ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/306888210

The Effect Of Crystallization Time And Temperature On Hydrothermal Synthesis Of Zeolite Nax From Bongawan Kaolin

Article *in* International Journal of Engineering and Technology · August 2016

CITATION
1

READS
2,418

1 author:

Sazmal Effendi Bin Arshad
Universiti Malaysia Sabah (UMS)

34 PUBLICATIONS **238** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project GRAPHENE TIN OXIDE NANOCOMPOSITES View project

Project Ion Exchanged Bentonite Based Zeolite NaX and A View project

All content following this page was uploaded by Sazmal Effendi Bin Arshad on 26 August 2016.

The user has requested enhancement of the downloaded file.

THE EFFECT OF CRYSTALLIZATION TIME AND TEMPERATURE ON HYDROTHERMAL SYNTHESIS OF ZEOLITE NAX FROM BONGAWAN KAOLIN

Johnson, E. B. G., Asik, J., Arshad, S. E.*
Faculty of Science and Natural Resources, University Malaysia Sabah, 88400, Sabah, Malaysia
* sazmal@ums.edu.my

ABSTRACT

Hydrothermally synthesised zeolite NaX was produced by using kaolin procured from Kg. Gading, Bongawan. The kaolin was treated using sodium hexametaphosphate and calcined at 800°C to form metakaolin. Treated kaolin and prepared metakaolin were characterized using X-ray Fluorescence (XRF) and X-ray Diffraction (XRD). Reaction mixture was obtained by mixing metakaolin, sodium hydroxide and sodium silicate. The reaction mixture underwent aging for 15 hours before they were crystallized at various crystallization times (0-48 hours) and temperatures (80–130°C). The effect of crystallization time and temperature was studied using SEM and XRD. Optimum time and temperature for the synthesis was found to be 8 hours at 100 °C, respectively.

Keywords: *Hydrothermal, kaolin, crystallization time, crystallization temperature*

INTRODUCTION

Zeolite is a crystalline aluminosilicate with a three dimensional framework structure that forms a microporous compound which contains uniform sized pores. These pores can absorb molecules that fit into it and leave the bigger molecules making zeolite known as molecular sieves. The framework consists of crystalline silica (SiO_2). At some point in the framework, Al^{3+} replaces Si^{4+} causing the framework to carry a negative charge. The cations that are held inside the cavities of the framework play a role to maintain the electroneutrality of zeolite. These cations are amenable to cation exchange [1]. Other properties that make zeolite widely used as a catalyst, ion-exchanger and adsorbents is its thermal stability, good shape selectivity, strong acidity and high ion exchange capacity [2,3]. The general formula for zeolite is $M_{2/n}O.\ Al_2O_3.ySiO_2.wH_2O$. The value of *y* is 2-200, while *n* is the cation valence and *w* represents the water contained in the intracrystalline channels of zeolite. By sharing oxygen ions, zeolite's framework which consists of four connected framework of AlO_4 and SiO_4 tetrahedra which are joined together. In the framework, each AlO_4 tetrahedron carries a net negative charge which is balanced by an extra framework cation [4].

Kaolin or china clay is very rich in kaolinite mineral. Kaolinite consists of a layer of silicate tetrahedral sheet and a layer of alumina octahedral sheet. These layers are connected by oxygen atoms [5,6]. Thermal treatment (550-900°C) on kaolinite group clay transforms it into metakaolin [7]. The transformation process of kaolin to metakaolin is known as metakaolinization or dehydroxylation [8]. Metakaolin is an amorphous material that contains approximately 40-45% of Al_2O_3 and 50-55% of SiO_2 in weight [9,10]. Previously, there were reports on zeolite synthesized from kaolin [11-18].

There are two reports on the effect of crystallization time and temperature on zeolite NaX synthesis by Chandrasekhar and Pramada [19] and Kovo [20] with different observations. Chandrasekhar and Pramada obtained zeolite NaX at 87$\pm$ 2 °C after 10 hours of crystallization time by synthesizing it in plastic bottles, while Kovo obtained zeolite X at 80–100 °C after 6 hours of crystallization in Teflon autoclave. The difference may be due to their different sources of clay and sample preparations. Nevertheless, Chandrasekhar and Pramada [19] and Kovo [20] used the hydrothermal synthesis technique. Hydrothermal synthesis is a reaction of aqueous solutions that occur in a closed system above room temperature and above the pressure of 1 bar [21,22]. This study discusses the effect of crystallization time and temperature when zeolite is hydrothermally synthesized in teflon bottles.

EXPERIMENTAL DETAILS

Metakaolinization of kaolin

A 10 kg sample of kaolin clay was procured from Kg. Gading, Bongawan, Sabah. The raw clay was treated with sodium hexametaphosphate (>65% w/w P_2O_5, System) before it underwent metakaolinization process at 800 ºC. The chemical composition of the metakaolin was determined by X-ray fluorescence (XRF). The structure of the metakaolin was identified using X-ray diffraction (XRD) technique.

Synthesis of Zeolite NaX

The method to synthesis zeolite NaX was modified from Caballero et al. [23]; Kovo [20]; Zhang et al. [24]. The chemicals used to prepare the reaction mixture did not undergo any purification. Sodium metasilicate (extra pure 7.5% w/w Na_2O, 25.5% w/w SiO_2, 67% w/w, H_2O; Merck) was used as the additional source of silica. 1 M aqueous solution of sodium hydroxide was prepared by mixing 20 g of NaOH pellet (>99% w/w, Merck KGaA) with distilled water. The reaction mixture of zeolite NaX was prepared in a Teflon bottle by adding 1 g of metakaolin into an aqueous solution of sodium hydroxide followed by an addition of sodium metasilicate. In this synthesis, usage of Teflon bottle is to replace the use of Teflon-lined stainless steel autoclave vessel. Throughout this study, the molar ratio of reaction mixture used was 2 NaOH: 0.1 Na_2SiO_3: 0.45 MK: 166 H_2O. The reaction mixture was stirred for 15 hours at room temperature and then crystallized in an oven at 100 ºC. The zeolite NaX samples were then taken out from the oven at: 0, 4, 8, 12, 24 and 48 hours respectively. Another set of zeolite NaX samples was prepared with the same molar ratio then crystallized for 8 hours at the following temperatures: 80 ºC, 90 ºC, 100 ºC, 110 ºC, 120 ºC and 130 ºC. All the finished products from the hydrothermal synthesis were filtered and washed using distilled water. Subsequently, the samples were dried in an oven at 80 ºC overnight. The samples were characterized using XRD and scanning electron microscopy (SEM).

Characterization Technique

XRF analysis was used to determine the chemical composition present in metakaolin performed by Rigaku X-ray Spectrometer model RIX 3000. The powder X-ray diffraction (XRD) pattern was obtained using a Philip Expert Pro X-Ray diffractometer model DY1496 (Cu Kα= 1.54056, 30 mA, 40kV). The data collection was carried out in the 2Θ range of 5º to 70º, with a step size of 0.02º. The SEM images were taken with Scanning Electron Microscopy (EVO MA10 XVP). The specific surface area (BET) and pore diameter of the synthesized zeolite NaX obtained at 100 ºC after 8 hours was determined by nitrogen adsorption-desorption on Micromeritic ASAP 2020 Tristar II 3020 KR, and the pore size distributions were calculated by the advanced Barrett-Joyner-Halenda (BJH) method [25] using the adsorption desorption branches of the isotherms. Prior to these measurements, the sample was degassed up to 200 ºC for 4 hours then analysed up to 300 ºC for 4 to 5 hours. The surface area and pore volume value obtained for zeolite NaX is 17.034 m^2/g and 0.03519 cm^3/g, respectively.

RESULTS AND DISCUSSION

Metakaolinization of Bongawan kaolin

Figure 1 shows the x-ray diffractogram of (a) treated kaolin and (b) metakaolin. The kaolinite peaks disappeared after dehydroxylation at 800 ºC for 5 hours. This indicates that the kaolin had transformed into metakaolin. Dehydroxylation leads to the breakdown of the kaolinite crystal lattice structure which becomes highly disordered and amorphous [26]. Table I indicates the chemical composition present in the metakaolin.

TABLE I. CHEMICAL COMPOSITION OF METAKAOLIN.

Chemical content (% weight)	Metakaolin
MgO	1.7
Al_2O_3	33.2
SiO_2	55.6
K_2O	4.4
TiO_2	0.8
Fe_2O_3	3.7

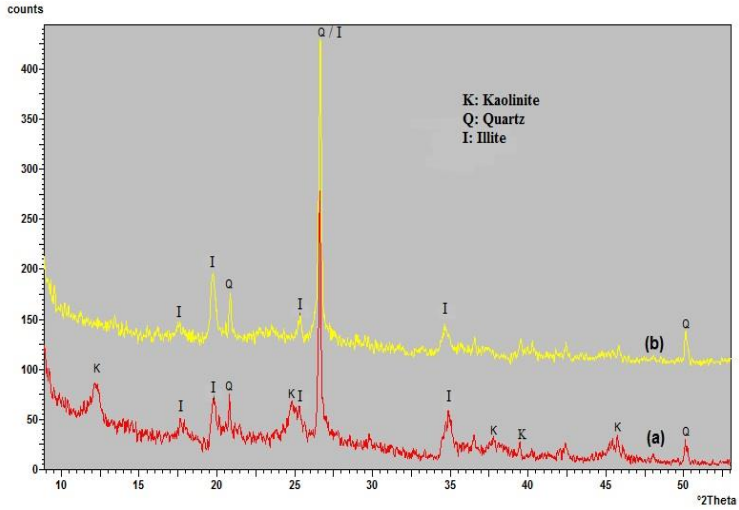

Figure 1. X-ray diffractograms of (a) treated kaolin (b) metakaolin.

Effect of crystallization time

The samples of reaction mixtures were prepared with a molar ratio of 2 NaOH: 0.1 Na_2SiO_3: 0.45 MK: 166 H_2O. All samples underwent aging for 15 hours before being crystallized at 100 °C. Figure 2 shows the X-ray diffractogram of zeolite NaX samples crystallized from 0 to 48 hours. After 4 hours of crystallization time, there was no zeolite NaX peak observed (Figure 2a, b). The only major peaks seen were the illite (19° and 26°) and quartz (21° and 27°) which were also seen in the X-ray diffractogram of treated clay and metakaolin (refer to Figure 1). This indicates that the sample still contained a large amount of amorphous material. This could be attributed to the fact that in the initial period of crystallization or heating, after mixing the metakaolin and alkali solution, some time is needed for the dissolution of metakaolin to complete [27]. After 8 hours of crystallization (Figure 2c), zeolite NaX peaks could clearly be seen. An extremely fast crystallization rate was observed between 4 to 8 hours of the hydrothermal synthesis. However, prolonging the crystallization time up to 12, 24 and 48 hours promoted the crystallization of zeolite P. Although the intensity of zeolite NaX increased with the increased crystallization time as reported in a review by Johnson and Arshad (2014), zeolite P comes as a co-product [28] (Figure 2d, e and f). Based on the XRD, zeolite NaX begins to produce the co-product (zeolite P) after 12 hours of crystallization and displays increasing intensity towards a longer time of crystallization. A longer time of crystallization produces zeolite P which is relatively more stable as a co-product. The nucleation of the more stable co-product could occur on the surface of the zeolite NaX, which is then regarded as the catalyst of the zeolite P formation.

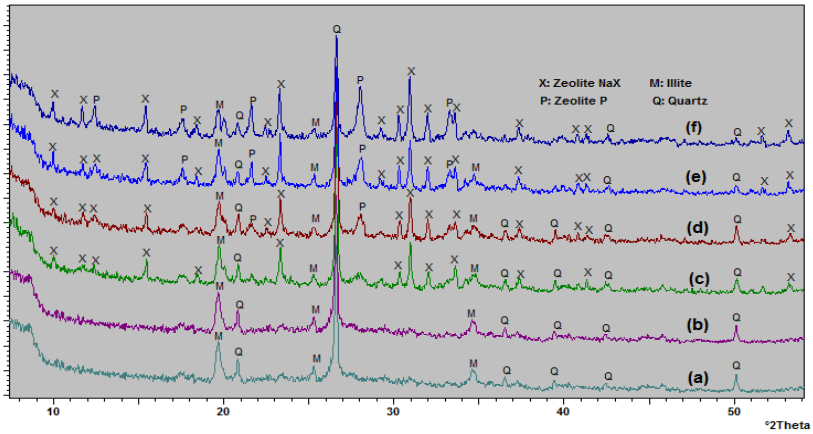

Figure 2. X-ray diffractograms of zeolite NaX samples obtained at different crystallization times. (a) 0 hour, (b) 4 hours, (c) 8 hours, (d) 12 hours, (e) 24 hours and (f) 48 hours.

Figure 3a shows the SEM image of the sample reaction mixture before it underwent the hydrothermal synthesis. There was no sign of zeolite crystals formed when the reaction mixture did not undergo any hydrothermal process. At 4 hours (Figure 3b) small and round shaped particles (1.5-2.0 µm) was observed. The round shape is strong evidence of the intergrowth formation and aggregation of crystals [28]. These features are evidence of an adhesive mechanism of growth at high supersaturated conditions. At this stage, the crystal morphology is usually without distinguishable facets and has a rough surface due to rapid secondary nucleation. After 8 hours of synthesis, the crystals had grown larger (5-8 µm) and more faceted. The smooth surface of the zeolite crystals indicated that supersaturation had now dropped and growth had taken place via layer growth or single nucleation mechanism [29]. After 12 hours, the zeolite NaX (Figure 3d) still showed a smooth surface. However after 24 hours, the zeolite NaX began to transform (Figure 3e). Optimum crystallization time is required to avoid the target crystal from transforming to a more stable phase of zeolite P. This is because most of the target zeolites themselves are metastable in the reaction medium and are not true thermodynamic products [30].

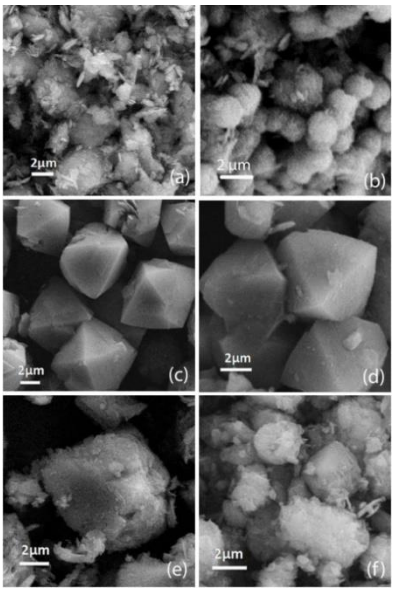

Figure 3. SEM images of zeolite NaX samples obtained at different crystallization times. (a) 0 hour, (b) 4 hours, (c) 8 hours, (d) 12 hours (e) 24 hours and (f) 48 hours.

Effect of crystallization temperature

Figure 4 shows the X-ray diffractograms of zeolite NaX samples crystallized at different temperatures. The reaction mixture with a molar ratio of 2 NaOH: 0.1 Na_2SiO_3: 0.45 MK: 166 H_2O was used to study the effect of crystallization temperature on zeolite NaX formation. All samples underwent aging for 15 hours before being crystallized at 80 ºC, 90 ºC, 100 ºC, 110 ºC, 120 ºC and 130 ºC for 8 hours. The X-ray diffractogram clearly showed that the crystallinity of the zeolite NaX gradually increased when crystallization temperature was raised

from 80 °C to 100 ° C (Fig. 4a, b, c). This result is in agreement with observations by Zhang et al. [24] whereby the reaction temperature strongly affected the nucleation and crystal growth process. The higher the temperature, the larger the energy and the shorter would be the crystallization time. At the same time, higher temperatures can enhance the concentration of chemical groups in sol, and it is also beneficial to crystalline [31]. At temperatures: 110 ºC, 120 ºC and 130 ºC, (Figure 4d, e, f) other phases of zeolite (zeolite P and sodalite) appeared to be more stable as compared to zeolite NaX. At 130 ºC, pure sodalite was formed; similar observations were obtained by Zhang et al. [24]. However it was in contrast with a study by Kovo [20], whereby zeolite X could still be detected at 150 ºC.

Zeolite NaX is a metastable phase that would transform to a more thermodynamically stable phase zeolite P, followed by the formation of sodalite. This result is in agreement with Ostwald's law of successive transformations [32,33]. This law states that an initial metastable phase is successively converted into a thermodynamically more stable phase until the most stable phase is produced [34].

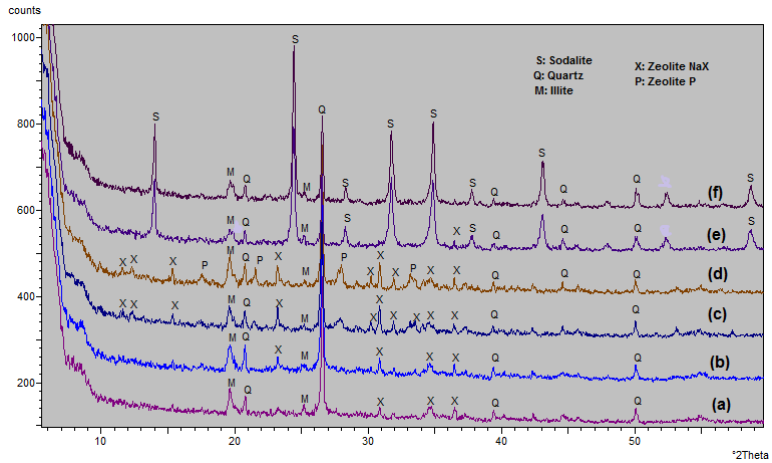

Figure 4. X-ray diffractograms of samples obtained at different crystallization temperatures. (a) 80 ºC, (b) 90 ºC, (c) 100 ºC, (d) 110 ºC, (e) 120 ºC and (f) 130 ºC.

The SEM micrographs of zeolite NaX samples displayed in Figure 5 shows there is no octahedral morphology observed at 80 ºC (Figure 5a). The formation of the octahedral shape crystals (2-10 µm) could only be seen at 90 ºC, 100 ºC and 110 ºC (Figure 5b, c, d). At higher temperatures, 120 ºC and 130 ºC (Figure 5e, f) a thread ball-like cluster (4-12 µm) using SEM was observed. These thread ball-like clusters are sodalite crystals, which only develop in a special environment. Similar images were obtained by Greer et al. for sodalite morphology [35]. An increase in crystallization temperatures increases both the nucleation rate and linear crystal growth rate [33]. Thus, larger crystals are obtained at higher crystallization temperatures as a result of a faster crystal growth rate.

A comparison on the size of crystals could be seen in crystals synthesised at 100 ºC (Figure 5c) and 120 ºC (Figure 5e), whereby the crystals crystallized at higher temperatures had a larger size (4-12 µm). At high temperatures, reaction mixtures can reach supersaturation at a faster rate due to the higher nucleation and growth rate of zeolite. At supersaturation, zeolite NaX is at a metastable phase, and when supersaturation decreases, it is transformed into sodalite which is a more stable phase. Zeolite synthesis is a dynamic equilibrium between crystal growth and crystal dissolution, as the metastable phase of zeolite NaX dissolves, a sodalite phase is formed. The higher the crystallization temperature, the faster is the dissolution of the zeolite NaX (metastable), and sodalite is formed at a shorter time [2].

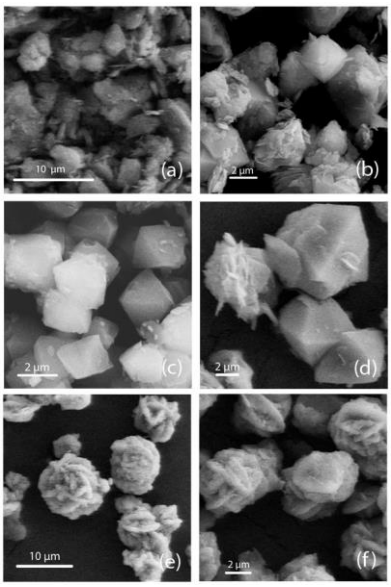

Figure 5. SEM images of samples obtained at different crystallization temperatures: (a) 80 ºC, (b) 90 ºC, (c) 100 ºC, (d) 110 ºC, (e) 120 ºC and (f) 130 ºC.

CONCLUSION

In this study, it was found that 8 to 12 hours of hydrothermal treatment is the optimum time range for the crystallization of zeolite NaX. Shorter crystallization time did not produce any zeolite since the reaction mixture remained in the amorphous phase, while a longer crystallization time (more than 12 hours) produced zeolite P as a major product of crystallization. Crystallization in the range of 80 ºC to 100 ºC is suitable for the synthesis of zeolite NaX. At a temperature of 110 ºC, zeolite NaX exists with some traces of zeolite P which appear as a co-product. At 120 ºC and 130 ºC, sodalite becomes the major product of the synthesis without any traces of zeolite NaX or zeolite P.

ACKNOWLEDGMENT

The authors gratefully acknowledge the Universiti Malaysia Sabah for the financial help in this research.

REFERENCES

[1] Theo, M. 2007. Studies in Surface Science and Catalysis. *In* Jiří Čejka, H. v. B. A. C. And Ferdi, S. (eds.). Chapter 1 The zeolite scene — an overview. Elsevier. 168:1-12.
[2] Cundy, C. S., & Cox, P. A. (2003) The hydrothermal synthesis of zeolites: History and development from the earliest days to the present time. Chemical Reviews, 103, 663–701.
[3] Tosheva, L., & Valtchev, V. P. (2005) Nanozeolites: synthesis, crystallization mechanism and applications. Chemistry of Materials, 17, 2494–2513.
[4] Flanigen, E. M., Broach, R. W., & Wilson, S. T. (2010). Introduction. In Kulprathipanja, S. (Ed.), Zeolites in Industrial Separation and Catalysis (pp. 1-26). Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA.
[5] Deer, W. A., Howie, R. A., & Zussman, J. *(1992). An introduction to the rock-forming minerals (2*nd ed.). Harlow: Longman.
[6] Pohl, W. L. (2011). Economic geology: principles and practice : metals, minerals, coal and hydrocarbons - Introduction to formation and sustainable exploitation of mineral deposits. Chichester, West Sussex: Wiley-Blackwell.
[7] Bellotto, M., Gualtieri, A., Artioli, G., & Clark, S.M. (1995). Kinetic study of the kaolinite-mullite reaction sequence. Part I: Kaolinite dehydroxylation. Phys. Chem. Minerals, *22*(4), 207–214.
[8] Kovo, A. S., Hernandez, O., & Holmes, S. M. (2009). Synthesis and characterization of zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a novel, lower temperature, metakaolinization technique. Journal of Materials Chemistry, 19(34), 6207-6212.

[9] Poon, C. S., Lam, L., Kou, S. C., Wong, Y. L. and Wong, R. 2001. Rate of pozzolanic reaction of metakaolin in high-performance cement pastes. Cement and Concrete Research. 31(9): 1301-1306.
[10] Shvarzman, A., Kovler, K., Grader, G. S., & Shter, G. E. (2003). The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite. Cement and Concrete Research, 33(3), 405-416.
[11] Bosch, P., Ortiz, L., & Schifter, I. (1983). Synthesis of faujasite type zeolites from calcined kaolins. Industrial & Engineering Chemistry Product Research and Development, *22*(3),401-406.
[12] Costa, E., De Lucas, A., Uguina, M. A., & Ruíz, J. C. (1988). Synthesis of 4A zeolite from calcined kaolins for use in detergents. Industrial and Engineering Chemistry Research, *27*(7), 1291-1296.
[13] Basaldella, E. I., Bonetto, R., & Tara, J. C. (1993). Synthesis of NaY zeolite on preformed kaolinite spheres. Evolution of zeolite content and textural properties with the reaction time. Industrial & Engineering Chemistry Research, *32*(4),751-752.
[14] Chandrasekhar, S., & Pramada, P. N. (2001). Sintering behaviour of calcium exchanged low silica zeolites synthesized from kaolin. Ceramics International, *27*(1),105-114.
[15] Covarrubias, C., García, R., Arriagada, R., Yánez, J., & Garland, M. T. (2006). Cr (III) exchange on zeolites obtained from kaolin and natural mordenite. Microporous and mesoporous materials, 88(1), 220-231.
[16] Zwingmann, N., Mackinnon, I. D., & Gilkes, R. J. (2011). Use of a zeolite synthesised from alkali treated kaolin as a K fertiliser: Glasshouse experiments on leaching and uptake of K by wheat plants in sandy soil. Applied Clay Science, 53(4): 684-690.
[17] Holmes, S. M., Alomair, A. A., & Kovo, A. S. (2012). The direct synthesis of pure zeolite A using 'virgin' Kaolin. RSC Advances, *2*(30), 11491-11494.
[18] Johnson, E. B. G., Asik, J., & Arshad, S. E. (2014). Hydrothermal Synthesis of Zeolite A Using Natural Kaolin from Kg. Gading Bongawan Sabah. Journal of Applied Sciences, 14: 3282-3287.
[19] Chandrasekhar, S. and Pramada, P. N. 1999. Investigation on the Synthesis of Zeolite NaX from Kerala Kaolin. Journal of Porous Materials. 6(4): 283-297.
[20] Kovo, A. S. 2012. Effect of temperature on the synthesis of zeolite X from Ahoko Nigerian kaolin using novel metakaolinization technique. Chemical Engineering Communications. 199(6):786-797.
[21] Rabenau, A. 1985. The Role of Hydrothermal Synthesis in Preparative Chemistry. Angewandte Chemie International Edition in English, 24(12): 1026-1040.
[22] Byrappa, K., & Yoshimura, M. (2001). Handbook of Hydrothermal Technology. (McGuire, G. E., & Rossnagel, S. M. (Eds.). Park Ridge, NJ: Noyes Publications.
[23] Caballero, I., Colina, F. G. and Costa, J. 2007. Synthesis of X-type Zeolite from Dealuminated Kaolin by Reaction with Sulfuric Acid at High Temperature. Industrial & Engineering Chemistry Research. 46(4): 1029-1038.
[24] Zhang, X., Tang, D., Zhang, M., & Yang, R. (2013). Synthesis of NaX zeolite: Influence of crystallization time, temperature and batch molar ratio SiO_2/Al_2O_3 on the particulate properties of zeolite crystals. Powder Technology, 235(2): 322-328.
[25] Gregg, S.J. & Sing, K.S.W. (1982) Adsorption, Surface Area and Porosity (2nd ed.). Academic Press, New York.
[26] Said-Mansour, M., Kadri, E. H., Kenai, S. Ghrici, M., & Bennaceur, R. (2011). Influence of calcined kaolin on mortar properties. Construction and Building Materials. 25(5), 2275-2282.
[27] Chandrasekhar, S., & Pramada, P. N. (2008). Microwave assisted synthesis of zeolite A from metakaolin. Microporous and Mesoporous Materials, *108*(1): 152-161.
[28] Johnson, E. B. G., & Arshad, S. E. (2014). Hydrothermally synthesized zeolites based on kaolinite: A review. Applied Clay Science, 97: 215-221.
[29] Cubillas, P., & Anderson, M. W. (2010). Synthesis mechanism: crystal growth and nucleation. In Cejka, J., Corma, A., & Zones, S. (Eds.), Zeolites and Catalysis: Synthesis, Reactions and Applications (pp. 1–55). Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KgaA.
[30] Barrer, R. M. (1982). Hydrothermal Chemistry of Zeolites. London: Academic Press.
[31] Kim, G. J. and Ahn, W. S. 1991. Synthesis and characterization of iron-modified ZSM-5. Applied Catalysis. 71:55–68.
[32] Tounsi, H. Mseddi, S. and Djemel, S. 2009. Preparation and characterization of Na-LTA zeolite from Tunisian sand and aluminum scrap. Physics Procedia. 2:1065–1074.
[33] Molina, A., & Poole, C. (2004). A comparative study using two methods to produce zeolites from fly ash. Minerals Engineering, 17, 167–173.
[34] Dyer, A. (1988). An Introduction to Zeolite Molecular Sieves. Chichester, UK: Wiley & Sons Ltd.
[35] Greer, H., Wheatley, P. S., Ashbrook, S. E., Morris, R. E., & Zhou, W. (2009). Early stage reversed crystal growth of zeolite A and its phase transformation to sodalite. Journal of the American Chemical Society, 131(49): 17986-17992.

View publication stats