



## 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.

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*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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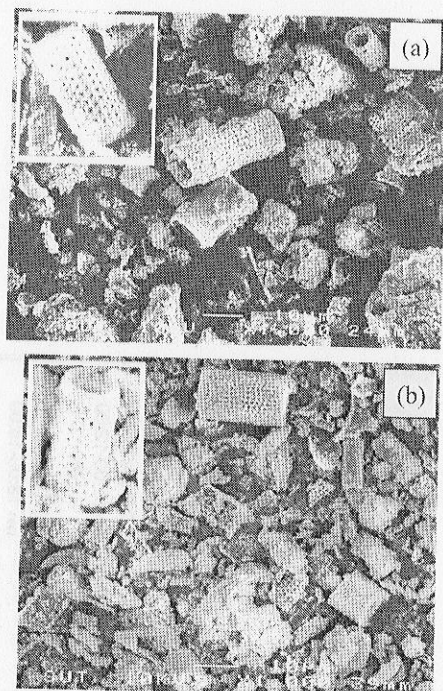


Fig. 1. Scanning electron micrograph of (a) natural raw diatomite and (b) modified diatomite with 10 kV and 5000 magnification.

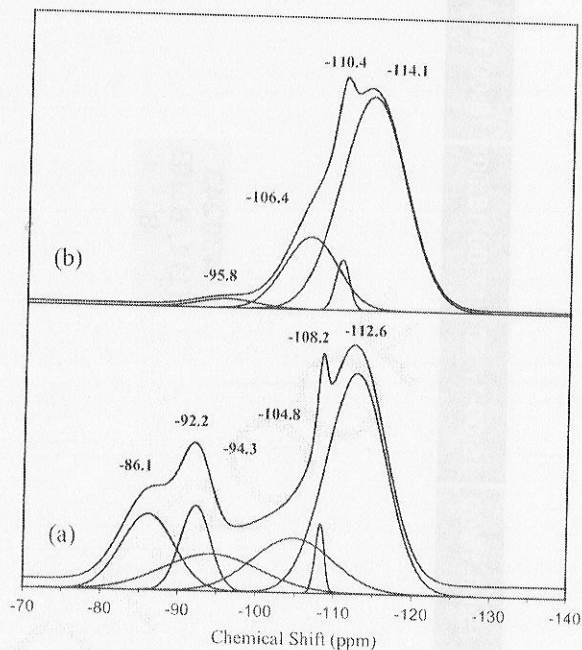


Fig. 2.  $^{29}\text{Si}$  MAS NMR spectra of (a) natural diatomite material and (b) modified diatomite material.

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

65 This study focuses on the synthesis of sodium  
 66 zeolites, i.e. Na-P1, analcime, canerinite and hydroxysol-  
 67 dalite from natural raw diatomite and modified diatomite  
 68 employing an inexpensive and simple treatment with  
 69 sodium hydroxide solution. The effectiveness of the  
 70 resulting sodium zeolite products was determined in  
 71 terms of cation exchange capacity (CEC).

## 72 2. Experimental procedure

73 Natural raw diatomite samples collected from Ban  
 74 Keuw in Mae Tha District, Lampang Province, Thailand,  
 75 were crushed into aggregate-size pieces in roller mills,  
 76 air-dried and gently ground to pass through a 63- $\mu\text{m}$

77 mesh metal sieve. The fraction of particles less than 63  
 78  $\mu\text{m}$  in size was used for zeolitization experiments. The  
 79 modified diatomite was obtained by activation treatment  
 80 of the natural raw diatomite with 6 M  $\text{H}_2\text{SO}_4$  refluxed at  
 81  $100^\circ\text{C}$  for 24 h, and then followed by calcination at  
 82  $1100^\circ\text{C}$  for 5 h. The particle size distribution of both  
 83 diatomites was measured by a Malvern Mastersizer  
 84 Ver.2.15 and they were characterized structurally by  $^{29}\text{Si}$   
 85 magic-angle spinning nuclear magnetic resonance ( $^{29}\text{Si}$   
 86 MAS NMR, Bruker MSL 300). X-ray fluorescence  
 87 (Philips, PW 2404, Magix Pro) was used to determine  
 88 the composition of materials by borate fusion technique  
 89 [8]. The zeolitizations were carried out by mixing the  
 90 natural raw diatomite or modified diatomite powder with  
 91 10%, 20% and 30% w/v of sodium hydroxide (Merck)  
 92 with the ratios (g/ml) of solid to liquid 1:10 and 1:30.  
 93 The reaction was carried out in digestion bombs with  
 94 autogenous pressure at the temperatures 100, 140 and 180  
 95  $^\circ\text{C}$  with various reaction periods from 24 to 168 h. In  
 96 addition,  $\text{Al}(\text{OH})_3$  was used to adjust the  $\text{SiO}_2/\text{Al}_2\text{O}_3$   
 97 molar ratio of the modified diatomite for the same  
 98 composition as the natural raw diatomite. The experi-  
 99 ments were performed in an oven with a controller ( $\pm 1$

t1.1 Table 1  
 t1.2 Chemical composition of the starting materials for synthesis of zeolites determined by XRF

t1.3 Material	Weight (%)							
t1.4	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{MnO}$	$\text{TiO}_2$
t1.5 Natural raw diatomite	71.90	14.60	5.78	1.95	0.17	0.69	0.01	0.51
t1.6 Modified diatomite	94.42	3.68	0.50	0.68	0.00	0.14	0.00	0.43

100 °C). Once the activation time was reached, the digestion  
 101 bomb was quenched in cold water to stop the reaction.  
 102 The solid product was filtered and washed with deionized  
 103 water to remove excess alkali until the pH of the filtrate  
 104 became 7. Then, the sample was dried at 110 °C for 24 h  
 105 and stored in a desiccator. Powder X-ray diffractometry  
 106 (Bruker D5005, CuK $\alpha$ , Ni filter,  $\lambda=1.54 \text{ \AA}$ ) and scanning  
 107 electron microscopy (JEOL JSM-6400) were used,

respectively, to identify the crystalline solid products  
 and to investigate the morphology of the solids. The  
 existence of zeolite framework was confirmed by Fourier  
 transform infrared (FTIR) spectroscopy (Perkin-Elmer  
 Spectrum GX). The CEC values were determined using  
 a modified ammonium acetate method, as previously  
 reported [9], and the results were expressed as milli-  
 equivalents per 100 g of solid.

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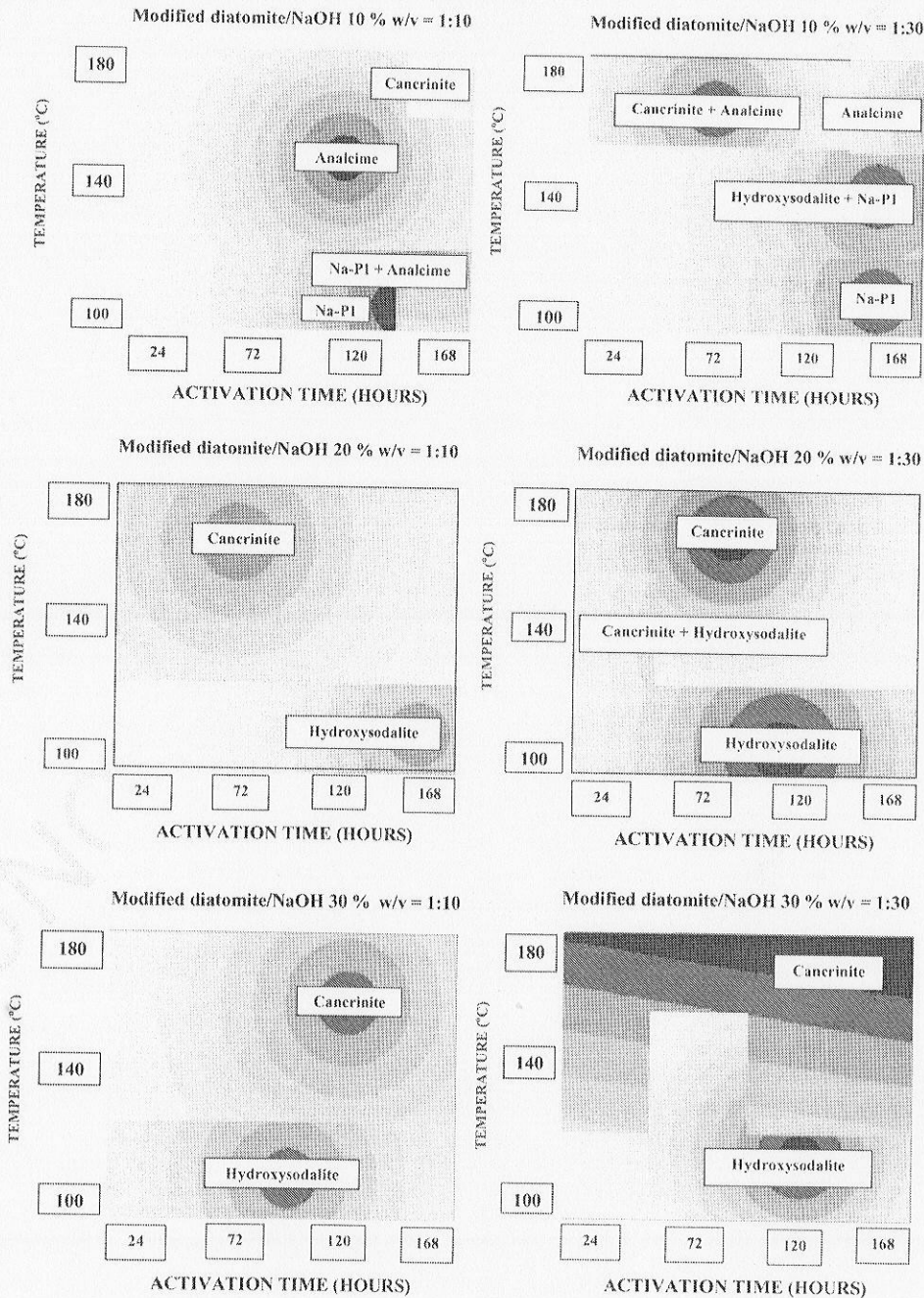


Fig. 3. Different types of zeolite products and their relative intensities obtained from synthesized modified diatomite depending on various experimental conditions.

### 116 3. Results and discussion

117 The natural raw diatomite and modified diatomite  
 118 with mean particle size 9.88 and 8.97  $\mu\text{m}$ , respectively,  
 119 having the morphology are shown in Fig. 1. The natural  
 120 raw diatomite obtained from Mac Tha District, Lampang  
 121 Province, contains mainly *A. granulata* species [10]. The  
 122 morphology of both diatomites is similar although the  
 123 modified diatomite was processed by hot acid and heat.  
 124 From the X-ray diffraction patterns, the natural raw  
 125 diatomite is mostly biogenic hydrous silica identified as  
 126 Opal-A (A-amorphous) [11] mixed with a minority  
 127 amount of quartz, kaolinite, montmorillonite and illite,  
 128 while the modified diatomite shows only an amorphous  
 129 phase mixed with a minute amount of quartz. This  
 130 indicates that clay minerals can be easily removed by  
 131 hot  $\text{H}_2\text{SO}_4$ . The elemental composition of the natural  
 132 raw diatomite and modified diatomite expressed as  
 133 weight percentages is shown in Table 1. The main  
 134 components of the natural raw diatomite are oxides of  
 135 Si, Al and Fe, whereas the main components of the  
 136 modified diatomite are oxides of Si and Al. The acid  
 137 treatment reduces or eliminates all other oxides relative  
 138 to  $\text{SiO}_2$ . The  $^{29}\text{Si}$  MAS NMR spectra of natural raw  
 139 diatomite and modified diatomite are given in Fig. 2. All  
 140 the spectra were simulated using essentially Gaussian  
 141 functions as illustrated below the spectral traces in Fig.  
 142 2.  $\text{SiO}_4$  site can be labeled as  $Q^n$ , where  $n$  designates  
 143 the number of bridging oxygen atoms (those shared with  
 144 tetrahedral silicon). The  $^{29}\text{Si}$  MAS NMR spectrum of  
 145 natural raw diatomite consists of 6 resonances at  $-86.1$ ,  
 146  $-92.2$ ,  $-94.3$ ,  $-104.8$ ,  $-108.2$  and  $-112.6$  ppm,  
 147 characteristic of  $Q^2$  ( $-86.1$ ,  $-92.2$ ),  $Q^3$  ( $-94.3$ ) and  
 148  $Q^4$  ( $-104.8$ ,  $-108.2$ ,  $-112.6$ ), respectively. The modi-  
 149 fied diatomite shows two components that appear at  
 150  $-95.8$  ppm corresponding to  $Q^3$  site and others in the

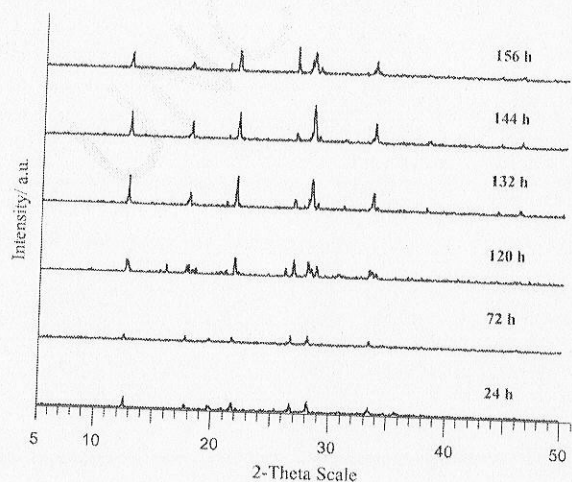


Fig. 4. XRD patterns of Na-P1 obtained from a transformation of the modified diatomite with 10% NaOH concentration, S/L=1/10 and reaction temperature of 100 °C at various reaction times.

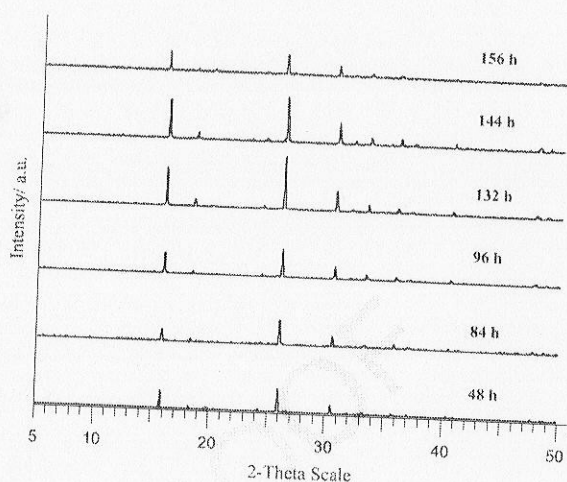


Fig. 5. XRD patterns of analcime obtained from a transformation of the modified diatomite with 10% NaOH concentration, S/L=1/10 and reaction temperature of 140 °C at various reaction times.

range of  $-106.4$  to  $-114.1$  ppm attributed to  $Q^4$  site  
 [12]. The both spectrum are dominated by a large  $Q^4$   
 ( $[\text{Si}(\text{OSi})_4]$ ) and a secondary  $Q^3$  ( $[(\text{OH})\text{Si}(\text{OSi})_3]$ ) resonance.  
 A percentage of amorphous silica with different  
 types  $Q^n$  calculated from Gaussian curve fitting shows  
 the natural raw diatomite structure contains  $[\text{Si}(\text{OSi})_4]$ ,  
 $[(\text{OH})\text{Si}(\text{OSi})_3]$  and  $[(\text{OH})_2\text{Si}(\text{OSi})_2]$  in the ratio 63.89%,  
 23.33% and 12.78%, respectively, while the modified  
 diatomite consists of 97.21%  $[\text{Si}(\text{OSi})_4]$  group and only  
 2.79%  $[(\text{OH})\text{Si}(\text{OSi})_3]$  but no  $[(\text{OH})_2\text{Si}(\text{OSi})_2]$ .  
 Phase identification was performed by comparing the  
 observed powder patterns with calculated ones reported  
 in the collection of simulated XRD patterns for zeolites  
 [13]. The relative intensity yields were obtained from  
 normalized XRD intensities of the major reflection for  
 each zeolite. Natural raw diatomite used as a starting  
 material yields the same types of zeolite as does the  
 modified diatomite under the same experimental con-  
 ditions. Nevertheless, the solid products synthesized from  
 the modified diatomite contain a higher amount of  
 zeolite crystallinity than those from natural diatomite. It  
 may be due to the natural raw diatomite containing a  
 higher amount of ferric oxide, SiOH groups and clay. In  
 addition, the particle size of the natural raw diatomite is  
 larger than that of the modified diatomite. Fig. 3  
 summarizes the different types of zeolite synthesized  
 from the modified diatomite under various experimental  
 conditions (temperature, concentration of the activation  
 solution, starting material/solution ratio and reaction  
 time). Na-P1 is obtained in higher yields at low  
 temperatures (100 and 140 °C) and low alkali concen-  
 tration (10% NaOH), while under the extreme conditions  
 (140, 180 °C and 20% NaOH, 30% NaOH) hydrox-  
 ysodalite and cancrinite were obtained instead. Additional  
 experiments, where natural diatomite was treated only  
 with hot 6M  $\text{H}_2\text{SO}_4$  before using it for zeolite synthesis,

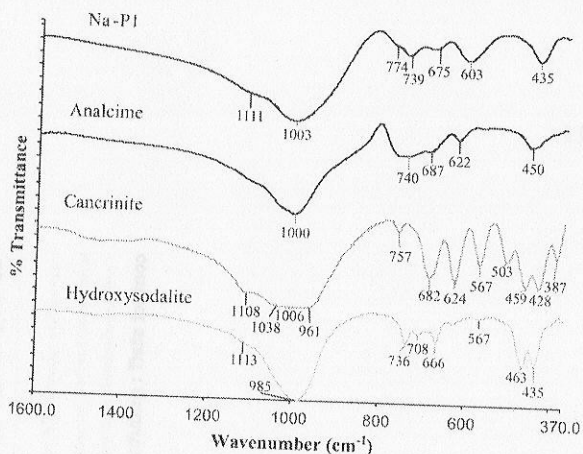


Fig. 6. IR spectra of each sodium zeolite synthesized from the modified diatomite.

187 also gave Na-P1 as the product but in approximately  
188 20% lower yields than that from the modified diatomite  
189 [14].

190 NaOH concentration and temperature are the most  
191 important parameters influencing the transformation of the  
192 diatomites, whereas the solid/liquid (S/L) ratio seems to  
193 be less influential on the type of sodium zeolites formed.  
194 Another important parameter for the zeolitization of  
195 diatomite starting material is the activation time. Figs. 4  
196 and 5 show some examples of XRD patterns of Na-P1  
197 and analcime produced at the optimum synthesis con-  
198 ditions at different times, showing that the maximum  
199 efficiency for Na-P1 formation was reached after 144 h at  
200 100 °C with 10% NaOH and S/L=1/10 ratio, and for  
201 analcime with 10% NaOH (S/L=1/10) at 140 °C after 132

202 h. The optimum condition for cancrinite crystallization is  
203 found to be 20% NaOH, S/L=1/10 at 180 °C after 72 h,  
204 and for hydroxysodalite, 100 °C, 30% NaOH, S/L=1/30  
205 and 96 h.

206 The IR spectra of the highest yield products of each  
207 sodium zeolite are shown in Fig. 6. Bands at 800 and 780  
208 cm<sup>-1</sup>, which indicate the Si-O-Si vibration of quartz [4], do  
209 not appear in the final products. The absorption spectra in  
210 this study are similar to previous reports [15,16]. SEM  
211 images of the sodium zeolites corresponding to the XRD  
212 pattern with the highest intensity are given in Fig. 7. It is  
213 found that Na-P1 appears in fairly equant, but somewhat  
214 irregular shapes having diameters of 10–20 μm. The  
215 analcime has icosahedral shape with a diameter of approx-  
216 imate 100 μm. The cancrinite appears in fractal shape  
217 comprised of extended bars with lengths of approximately  
218 30 μm. Additionally, Fig. 7(d) shows the prismatic particle  
219 shape of the hydroxysodalite having diameters of approx-  
220 imately 5 μm. The CEC was found to be high for Na-P1  
221 (173 meq/100 g), while it is quite low for analcime (36 meq/  
222 100 g). In the case of hydroxysodalite and cancrinite, the  
223 CEC was 87 and 67 meq/100 g, respectively. From the point  
224 of view of the potential industrial application, the more  
225 interesting zeolitic product is Na-P1, due to the high ion  
226 exchange capacity.

#### 4. Conclusions

227 The sodium zeolites were successfully synthesized from  
228 natural diatomite and modified diatomite materials by the  
229 hydrothermal process, demonstrating that these materials  
230 are suitable for zeolite synthesis. Regardless of the starting  
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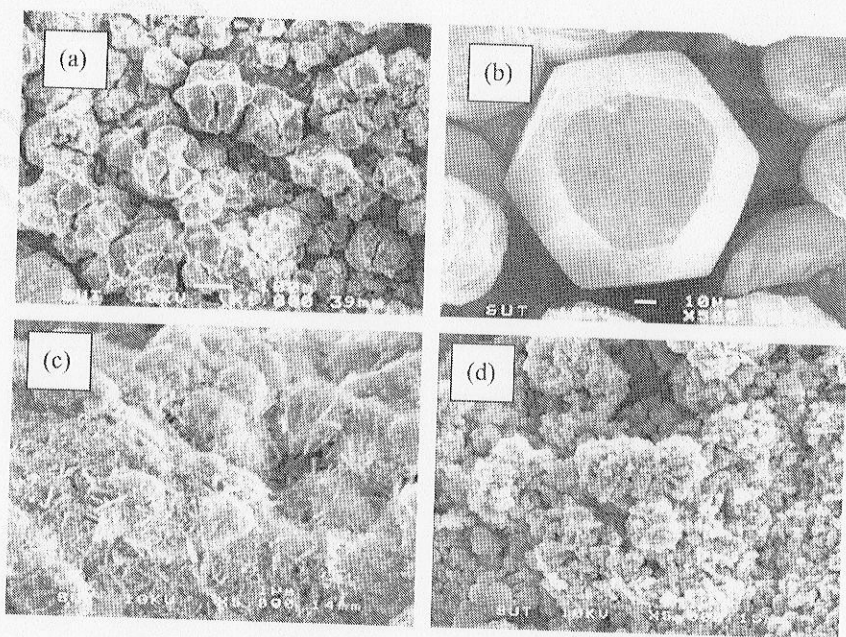


Fig. 7. SEM micrographs of (a) Na-P1, (b) analcime, (c) cancrinite and (d) hydroxysodalite.

232 material, the zeolite products synthesized were Na-P1,  
 233 analcime, cancrinite and hydroxysodalite, and their for-  
 234 mation and proportion mainly depends on concentration of  
 235 solution, reaction temperature and reaction time. Optimum  
 236 conditions were obtained using modified diatomite material  
 237 with 10% NaOH, a S/L ratio 1/10, 100 °C and 144 h,  
 238 which produced highly crystalline zeolite Na-P1 with a  
 239 CEC value of 173 meq/100 g.

240 From our preliminary experiments, we see that only  
 241 acid treatment is sufficient to provide a good starting  
 242 material, which contains lower amount of ferric oxide  
 243 and other impurities, and also contains more amount of  
 244 Si(SiO)<sub>4</sub> units as well, suggesting that a modification of  
 245 the process, eliminating the heating step, may be more  
 246 economical.

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