthesis of zeolite in the present work.

The X-ray diffraction analysis indicates that the synthesized zeolites with different cations have different

Table 1 Percentage of chemical composition of Fajr RHA determined by XRF

SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MnO	TiO_2	MgO	P_2O_5	LOI[a]
96.08	0.21	0.14	0.24	0.20	0.51	0.16	0.01	0.48	0.33	1.64

[a] Loss of ignition

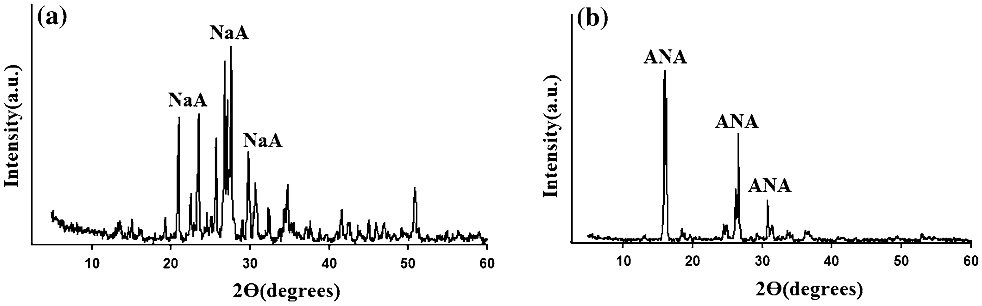

Fig. 1 The effect of cation Na^+ (**a**) and K^+ (**b**) on the synthesis of zeolite with composition of $2SiO_2:Al_2O_3:2(NaOH/KOH)$

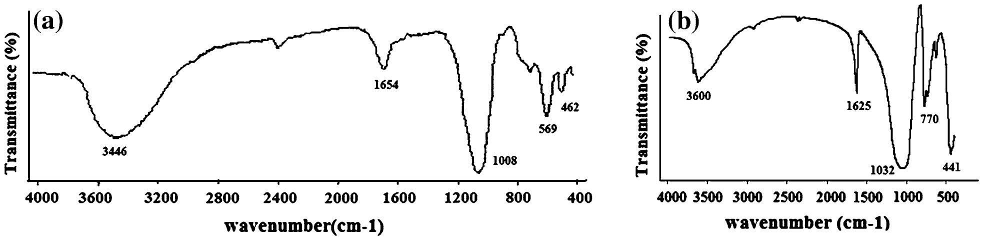

Fig. 2 FT-IR spectrum of **a** NaA and **b** analcime zeolite

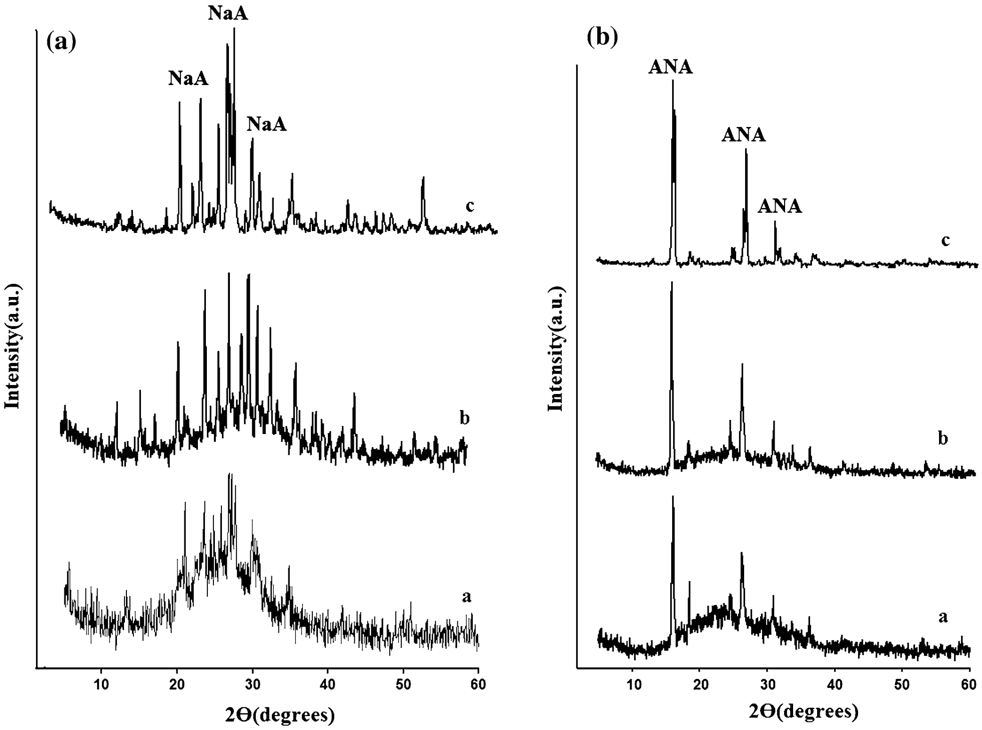

Fig. 3 XRD pattern of **a** NaA, using NaOH and **b** analcime, using KOH crystallized at different temperatures: (*a*) 120, (*b*) 150 and (*c*) 180 °C at the heating time 18 h (2 h microwave irradiation and 16 h hydrothermal)

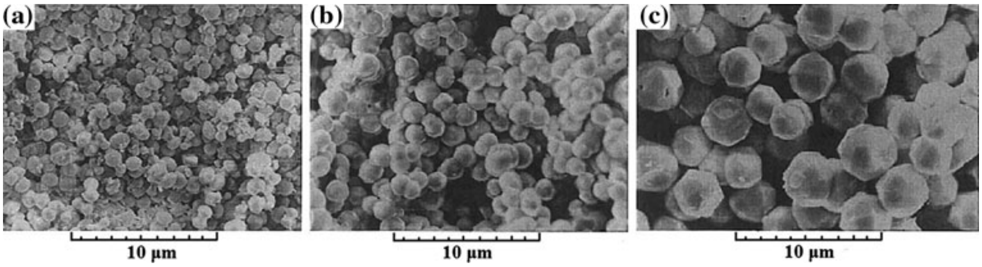

Fig. 4 SEM images of synthesized NaA in different temperatures **a** 120, **b** 150 and **c** 180 °C

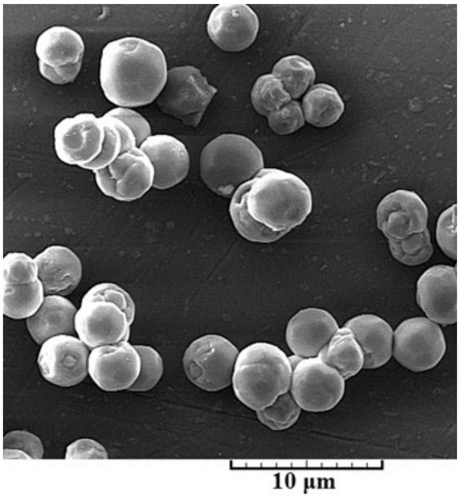

Fig. 5 SEM image of analcime prepared from initial composition [$2SiO_2$:Al_2O3:2KOH] at the heating time 18 h (2 h microwave irradiation and 16 h hydrothermal)

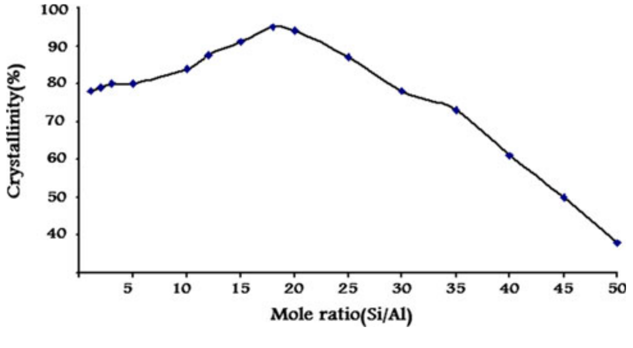

Fig. 6 Plot of the effect of different Si/Al ratio on crystallinity of NaA

crystalline structure at the similar temperature, concentration and conditions (see Fig. 1). On the other hand, when using NaOH, the X-ray diffraction shows sharp peaks at 2θ 21° and 27° due to NaA. In comparison to that under using KOH, peaks at 2θ 17° and 26° reveals analcime zeolite.

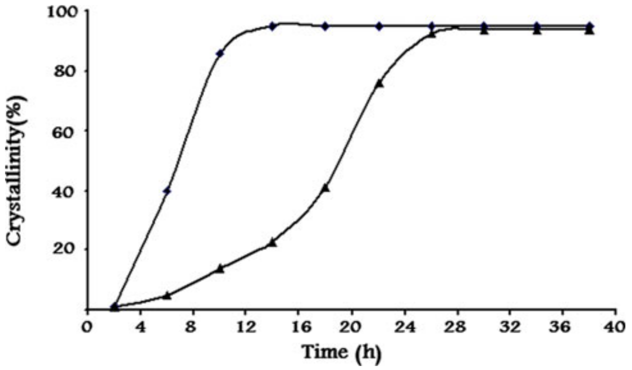

Fig. 7 Plots of crystallinity % against heating time in synthesis of NaA zeolite using conventional heating (*filled triangle*) and an improved method (2 h microwave irradiation continued by hydrothermal) (*filled square*)

Therefore, it could be concluded that the type of zeolite crystallized from aluminosilicate hydrogel depends on the type of cations which are present in solution (template directing rule).

All the characteristic reference IR bands of the zeolite NaA are observed for the synthesized NaA (Fig. 2) as well as for the analcime. The reference IR wavenumbers were given as 1003, 664, 557 and 466 cm^{-1} for NaA and 449, 740, 1026, 1639, 3620 for the analcime [19]. The broad band at about 3440 cm^{-1} and band at about 1650 cm^{-1} are attributed to zeolitic water, the bands at about 452 cm^{-1} is due to internal vibrations of (Si, Al)O$_4$ tetrahedral of NaA and analcime, whereas the band at about 1008 cm^{-1} is due to unsymmetrical vibrations related between tetrahedra. Generally, the absorption bands within the range 420–500 cm^{-1} are related to the T–O–T bending of vibration mode (T = Al, Si) and within the range 950–1250 are related to the T–O–T stretching vibration mode. It can be observed that the infrared data of zeolites synthesized from RHA were quite identical with the references and proved the successful conversion of RHA to zeolites NaA and analcime. In addition, there are no impurities or other phases in the products since no other peaks emerge in the infrared spectra of each synthesized zeolites.

The results of XRD and SEM show that a total heating temperature of 180 °C is needed for obtaining pure crystallized NaA and analcime zeolites (Figs. 3, 4). As a result, agglomeration of amorphous material at 120 °C with some characteristic peaks of zeolites is obvious in Fig. 3a-*a*, b-*a*. The broad amorphous XRD peak decreased when the sample mixture was heated at 150 °C. However, a little amount of amorphous material is seen in Fig. 3b at this temperature. It is obvious that the temperature 180 °C is ideal for the crystallization of pure NaA and analcime zeolites. These results demonstrate that temperature strongly influences the formation of zeolite NaA and analcime. It is obvious from Fig. 4a–c that lowering the temperature in synthesis of NaA will produce smaller particle of zeolite. Also, the spherical shapes are observed after 16 h of conventional heating and 2 h of microwave irradiation, shown in Figs. 4 and 5.

The results obtained in optimizing of Si/Al ratio (Fig. 6) reveal that the high and low Si/Al ratios are not suitable for zeolite synthesis (78% and 37% crystallinity, respectively). The maximum of crystallinity was found at the Si/Al mole ratio of 18 after 18 h heating (2 h microwave irradiation and 16 h hydrothermal as an improving method). This molar ratio was used in the most of experiments.

The effect of the heating method in synthesis of zeolite was displayed by XRD and the SEM images (Figs. 7, 8). Figure 7 shows that the improved method leads to maximum crystallinity and is almost twice faster than the conventional method. However, Fig. 8a, b shows that the crystal size of NaA synthesized using improved method was less than one synthesized by conventional heating (3.8 µm in comparison of 10 µm). Therefore, a special crystallite size of zeolite at a reliable time could be synthesized using these two heating methods together.

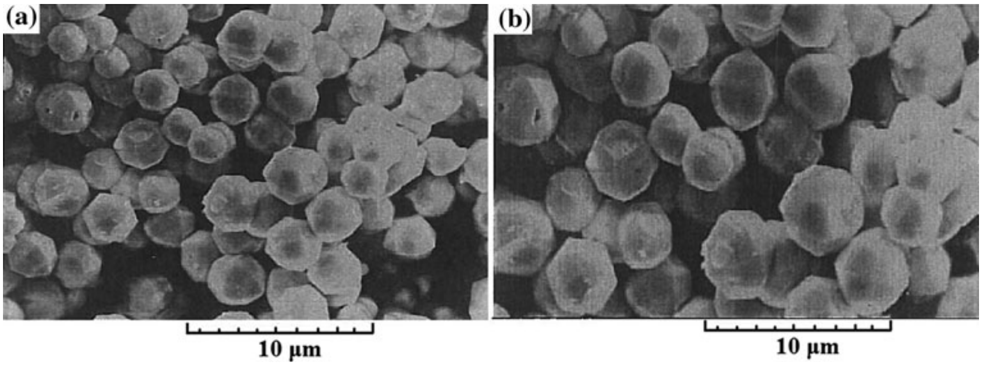

Fig. 8 SEM images of NaA zeolite synthesized with **a** improved and **b** hydrothermal method

Conclusion

The NaA and analcime were successfully synthesized using RHA silica with NaOH and KOH, respectively. The Si/Al molar ratio of 18 is the optimum for successful synthesis of NaA zeolite. Zeolite NaA and analcime can be synthesized by an improved method in a short time (2 h microwave and 16 h hydrothermal) at 180 °C. The heating time, heating temperature and the heating source are important in crystallinity and the size of zeolite. Although the zeolite NaA obtained with the two methods showed the same XRD patterns but the size of particles was changed from 10 to 3.8 μm. The successful synthesis of NaA and analcime using RHA silica without organic template makes our synthesis method attractive for commercial production of NaA and analcime.

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