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Synthesis of sodium zeolites from natural and modified diatomite

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Abstract

This project is related with the synthesis of sodium zeolites using natural and modified diatomite as starting materials. The synthesis process consisted of conventional hydrothermal alkaline activation, using NaOH as reagent. The process was studied as a function of the starting material, temperature, time, solid/liquid ratio and activation reagent concentration. The resulting crystals were identified by X-ray diffraction, and characterized by Fourier transform IR and SEM, and they also determined the cation exchange capacity value (CEC). While Na-P1, analcime, cancrinite and hydroxysodalite were obtained under the same conditions, the highest yield was obtained when modified diatomite was used as a starting material. The solid/liquid ratio proved to have less effect on the type of zeolite obtained and the degree of zeolitization achieved.

Keywords: Diatomite; Na-P1; Analcime; Cancrinite; Hydroxysodalite; X-ray diffraction

1. Introduction

Zeolites have gained a great deal of public attention from the chemical industry due to their special properties. Zeolites are crystalline aluminosilicates with an indefinitely extending three-dimensional network of aluminium and silicon tetrahedra linked by sharing of oxygen atoms. Zeolites may be obtained from both natural deposits and laboratory synthesis. Generally, zeolites are synthesized from freshly prepared sodium aluminosilicate gel, from various silica and alumina sources by hydrothermal treatment. Due to their abundant uses as catalyst, ion exchanger, adsorption agent and water softener, there is considerable research on the synthesis of zeolites. The rapid increase in consumption of zeolites calls for further work seeking cheaper raw materials for their synthesis. Clay minerals constitute one such material. Not only is the synthesis of zeolites from kaolin well known, but also the other raw materials such as high silica bauxite, halloysite, interstratified illite-smectite, montmorillonite and bentonite are also used for zeolite syntheses [1–6]. Diatomite is another interesting material because of its low cost and its advantage over other materials due to the highly reactive amorphous state of its silica skeletons, which makes it unnecessary to carry out thermal activation to transform an unreactive state into a reactive state.

Diatomite is a material of sedimentary origin consisting mainly of an accumulation of skeletons formed as a protective covering by diatoms. The skeletons are essentially amorphous hydrated or opaline silica but occasionally are partly composed of alumina. Diatomite usually contains other sediments such as clay and fine sand but its deposits sometimes consists of diatom shells only. In Thailand, the Thai Department of Mineral Resources has found 500,000,000 tons of natural raw diatomite mainly in Lampang Province. Thus, diatomite is naturally available in large quantities at an extremely low cost. On complete calcination, diatomite yields porous, cellular grade material in the form of highly gray colored material containing up to 89 wt.% of silica.

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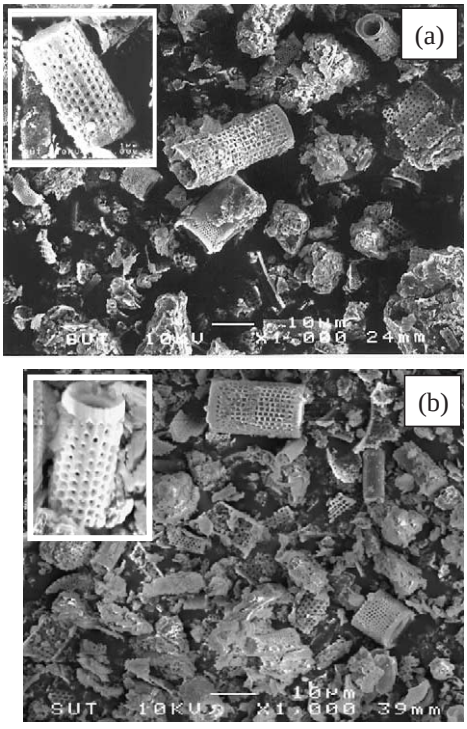

Fig. 1. Scanning electron micrograph of (a) natural raw diatomite and (b) modified diatomite with 10 kV and 5000 magnification.

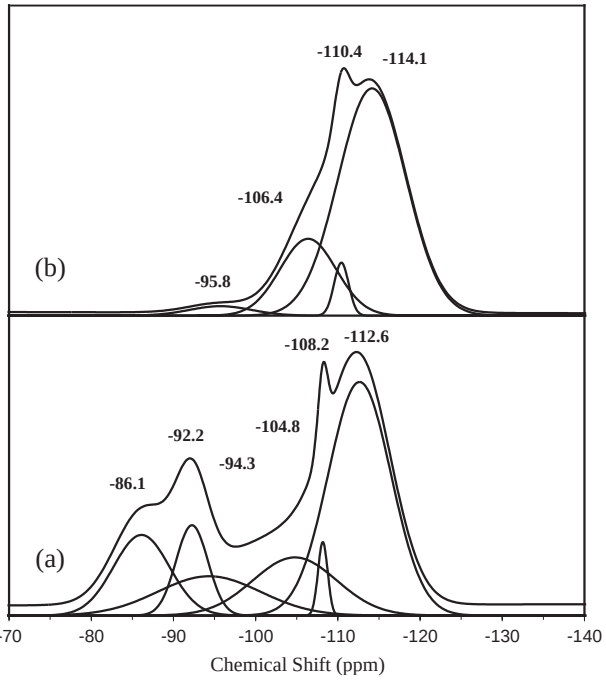

Fig. 2. ^{29}Si MAS NMR spectra of (a) natural diatomite material and (b) modified diatomite material.

Being cellular, this silica is in a highly reactive state. As such, diatomite is an important source of silica offering great potential for its use in the synthesis of zeolite under leaching condition with sodium hydroxide. However, synthesis of zeolite from diatomite is a structurally and chemically complicated problem and depends on a large number of factors [7].

This study focuses on the synthesis of sodium zeolites, i.e. Na-P1, analcime, cancrinite and hydroxysodalite from natural raw diatomite and modified diatomite employing an inexpensive and simple treatment with sodium hydroxide solution. The effectiveness of the resulting sodium zeolite products was determined in terms of cation exchange capacity (CEC).

2. Experimental procedure

Natural raw diatomite samples collected from Ban Keuw in Mae Tha District, Lampang Province, Thailand, were crushed into aggregate-size pieces in roller mills, air-dried and gently ground to pass through a 63-μm mesh metal sieve. The fraction of particles less than 63 μm in size was used for zeolitization experiments. The modified diatomite was obtained by activation treatment of the natural raw diatomite with 6 M H_2SO_4 refluxed at 100 °C for 24 h, and then followed by calcination at 1100 °C for 5 h. The particle size distribution of both diatomites was measured by a Malvern Mastersizer Ver.2.15 and they were characterized structurally by ^{29}Si magic-angle spinning nuclear magnetic resonance (^{29}Si MAS NMR, Bruker MSL 300). X-ray fluorescence (Philips, PW 2404, Magix Pro) was used to determine the composition of materials by borate fusion technique [8]. The zeolitizations were carried out by mixing the natural raw diatomite or modified diatomite powder with 10%, 20% and 30% w/v of sodium hydroxide (Merck) with the ratios (g/ml) of solid to liquid 1:10 and 1:30. The reaction was carried out in digestion bombs with autogenous pressure at the temperatures 100, 140 and 180 °C with various reaction periods from 24 to 168 h. In addition, $Al(OH)_3$ was used to adjust the SiO_2/Al_2O_3 molar ratio of the modified diatomite for the same composition as the natural raw diatomite. The experiments were performed in an oven with a controller (±1

Table 1
Chemical composition of the starting materials for synthesis of zeolites determined by XRF

Material	Weight (%)							
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	MnO	TiO_2
Natural raw diatomite	71.90	14.60	5.78	1.95	0.17	0.69	0.01	0.51
Modified diatomite	94.42	3.68	0.50	0.68	0.00	0.14	0.00	0.43