

Research Article

Phase Transformation of Zeolite P to Y and Analcime Zeolites due to Changing the Time and Temperature

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In the present study, the synthesis of template free zeolite P under hydrothermal condition was investigated. The effects of parameters such as Si/Al ratios (3–45), crystallization temperatures (80–160°C), and cry (40–60 h) on the synthesis of zeolite P were studied. The phase transformation of zeolite P to two types of high crystallinity Y and analcime zeolites due to change of temperature was observed. The effect of temperature on the achievement of two different zeolite types (Y and analcime) with a constant initial synthetic composition under organic free synthesis of zeolite P was studied. The zeolitic products were characterized by X-ray diffraction, scanning electron microscopy, and IR spectroscopy techniques.

1. Introduction

Zeolitic materials are microporous high-internal-surface crystalline and hydrated aluminosilicates of alkali and alkaline earth cations with an infinite open and rigid three-dimensional structure [1]. Breck et al. in 1956 reported the synthesis of “species very similar to gismodine” [2]. Later these types of zeolites were thought to belong to the harmotome-phillipsite group, which is called P zeolites [3, 4]. Zeolite P is the synthetic analogue of the GIS-type (gobbinsite-NaP1) zeolites and has a two-dimensional pore system with two intersecting 8-ring channels [5]. Zeolite P with Si/Al ratio of 1 has been described as a commercially detergent builder [6, 7]. On the other hand, the analcime structure is made up of small pores that are arranged in four-, six-, and eightfold ring. The crystal structure of analcime for the first time was determined by Taylor [8] and refined by Calleri and Ferraris [9]. Analcime may be used in selective adsorption reactions and in heterogeneous catalysis. Zeolite Y is in the faujasite (FAU) family with a framework containing double 6 rings linked through sodalite cages that generate supercages with average pore diameter of 7.4 Å. There are several applications of FAU zeolites such as fluid cracking catalysts and sorbents for volatile organic removal [10].

Phase transformation processes include the transition from one structure or symmetry into another structure or symmetry, and the intermediate phases can be observed by analysis techniques. This means that from an initial gel with defined composition, one can obtain two or more pure types of zeolite depending on the conditions of crystallization such as alkalinity, crystallization temperature and time, and organic additives (template). However, such a possibility may represent a serious disadvantage in the attempt to achieve the desired group of zeolite in pure form without admixtures of alternative types of zeolite. Then it is possible to know the conditions under which a certain type of zeolite transform into other ones, in order to determine useful crystallization conditions for synthesis of zeolites in pure form. The role of organic template on phase transformation process of Y zeolite to zeolite P and analcime was reported in our previous work [11]. Recently, due to the poisonous effects and high expenses of organic templates for synthesis of zeolite, the template free synthesis of zeolites has been frequently investigated and whenever it comes to the commercial-scale production of zeolites; there is a high incentive for template free syntheses, both for ecological and economical reasons [12, 13]. In this study, the synthesis of template free zeolite P and its phase transformation to two types of high crystalline zeolites Y

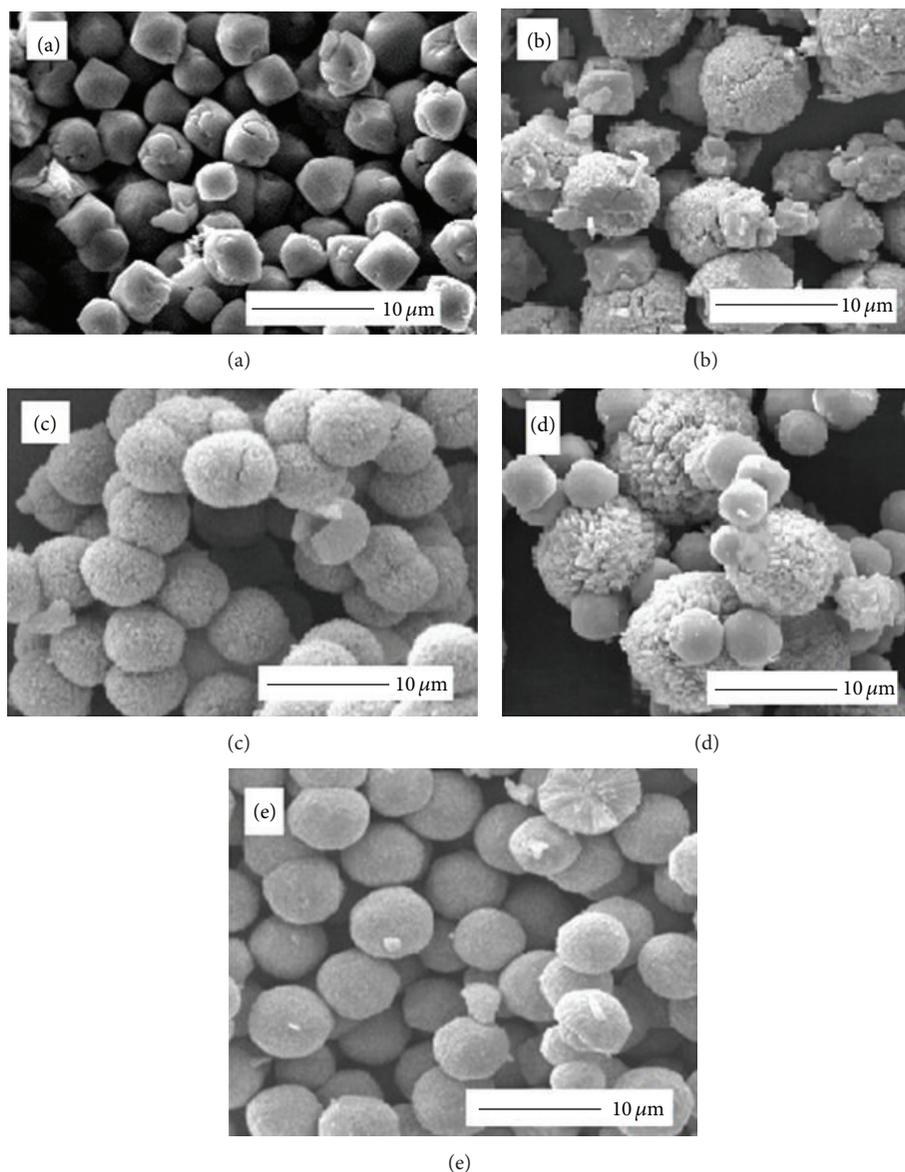


FIGURE 1: Scanning electron micrographs of synthesized zeolites at different temperatures: (a) 90°C, (b) 96°C, (c) 100°C, (d) 110°C, and (e) 130°C.

and analcime with changing crystallization temperature (80–160°C) and additionally the effect of different Si/Al ratios (3–45) and crystallization times (40–60 h) were investigated. To the best of our knowledge this is the first time that organic free synthesis of three pure phase zeolite types with the same sol-gel composition at certain crystallization times with only changing crystallization temperature was investigated. The aim of this work was to study the effect of temperature on the phase transformation as a key factor on the organic free synthesis of mentioned zeolites. The syntheses were carried out under hydrothermal conditions. The obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and FT-IR spectroscopy techniques.

2. Experiment

2.1. Synthesis. The reagents silicic acid, sodium hydroxide, and aluminum powder (all purchased from Merck) were used in the synthesis. All aqueous solutions were prepared using deionized doubly distilled water. The zeolite was synthesized from gel with initial Si/Al molar ratio in composition of 14.5. The sol-gel mixture was prepared by mixing an aluminate and a silicate solution. Then the synthesis gel was introduced to Teflon-lined stainless steel autoclave and sealed autoclave was put into an air oven and heated for 60 hours at 100°C. The solid products were filtered and washed with deionized water, dried overnight at 100°C, and calcinated at 550°C for 5 h in an electric furnace.

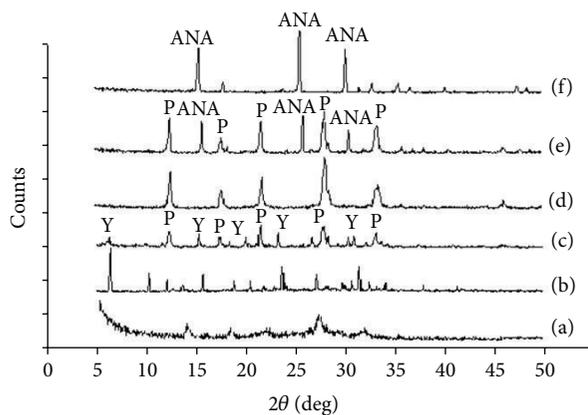


FIGURE 2: X-ray patterns of synthesized zeolites at different temperatures: (a) 85°C, (b) 90°C, (c) 96°C, (d) 100°C, (e) 110°C, and (f) 130°C.

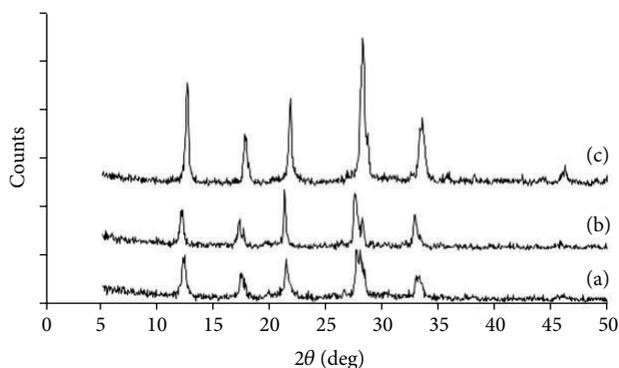


FIGURE 3: X-ray patterns of synthesized P zeolites after different crystallization times: (a) 30 h, (b) 40 h, and (c) 60 h.

2.2. Characterization Techniques. The X-ray powder diffraction (XRD) patterns were collected on a GBC MMA instrument. The patterns were run with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$ Angstrom) at 35.4 kV and 28 mA with a scanning speed of $2\theta = 10^\circ \text{ min}^{-1}$. FT-IR spectra were recorded at room temperature using FT-IR spectrometer (Vector 22-Bruker), over the range of $400\text{--}1500 \text{ cm}^{-1}$ with a resolution of 2 cm^{-1} on KBr pellets. Scanning electron microscopy was performed on selected samples to determine the crystallite size and morphology using a JEOL JXA-840 SEM instrument.

3. Results and Discussion

3.1. The Effect of Crystallization Temperature. The crystallization temperature was varied from 80°C to 160°C in order to find the appropriate temperature for the formation of each pure zeolitic phase. The results indicated that the pure zeolite P was obtained at 100°C whereas the pure phase zeolite Y was produced at 90°C and changing temperature to 95–97°C resulted in a mixture of zeolites Y and P. By increasing temperature from 100°C up to 110°C a mixture of zeolites P and analcime was produced. The pure phase analcime can be obtained at 130°C. All investigations about the effect of temperature were carried out with a same initial

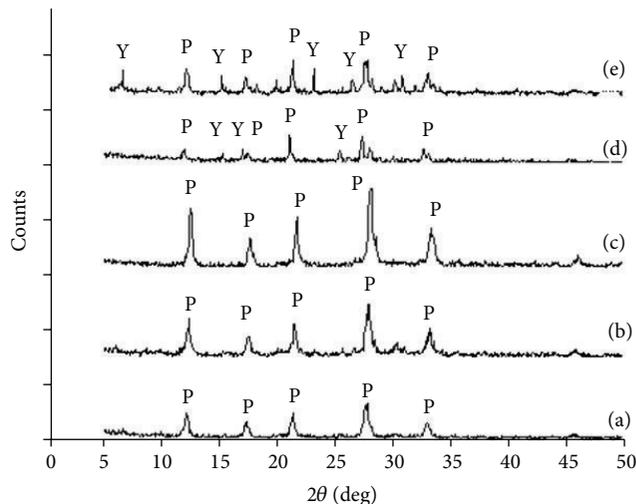


FIGURE 4: X-ray patterns of synthesized zeolites from initial synthetic gel with various Si/Al mole ratios: (a) 3, (b) 5, (c) 15, (d) 30, and (e) 45.

gel composition without using any organic additive. The scanning electron micrographs and XRD patterns, which showed the effect of temperature on the synthesis of three types of mentioned zeolites, are illustrated in Figures 1 and 2. One can obtain the pure phase of zeolites Y, P, and analcime at 90, 100, and 130°C with a parent composition in ratio of $30 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 24 \text{ Na}_2\text{O} : 1360 \text{ H}_2\text{O}$ by the conventional hydrothermal technique, respectively. The synthesis of analcime at 160°C using $\text{N,N}'$ -dibenzyl- $\text{N,N,N}',\text{N}'$ -tetramethyl ethylene diamine (DBTMED) as organic template was reported in our previous work [14] and now we can introduce a new method to achieve pure phase analcime at lower temperature without using organic additive in initial synthetic sol-gel.

3.2. Crystallization of Zeolite P versus Time. The crystallization of zeolite P from initial gel composition of $30 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 24 \text{ Na}_2\text{O} : 1360 \text{ H}_2\text{O}$ with different crystallization times at a temperature of 100°C was followed by X-ray powder diffraction (Figure 3). The XRD patterns showed that, after 40 h, a product with poor crystalline system was formed, and the high crystalline zeolite P could be obtained after 60 h at 100°C. With an increase in the crystallization time at 100°C, zeolite P with high crystallinity was achieved whereas the mixture of zeolite P and analcime was obtained with the increase of crystallization time up to 60 h when D-Methionine was used as organic template in initial gel composition [11].

3.3. The Effects of Si/Al Ratio on the Synthesis of Zeolite P. In order to synthesize zeolite P the initial gel composition $30 \text{ SiO}_2 : a \text{ Al}_2\text{O}_3 : 24 \text{ Na}_2\text{O} : 1360 \text{ H}_2\text{O}$, in which coefficient a has been varied from 0.33 to 5, was investigated at 100°C for 60 h. The results indicated that the crystallinity of pure zeolite P was increased from Si/Al ratio of 3 followed by 5 and 15. For higher Si/Al ratio (Si/Al = 30) a mixed phase of P and Y zeolites was obtained. An increase in the Si/Al ratio to 45

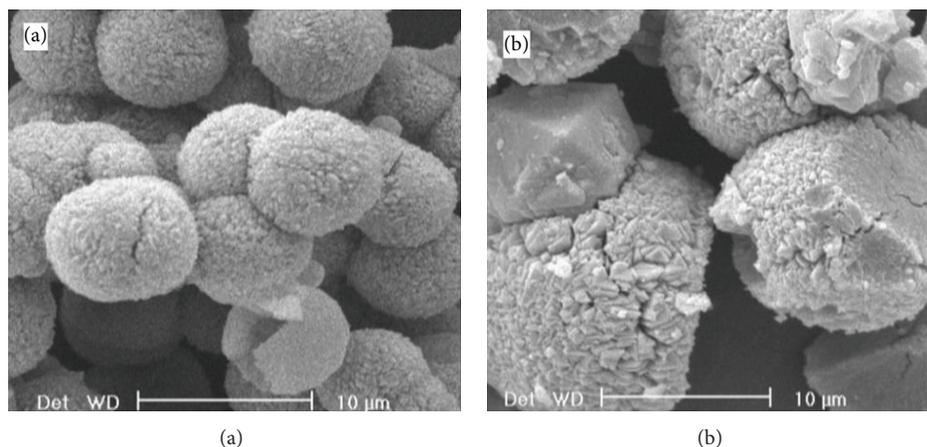


FIGURE 5: SEM images of synthesized zeolites from initial synthetic gel compositions with Si/Al mole ratios of (a) 15 and (b) 30.

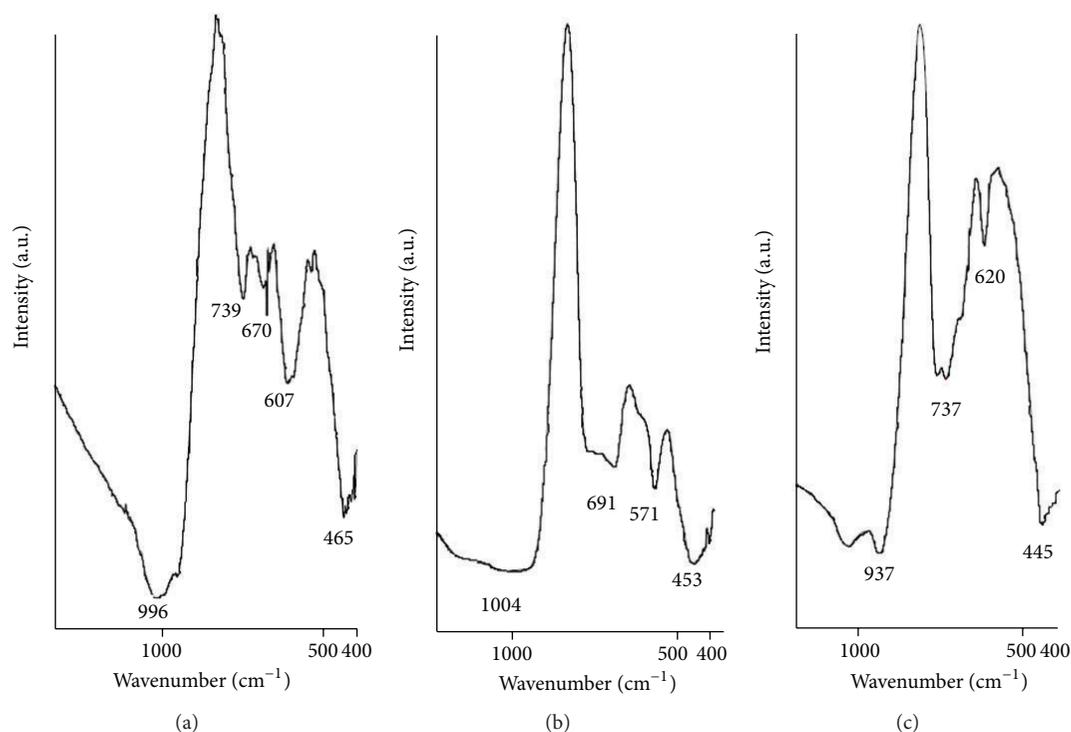


FIGURE 6: FT-IR spectra of synthesized three types of zeolites under template free condition from the same initial gel compositions (a) zeolite Y, (b) zeolite P, and (c) analcime.

maximizes the intensity of zeolite Y peaks and for Si/Al ratio >45 no solid product was obtained. One can see that the Si/Al ratio has a great influence in the phase transformation during template free synthesis of zeolite P (Figure 4). Figure 5 shows the SEM images of obtained zeolitic products with the Si/Al ratios of 15 and 30 in initial synthetic compositions.

3.4. FT-IR Spectra of Synthesized Zeolites. Figure 6 illustrates the FT-IR spectra of synthesized zeolitic samples of zeolites P, Y, and analcime with initial gel composition of $30 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 24 \text{ Na}_2\text{O} : 1360 \text{ H}_2\text{O}$. The FT-IR spectrum of zeolite

P is shown in Figure 6(a). The obtained peaks are similar to those of zeolite P that were reported by Flanigen et al. [15]. The peaks at $453\text{--}571 \text{ cm}^{-1}$ and 996 cm^{-1} were assigned to T-O (T = Si, Al) bending and Si-O, Al-O tetrahedral vibration, respectively. The band at 739 cm^{-1} is attributed to symmetrical stretching of Si-O (Al-O). Figure 6(b) shows the FT-IR spectrum of zeolite Y. The signal at 453 cm^{-1} is assigned to the structure insensitive internal TO_4 tetrahedral bending and the signal at 571 cm^{-1} is attributed to the double ring external linkage band assigned to zeolite Y. The signal at 691 cm^{-1} is assigned to external linkage symmetrical

stretching. The peak at 1004 cm^{-1} is assigned to internal tetrahedral asymmetrical stretching. Figure 6(c) shows the FT-IR spectrum of analcime. The band at about 937 cm^{-1} is due to internal vibrations of the $(\text{Si}, \text{Al})\text{O}_4$ tetrahedral of analcime, whereas the band at about 1100 cm^{-1} is due to vibrations related to external linkages between tetrahedral. The absorption bands at 445 , 620 , and 737 cm^{-1} are related to T–O–T symmetrical stretching mode.

4. Conclusion

In this study a new method for organic free synthesis of zeolite P under hydrothermal condition was investigated. The effect of temperature on the phase transformation of the structure of zeolite p to analcime and to zeolite Y was studied. By changing temperature, the Y and analcime zeolitic phases were observed. The organic free synthesis of analcime and zeolite Y through synthesis of zeolite P with changing temperature for the first time in this study was reported. The effect of heating time, Si/Al ratios in the initial gel, and heating temperature on the obtained zeolite were investigated. A mixture of P and Y zeolites was obtained in $95\text{--}97^\circ\text{C}$ and this mixture was transferred to high crystalline zeolites P and analcime phases with the increase of temperature to 100° and 130°C , respectively.

References

- [1] H. Kazemian, H. Modarres, and H. G. Mobtaker, "Iranian natural clinoptilolite and its synthetic zeolite P for removal of cerium and thorium from nuclear wastewaters," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 258, no. 3, pp. 551–556, 2003.
- [2] D. W. Breck, W. G. Eversole, and R. M. Milton, "New synthetic crystalline zeolites," *Journal of the American Chemical Society*, vol. 78, no. 10, pp. 2338–2339, 1956.
- [3] W. C. Beard, "Linde type B zeolites and related mineral and synthetic phases," *Advances in Chemistry*, vol. 101, pp. 237–249, 1971.
- [4] E. M. Flanigen, H. Khatami, and H. A. Szymanski, "Infrared structural studies of zeolite frameworks," *Advances in Chemistry*, vol. 101, pp. 201–229, 1971.
- [5] R. Szostak, *Handbook of Molecular Sieves*, Van Nostrand Reinhold, New York, NY, USA, 1992.
- [6] A. Araya, "The invention describes a process for preparing P zeolites in which aluminate and silicate solutions are reacted in the presence of a P-zeolite seed," US Patent. 5362466, 1994.
- [7] C. J. Adams, A. Araya, S. W. Carr et al., "Zeolite map: a new detergent builder," *Studies in Surface Science and Catalysis*, vol. 98, pp. 206–207, 1995.
- [8] W. H. Taylor, "The structure of analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$)," *Zeitschrift für Kristallographie*, vol. 74, pp. 1–19, 1930.
- [9] M. Calleri and G. Ferraris, "Struttura dell'analcime: $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$," *Atti della Accademia delle Scienze di Torino*, vol. 98, pp. 821–846, 1964.
- [10] C. S. Cundy and P. A. Cox, "The hydrothermal synthesis of zeolites: Precursors, intermediates and reaction mechanism," *Microporous and Mesoporous Materials*, vol. 82, no. 1–2, pp. 1–78, 2005.
- [11] S. N. Azizi and S. E. Tilami, "Recrystallization of zeolite Y to analcime and zeolite P with D-methionine as structure-directing agent (SDA)," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 635, no. 15, pp. 2660–2664, 2009.
- [12] W. Chang, C. H. Lee, M. Y. Kim, and B. J. Ahn, *Journal of Industrial and Engineering Chemistry*, vol. 7, p. 121, 2001.
- [13] R. A. Rakoczy, M. Breuninger, M. Hunger, Y. Traa, and J. Weitkamp, "Contents," *Chemical Engineering & Technology*, vol. 25, no. 1, pp. 3–8, 2002.
- [14] S. N. Azizi and M. Yousefpour, "Synthesis of aluminum-rich analcime using an ethylene diamine derivative as template," *Zeitschrift für anorganische und allgemeine Chemie*, vol. 635, no. 11, pp. 1654–1658, 2009.
- [15] E. M. Flanigen, H. Khatami, and H. A. Szymanski, "Infrared structural studies of zeolite frameworks," in *Molecular Sieve Zeolites-I*, E. M. Flanigen and L. B. Sand, Eds., Adv. Chem. Ser. No. 101, p. 201, ACS, Washington, DC, USA, 1971.



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