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Phase Diagram of Zeolite Synthesized from Perlite and Rice Husk Ash

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ABSTRACT: This research aimed to synthesize zeolites from perlite obtained from Lopburi Province, Thailand, and from rice husk ash, under hydrothermal condition. The experiments were carried out in an autoclave with SiO_2/Al_2O_3 molar ratios of 1 to 40, NaOH concentrations of 1 to 4 N, and starting pressure of 1 atm. The rice husk ash and $AlCl_3 \cdot 6H_2O$ were used to adjust the SiO_2/Al_2O_3 molar ratio. The autoclave was heated with the rate of 1.5 °C/min to the set points of 140 and 170 °C at which it was kept isothermally for 2 h. The results showed that the products detected were analcime, Na-P1, and sodalite octahydrate. However, at very low SiO_2/Al_2O_3 ratio and NaOH concentration, no zeolite could be formed at 140 °C. The analcime could be formed at almost all conditions, except at low concentration of NaOH and the SiO_2/Al_2O_3 ratio below 25. Furthermore, the Na-P1 could be detected in every area except at high concentration of NaOH and high SiO_2/Al_2O_3 ratio at which only analcime and sodalite octahydrate were found. The sodalite octahydrate was formed preferably at high concentration of NaOH and high ratio of SiO_2/Al_2O_3. At temperature of 170 °C, the formation of analcime was enhanced, while the others seemed to be unaffected. Finally, phase diagrams of detected zeolites were constructed.

KEYWORDS: zeolite, perlite, rice husk ash, phase diagrams.

INTRODUCTION

Zeolites are a well-defined class of crystalline of naturally occurring aluminosilicate minerals. They have three-dimensional structures arising from framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, coordinated in a polyhedral structure linked by all corners. There are 39 naturally occurring zeolite species recorded and more than 100 species have been synthesized.[1] Because of their abundant utilization such as catalyst, ion exchanger, sorption agent, and water softener, there are many researches on synthesis of zeolites. The hydrothermal synthesis of aluminosilicate zeolites involves a few elementary steps by which a mixture of silicon and aluminum compounds, metal cations, organic molecules, and water is converted via an alkaline supersaturated solution into a microporous crystalline aluminosilicate.[2]

The synthesis of zeolites from low-cost silica-alumina sources has been the aim of many experiments. The sources of silica-alumina include fly ash, kaolinite, diatomite. In this experiment, perlite and rice husk ash were used.

Perlite or pearl stone is a natural glass generally of equivalent composition to granite, which has formed by rapid cooling of viscous lava or magma.[3] In Thailand, perlite is an abundant natural resource found in Lopburi Province. Rice husk is an agricultural waste, a by-product from rice milling. Because Thailand exports large amounts of rice, million tons of rice husk are produced. Some rice husk is used as fuel, brick making, animal feed, and fertilizer. When it is combusted under appropriate conditions, the ash having 70 to 97 percent by weight of amorphous silica is obtained. The amorphous silica can be utilized as a highly reactive reactant for many chemical processes.[4,5,6]

The objectives of this work were to identify the crystalline phases of zeolites synthesized from perlite and rice husk ash with varied SiO_2/Al_2O_3 molar ratio and NaOH concentrations, at 140 and 170 °C. Subsequently, the corresponding phase diagrams were constructed.

MATERIALS AND METHODS

Materials

Light color perlite with grain size less than 100 μm from Lopburi Province, Thailand was used as a starting material having the following chemical compositions: 80.44% SiO_2, 11.83% Al_2O_3, 5.68% K_2O, 1.60% Fe_2O_3, 0.39% TiO_2, and 0.06% MnO_2 by weigh. It should be noted that the original SiO_2/Al_2O_3 molar ratio of used perlite is 11.5. Its physical properties were as follows:

Table 1. Crystalline phases of zeolites synthesized at 140 °C (ANA = analcime, Na-P1 = Sodium P1, and SOD = Sodalite Octahydrate).

SiO_2/Al_2O_3	NaOH Conc. (N)	Detected Phase
4	0.5	SOD+Na-P1
1.0	1	Perlite
1.5	1	Perlite
2.0	1	Na-P1 + SOD
2.5	1	Na-P1 + SOD
3	1	SOD + Na-P1
5	1	Na-P1
7	1	Na-P1
9	1	Na-P1
1.0	1.5	SOD + Na-P1
2.5	1.5	SOD + Na-P1 + ANA
4	1.5	Na-P1 + ANA + SOD
25	1.5	ANA + Na-P1
1.0	2	SOD + Na-P1
1.5	2	SOD + Na-P1 + ANA
2.0	2	Na-P1 + SOD + ANA
2.5	2	Na-P1 + SOD + ANA
3	2	Na-P1 + SOD + ANA
5	2	Na-P1 + ANA
7	2	Na-P1 + ANA
7	2	Na-P1 + ANA
9	2	Na-P1 + ANA
11.54	2	Na-P1+ ANA
20	2	Na-P1+ ANA
30	2	Na-P1+ ANA
40	2	ANA + Na-P1
4	2.5	Na-P1 + SOD + ANA
10	2.5	Na-P1 + ANA
1.0	3	SOD + Na-P1
1.5	3	SOD + Na-P1
2.0	3	SOD + Na-P1 + ANA
2.5	3	SOD + Na-P1 + ANA
3	3	Na-P1 + SOD + ANA
5	3	Na-P1 + ANA+ SOD
7	3	Na-P1 + ANA+ SOD
9	3	Na-P1 + ANA+ SOD
11.54	3	Na-P1 + ANA
20	3	ANA + Na-P1
30	3	ANA + Na-P1
40	3	Na-P1 + ANA
10	3.5	Na-P1 + SOD + ANA
35	3.5	ANA + Na-P1
1.0	4	SOD + Na-P1
1.5	4	SOD + Na-P1
2.0	4	SOD + Na-P1 + ANA
2.5	4	SOD + Na-P1 + ANA
3	4	SOD + ANA + Na-P1
5	4	SOD + ANA + Na-P1
7	4	SOD + ANA + Na-P1
9	4	SOD + ANA + Na-P1
11.54	4	SOD + ANA
20	4	SOD + ANA
30	4	SOD + ANA
40	4	ANA + SOD

density of 2.452 g/cm^3, specific surface area of 20 m^2/g, and average pore size of 79 Å.

Table 2. Crystalline phases of zeolites synthesized at 170 °C (ANA = analcime, Na-P1 = Sodium P1, and SOD = Sodalite Octahydrate).

SiO_2/Al_2O_3	NaOH Conc. (N)	Detected Phase
11.54	1	Na-P1 + ANA
40	1	Na-P1 + ANA
20	1.5	ANA + Na-P1
11.54	2	ANA + Na-P1
40	2.5	ANA + Na-P1
15	2.5	ANA + Na-P1
11.54	3	ANA + SOD
20	3	ANA + Na-P1
40	3	ANA + Na-P1
15	3.5	Na-P1 + ANA+SOD
11.54	4	ANA + SOD
20	4	ANA + SOD
30	4	ANA + SOD
40	4	ANA + SOD

Methods

Rice husk was cleaned with water and boiled with 1 N HCl for 3 h to remove impurities. Then it was burned at 700 °C for 2 h under oxygen atmosphere. The obtained ash was found to be an amorphous phase having the following chemical compositions: 99.66% SiO_2, 0.10% Al_2O_3; 0.19% CaO, 0.03% K_2O, and 0.02% Fe_2O_3 by weight. Its physical properties were as follows: density of 1.834 g/cm^3, specific surface area of 332 m^2/g, and average pore size of 59 Å.

The synthesis was carried out hydrothermally in an autoclave with SiO_2/Al_2O_3 molar ratios of 1 to 40, NaOH concentrations of 1 to 4 N, and starting pressure of 1 atm. The rice husk ash and $AlCl_3 \cdot 6H_2O$ were used to adjust the SiO_2/Al_2O_3 molar ratio. The autoclave was heated with the rate of 1.5 °C/min to the set points of 140 and 170 °C at which it was kept isothermally for 2 h. Because the varied solid/liquid ratio may influence the kind of zeolite formed at higher temperature,[7,8] in this work the solid/liquid ratio was fixed at 15 (wt./vol.) for all experiments.

The crystalline structures of obtained products were identified by an X-Ray Diffractometer (Philips, X'pert). Types of zeolite were identified by comparing the peak positions (2θ and their intensities from the obtained XRD-pattern with that of pure phase).[9] The specific surface area and average pore size of zeolitic products were determined by the static volumetric gas adsorption technique using nitrogen at –196 °C as an absorbent gas and using the multipoint BET method setting P/P_o in the range of 0.05-0.3 (Quantachrome, Autosorb-I NOVA 2000). Finally, the crystal morphology was viewed by a Scanning Electron Microscopy (Jeol, JSM 5600 LV).

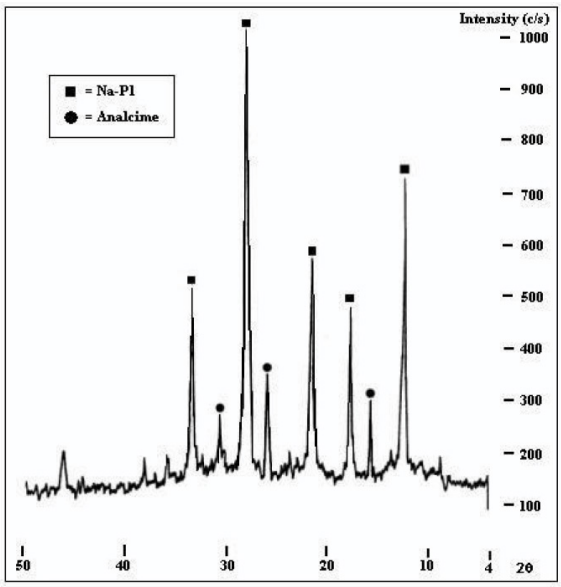

Fig 1. Typical XRD pattern of obtained zeolitic product.

Results and Discussion

After passing the hydrothermal process, the products were identified to be the analcime, Na-P_1 and sodalite octahydrate zeolites accompanied with trace amount of unreacted perlite. However, the formation of each phase was influenced by varied experimental conditions as summarized in Table 1 and 2. The types of zeolite shown are arranged in order of height of major peaks obtained from XRD. Figure 1 shows a typical XRD pattern of synthesized zeolites.

The results showed that at very low SiO_2/Al_2O_3 ratio and NaOH concentration, no zeolite could be formed at 140 °C. The analcime can be formed at almost all conditions except at concentration of NaOH below 1.5 N and the SiO_2/Al_2O_3 ratio below 25. Furthermore, the Na-P1 could be detected in every area except at high concentration of NaOH and high ratio of SiO_2/Al_2O_3 at which only analcime and sodalite octahydrate were found. The sodalite octahydrate was formed preferably at high concentration of NaOH and high ratio of SiO_2/Al_2O_3. When the processing temperature was raised to 170 °C, the formation of analcime was enhanced while the others appeared to be unaffected. Finally, phase diagrams of detected zeolites were constructed and presented in Figures 2 and 3.

In order to examine the morphology of obtained zeolites, the samples, whose XRD patterns were dominated by one type of zeolite were viewed under scanning electron microscopy and shown in Figures 4-6. The analcime had spherical shape with a diameter of approximately 10 μm (Figure 4). The Na-P1 appears in an aggregate of various shapes (Figure 5). The sodalite

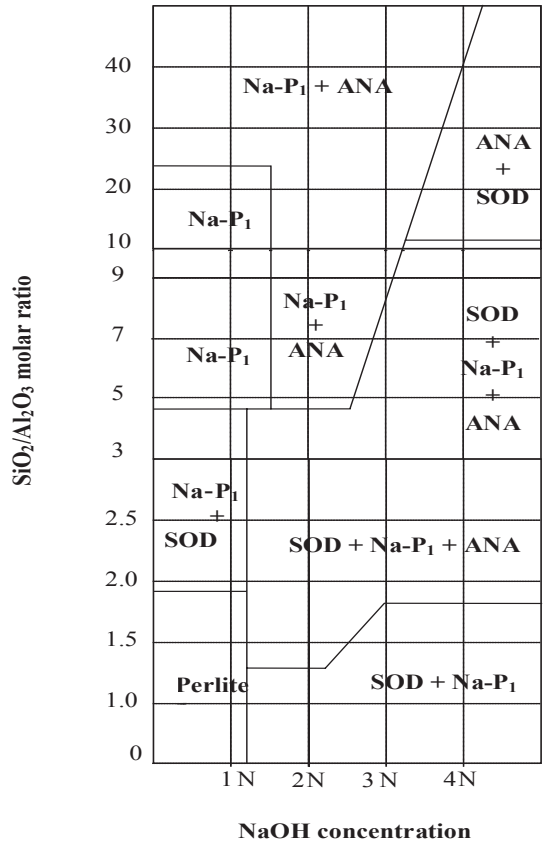

Fig 2. Phase diagram of zeolite synthesized at 140 °C.

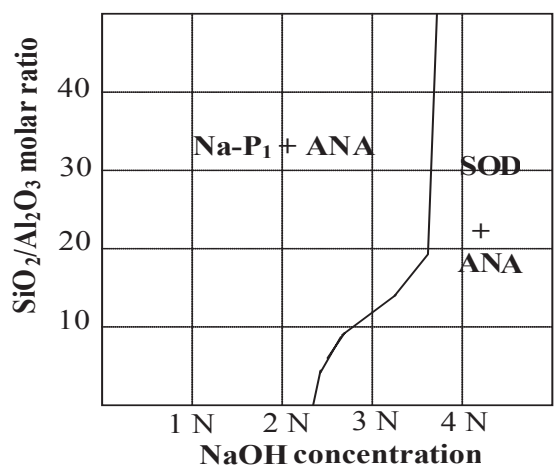

Fig 3. Phase diagram of zeolite synthesized at 170 °C.

octahydrate appeared spherical with a diameter of approximately 3 μm. Using the BET method, the obtained zeolites were found to have the specific surface areas in the range of 62 to 87 m^2/g and the average pore sizes in the range of 7 to 9 Å

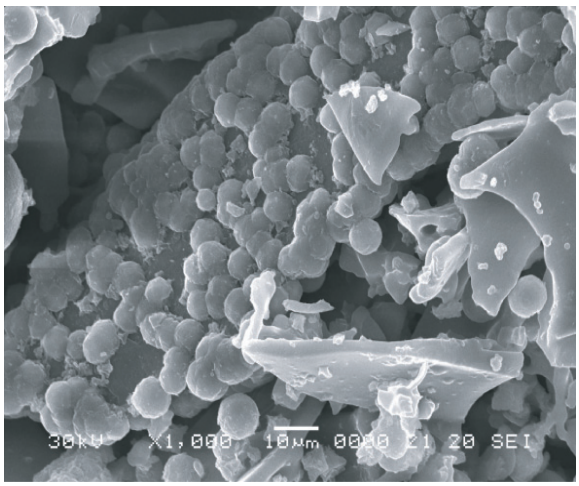

Fig 4. Scanning electron micrograph of analcime.

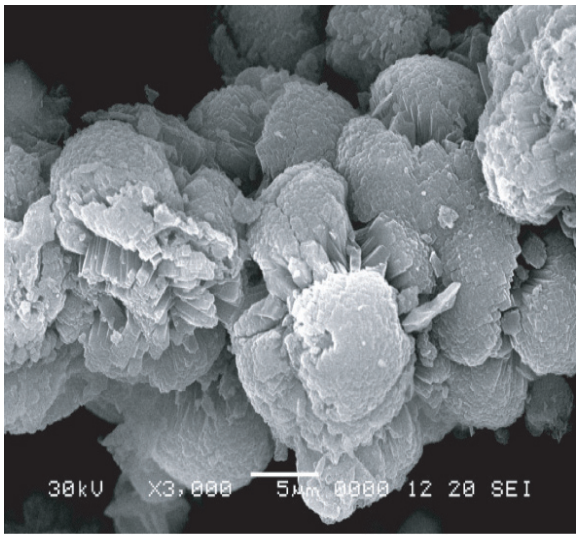

Fig 5. Scanning electron micrograph of Na-P1.

Fig 6. Scanning electron micrograph of sodalite octahydrate.

Conclusions

Three types of zeolites, namely analcime, Na-P1, and sodalite octahydrate, were successfully synthesized from perlite and rice husk ash by the hydrothermal process at 140 and 170 °C. The higher temperature significantly enhanced the formation of analcime only. The obtained zeolites have the specific surface areas in the range of 62 to 87 m^2/g and the average pore sizes in the range of 7 to 9 Å.

Acknowledgements

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