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Thermal and acid treatment on natural raw diatomite influencing in synthesis of sodium zeolites

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Abstract.

A natural raw diatomite and four modified diatomites by calcination and acidification were used as starting materials for the sodium zeolitization process. Iron impurity content present in the natural raw diatomite which was expressed as Fe_2O_3 is about 5.8% and Q^4 ($[Si(OSi)_4]$) unit 64%, whereas the modified diatomite which was treated with hot 6M H_2SO_4 (refluxed at 100 $^\circ$C) for 24 h and followed with calcination at 1100 $^\circ$C for 5 h, contains about 0.5% of Fe_2O_3 and 97% of Q^4. The results showed that under the studied conditions (NaOH 10-30%w/v, 100-180 $^\circ$C, solid:liquid 1:10 and 1:30, reaction time 24-180 h) only Na-P1, analcime, cancrinite and hydroxysodalite were obtained and the highest yield of each sodium zeolite product was obtained from the modified diatomite treated

with hot H_2SO_4 and followed with calcinations at 1100 °C. This results from the reduction of iron content by acid leaching and the elimination of silanol groups after calcination to form more siloxane groups in the structure of starting materials. In addition, a role of iron content was found to be significant in zeolite formation compared to a role of Q^4 sites. It was found that a percentage of crystallinity is very high in the case of all starting materials, which first underwent iron impurity elimination before further thermal treatments.

Introduction

Zeolites have gained a great deal of attention from many industrial sectors because of their special properties. They have been widely used in many applications, such as ion exchange, adsorbent and catalyst [1]. Therefore, an attempt to search for a zeolite synthesis process with economical value has been regularly of interest. In general, locally obtained raw materials used for silica or alumina source means the advantage of reduction of the operating budget. Useful information on factors affecting the synthesis specifically structure and chemical composition of starting materials to effectively promote the reaction to yield high zeolite crystallinity is necessary for good investment as well. Diatomite is another interesting material because of its relatively low cost, large reserves and its highly reactive amorphous state in silica skeletons which makes it unnecessary to transform an unreactive state into a reactive state with thermal activation like clay minerals [2-4]. Diatomite is natural amorphous silica engendered by the deposition of diatom skeleton. It is formed by closest packing of hydrous SiO_2 spheres and is classified as opal-A mineralogically. Diatomite usually contains other sediments such as clay and fine sand. In Thailand,

the Thai Department of Mineral Resources (DMR) found 500,000,000 tons of natural

raw diatomite mainly in Lampang Province; containing highly clay minerals and iron

oxide. In addition, it is low in silica but high in alumina compared to other countries

[5]. Our previous works [6,7] reported some physico-chemical properties of the

natural raw Lampang diatomite and diatomites treated with heat and acid, as well as

the use of these materials for preparing sodium zeolites by hydrothermal alkaline

activation under the influence of various conditions. However, the synthesis of zeolite

from diatomite depends on a lot of factors and so it is a structurally and chemically

complicated problem.

The objective of this work was to investigate the effect of diatomite structure and iron

impurity present in the diatomite on synthesis of sodium zeolites by means of

preparing a series of modified raw diatomite samples with thermal and acid before

using them as starting materials for zeolites synthesis. ^{29}Si magic angle spinning

nuclear magnetic resonance (^{29}Si MAS NMR), X-ray diffraction (XRD) and Fourier

transform infrared (FT-IR) spectroscopy were used to analyse the structure of

diatomite.

Experimental

Natural raw diatomite samples collected from the 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 particles less than

63 μm in size were used for zeolitization experiments. The researchers selected the

best thermal and acid treatment conditions from our previous study [6] to use for the

modifying of natural raw diatomite to be the starting materials for synthesizing

zeolites. The modified diatomites were obtained as follows: (1) calcined at 900 °C for

5 hours, (2) calcined at 1100 °C for 5 hours, (3) treated with hot 6M H_2SO_4 (refluxed at 100 °C) for 24 hours and (4) treated with hot 6M H_2SO_4 (refluxed at 100 °C) for 24 hours and followed with calcination at 1100 °C for 5 hours. The starting diatomite materials were designated as follows: D-H_2SO_4-C(T), D denoted the natural diatomite, H_2SO_4 denoted the acid treatment with hot 6 M H_2SO_4 and C(T) denoted calcined temperature when T being the calcination temperature. Thus, in this study there were five starting diatomite materials denoted as: D, D-C(900), D-C(1100), D-H_2SO_4 and D-H_2SO_4-C(1100). The structural analysis of starting diatomite materials were determined by ^{29}Si magic-angle spinning nuclear magnetic resonance (^{29}Si MAS NMR, Bruker MSL 300). The samples were spun at a frequency of 4.5 kHz in Bruker double air-bearing probes and recycle delay times of 60 seconds. X-ray fluorescence (Philips, PW 2404, Magix Pro) was used to determine their chemical compositions by borate fusion technique. The mean particle size distribution was determined by a laser light scattering-based particle sizer (Malven Mastersizer S series instrument). Identification of crystalline samples and investigation of morphology of the samples were determined by X-ray diffraction (XRD) and scanning electron microscope, respectively. X-ray diffractograms were recorded by Bruker D5005, with CuK$_\alpha$ radiation, Ni filter, λ = 1.54   SEM micrographs were performed in a JEOL JSM-6400 scanning electron microscope. The materials were put onto a conductive carbon tape and coated with gold to prevent charging. The framework was also confirmed by Fourier transform infrared (FT-IR) spectroscopy (Perkin-Elmer Spectrum GX). FT-IR was recorded in the region of 4000-370 cm^{-1} with the KBr pellet technique.

The optimal conditions of each sodium zeolite synthesis from the previous preliminary experiments [7] were selected to be used in the following experiments.

All zeolite synthesis procedures were carried out with constant ratio (g cm^{-1}) of solid

to liquid 1:10 and Al(OH)$_3$ was used to adjust the Si/Al molar ratio of the modified

diatomites with acid (D-H$_2$SO$_4$ and D-H$_2$SO$_4$-C(1100)) to make the Si/Al ratio to be

the same as natural raw diatomite. Zeolite Na-P1 was synthesized using five

diatomites mixed with 10% NaOH, and the reaction mixture was carried out in Parr

bombs with autogenous pressure of the temperature at 100 °C with reaction 72 hours.

The other zeolites were synthesized with 10% NaOH for analcime, 20% NaOH for

cancrinite and 30% NaOH for hydroxysodalite. These synthesis procedures were the

same as above but different in reaction temperatures and reaction times; synthesized

analcime under the condition of 140 °C for 72 hours, cancrinite of 180 °C for 120

hours and hydroxysodalite of 100 °C for 120 hours. The experiments were performed

in an oven with a controller (± 1 °C). Once the activation time was reached, the Parr

bomb was quenched in cold water to stop the reaction. The solid product was filtered

and washed with deionized water to remove excess alkali until the pH of the filtrate

became 7. Then, the sample was dried at 110 °C for 24 hours and stored in a

desiccator.

Results and discussion

The morphology of starting materials was shown in Figure 1. It showed the dominant

A. granulata species [8]. The micrograph of the diatomite calcined at 900 °C showed

the detail of diatomite structure, still in its original geometry. When calcinated at 1100

°C, the diatomite still showed a sign of its original diatomite structure, but the

concave and convex surfaces were almost all gone, and smoother surfaces were

formed instead. The SEM micrographs of hot acid activation and the ones of hot acid

activation and followed with calcination at 1100 °C both showed the original

geometry of the pores to be preserved, but there was collapse of skeleton structure. The mean particle sizes of all the starting materials varied in a range of 8.6-19.8 μm. It was found that the particle size distribution of natural diatomite, calcined diatomite at 900 $^\circ$C and 1100 $^\circ$C are 8.6, 17.6 and 19.8 μm, respectively. The diatomite treated with hot acid and the one treated with hot acid and followed with calcinations at 1100 $^\circ$C showed the particle size of 10.8 μm and 9.3 μm, respectively. The elemental composition of the natural raw diatomite and modified diatomite expressed as weight percentages of metal oxide was shown in Table 1. The main components of the natural raw diatomite are oxides of Si, Al and Fe, while the main components of the other samples activated with acid are oxides of Si and Al. The acid treatment reduces or eliminates all other oxides relative to SiO_2. From XRD patterns (see Fig.2-3), the natural diatomite showed a single diffuse band centered at about 23° 2θ which could be identified as biogenic hydrous amorphous silica and also showed quartz at 2θ = 26.6° and 20.9° and some clay minerals like kaolite, montmorillonite, etc. After calcination at 900°C, the XRD patterns look similar to raw diatomite whereas calcined diatomite at 1100°C showed a new peak at 21.8° 2θ as a result from crystalline phase of cristobalite. On the other hand, the sample, with acid before calcining at 1100 $^\circ$C, could eliminate some impurities, but cristobalite did not appear even at 1100°C. However, the sample still remained amorphous silica. This suggested that some impurities and/or sufficient amount of Si-OH in the amorphous silica matrix could promote the transformation of some amorphous silica into crystalline structure of cristobalite. It seemed that quartz still remained even when it was treated with hot acid. Our natural raw diatomite sample is yellow powder and becomes white color after acid treatment and becomes red brown color after calcinations. The red brown color appearance corresponds to hematile (α-Fe_2O_3), which exhibited two new

peaks at 33.50° and 36° 2θ. It is quite difficult from the XRD pattern of the natural

raw diatomite sample to indicate what type of compound contributing to its color.

However, yellow color of raw diatomite may be obtained from goethite (α-FeOOH) as

iron impurity, because its pigment is yellow. In addition to this, small broad band

appearing at about 35° 2θ may be attributed to akaganeite (β-FeOOH). After

calcinations FeOOH may be transformed into α-Fe$_2$O$_3$. The analysis of IR spectra

shown in Fig. 4. corresponded to the XRD results. The 3698 and 3621 cm^{-1} bands of

natural raw diatomite were attributed to OH vibration mode of hydroxyl groups of

kaolinite which were eliminated after calcination or acidification [9]. The broad band

centered around 3436 to 3439 cm^{-1} was attributed to OH vibration mode of the

physically adsorbed H$_2$O [10]. The IR band intensities of Si-OH or Al-Al-OH at 913

cm^{-1} and Si-O-Al related to the Al octahedral sheet found at 533 cm^{-1} was eliminated

with hot 6M H$_2$SO$_4$. The result indicates that clay minerals can be removed with hot

H$_2$SO$_4$. The band around 793 to 798 cm^{-1} (free silica and /or quartz) is always present

in all starting diatomite material and not affected by acid and thermal treatment [11].

The appearance of a new band at 616 cm^{-1} of diatomite calcined at 1100 °C was the

typical of critobalite [12]. The absorption bands of diatomite in the region of

stretching of vibration of Si-O are quite difficult to solve because of the band

interference of clay minerals and types of silica state. However, based on our curve-

fitting, the Si-O-T (T= Si or Al) stretch vibrations were assigned at around 1190 cm^{-1},

1090 cm^{-1} and 1030 cm^{-1}. It was found that the relative absorption band area at 1030

cm^{-1} was greatly reduced when natural raw diatomites were treated with heat or acid,

whereas the relative band area at 1090 cm^{-1} increased in all modified diatomites. The

relative band area at 1190 cm^{-1} for the samples treated with heat was rather similar to

the raw diatomite, but increased for the samples treated with acid. This may result

from the band at about 1030 cm^{-1}, which was assumed to correspond to the characteristic of clay minerals and/or less active silicate. The band was reduced after acid leaching and transformed after calcinations. After, reactive amorphous silica at about 1090 cm^{-1} and 1190 cm^{-1} was developed. Again, the ^{29}Si MAS NMR technique was used to provide the detailed information on the structure of the starting materials. The ^{29}Si MAS NMR spectra of natural raw diatomite and four modified diatomites were given in Figure 5. All the spectra were simulated using essentially Gaussian function as illustrated below the spectral traces in Figure 5. SiO$_4$ sites were labeled as Q^n, where n designated the number of bridging oxygen atoms (those shared with tetrahedral silicon). The ^{29}Si MAS NMR spectra of all samples consisted of 4 resonances at -95±0.5, -105±1.0, -109.5±1.0 and -113.0±1.0 ppm, except natural raw diatomite having two additional resonances at -86.1 and -92.2 ppm. The characteristic of Q^2 ([(OH)$_2$Si(OSi)$_2$]) was assigned at -86.1 and -92.2 ppm, Q^3 ([(OH)Si(OSi)$_3$]) at -95±0.5 and Q^4 ([Si(OSi)$_4$]) at, -105±1.0, -109.5±1.0 ppm and 113.0±1.0 ppm [13]. The percentage of Q^n compositions of all starting materials from the fitting were shown in Figure 6. It showed that Q^2 was eliminated after thermal and acid treatment. The total Q^4 increased continuously after calcination due to dehydroxylation in the order of D, D-C(900), D-C(1100), D-H$_2$SO$_4$ and D-H$_2$SO$_4$-C(1100). The Q^4 site at around -109 ppm is quite consistent and may be attributed to the crystalline silica phase.

After the hydrothermal process, the received products were identified by comparing the observed powder patterns with calculated ones reported in the collection of simulated XRD patterns for zeolites [14]. The relative intensity yields were obtained from the integrated XRD intensities of the major reflection for each zeolite. The XRD patterns of four series of analcime, cancrinite, Na-P1 and

hydroxysodalite obtained from the different starting materials, were shown in Figure 7-10, respectively. It is clear that under the optimal conditions for synthesizing each zeolite [7], the maximum intensity yield for all zeolites was obtained from the starting material of D-H_2SO_4-C(1100). The pure phase of analcime and cancrinite can be synthesized with almost all starting materials, whereas in the synthesis of Na-P1 and hydroxysodalite, quartz still remained and small amounts of other zeolitic mixed phases appeared. It showed that quartz might not involve in the synthesis under mild condition such as synthesis of Na-P1. To compare the effects of the starting materials to yield the maximum final products, the relative amount of zeolite crystallinity was represented by relative intensity yield (see Fig. 11) which was obtained from integrated XRD intensities of the major reflections with relative intensities more than 50%, such as at 2θ = 12.46°, 17.66°, 21.67°, 28.10° for zeolite Na-P1. In all cases of zeolitization, the relative intensity yields were found to be significantly high in the case of using D-H_2SO_4 and D-H_2SO_4-C(1100) compared to the others (see Fig. 10). Regardless of added $Al(OH)_3$ to adjust Si/Al in the synthesis which propably affected the zeolite formation, it may cause form iron content in the starting materials. There is a small amount of iron in D-H_2SO_4 and D-H_2SO_4-C(1100), about 0.5wt% as Fe_2O_3, but large amount in the others (about 5.8%). In cases of D-H_2SO_4 and D-H_2SO_4-C(1100), the maximum of total Q^4 sites which appeared in D-H_2SO_4-C(1100) gave the highest yields. It may result from D-H_2SO_4-C(1100) containing more Q^4 sites at -113 ppm. However, from the natural raw diatomite and two thermal treated samples, the relative intensity yields seemed to be not much different and they were much less than from the samples treated with acid. Even though these two starting materials contained more and more Q^4 as the temperature of calcination increased due to dehydroxylation [15]. It indicates that iron content affects significantly on the zeolite

crystallization [16]. Since the natural raw diatomite occurred with clay minerals and iron. Therefore, the calcination of natural raw diatomite affects inactive clay minerals to transform into active forms for zeolite synthesis, such as kaolinite to be metakaolinite or mullite depending on the temperature of calcinations. Consequently, the relative intensity yields of products obtained from D-C(900), D-C(1100) should be higher than from the natural raw diatomite. However, the present experimental results indicate that amount of iron impurity in natural raw diatomite plays an important role in zeolite synthesis. Amorphous silica containing more Q^4 sites attributes more in zeolitization. Hence, the step of iron elimination in starting raw diatomite is more reasonable to provide high zeolite crystallinity compared to the calcination step.

Conclusions

1. Thai natural raw diatomite collected from the main resource in Lampang Province contains quite high amount of iron impurity (about 5.8wt% expressed as Fe_2O_3) and some clay minerals especially kaolinite.

2. The thermal treatment step gives high amount of Q^4 sites in diatomite structure, depending on the temperature used.

3. Acid treatment can remove iron impurity and some clay minerals from natural raw diatomite and cause the amount of Q^4 sites to increase more than thermal treatment. However, the highest total Q^4 sites are still in the sample treated with hot acid and followed with calcinations at 1100 °C.

4. The crystalline zeolites obtained from the natural raw diatomite and two diatomites treated with heat are much less than from the samples treated with acid. This indicates the influence of iron content on the zeolite formation.

5. The yields from the natural raw diatomite and two calcined diatomites are not much different, even though both of them contain much more amount of the total Q^4 or Q^4 at -113 ppm than the natural raw diatomite, and they also contain some active forms of clay minerals. This indicates that the effect of iron content is significant.

6. In the case of two starting materials from which iron impurity were eliminated first, the highest yields were obtained from the sample after calcining at 1100 °C. It may result from more reactive silica corresponding to Q^4 sites at about -113 ppm. Nevertheless, we suggest that the modification process, eliminating the calcinations step, is more economical.

Acknowledgement

References

1. DW. Breck, *Zeolite molecular sieve.* (John Wiley and Sons, New York, 1974).

2. G. Biswajit, C.Dinesh, and B. Subhash, Ind Eng Chem Res, **33**, 2107 (1994).

3. D. Boukadir, N. Bettahar, and Z. Derriche, Analytical Chimica-Science Materials, **27**, 1 (2002).

4. V. Sanhueza, U. Kelm, and R. Cid, J Chem Technol Biotechnol, **78**, 485 (2003).

5. R. Goren, H. Gocmez, and C. Ozgur, Ceramics International, **32**, 407 (2006).

6. A. Chaisena, and K. Rangsriwatananon, Suranaree J Sci Technol, **11**, 289 (2004).

7. A. Chaisena, and K. Rangsriwatananon, Mater Lett, **59**, 1474 (2005).

8. RB. Owen, and C. Utha-arron, J Paleolimnol, **22**, 81(1999).

9. VC. Farmer, *Infrared spectra of minerals, Mineralogical Society.* (London, 1974).

10. P. Yuan, DQ. Wu, HP. He, and ZY. Lin, Appl Surf Sci, **227**, 30 (2004).

11. C. Belver, MAB. Munoz, and MA. Vicente, Chem Mater, **14**, 2033 (2002).

12. E. Gorlich, Ceram Int, **8**, 3 (1982).

13. E. Gunter, Trends Anal Chem, **8**, 343 (1989).

14. MMA. Treacy, and JB. Higgins, *Collection of simulated XRD powder patterns for zeolites.* (Elsevier Science Publishers, Amsterdam, 2003).

15. H. Halimaton, NMD. Mohd, E. Salasiah, and L. Endang, J Non-Crys Solids **211**, 126 (1997).

16. EI. Basaldella, SRM. Torres, and JC. Tara, Clays Clay Miner, **5**, 481 (1998).
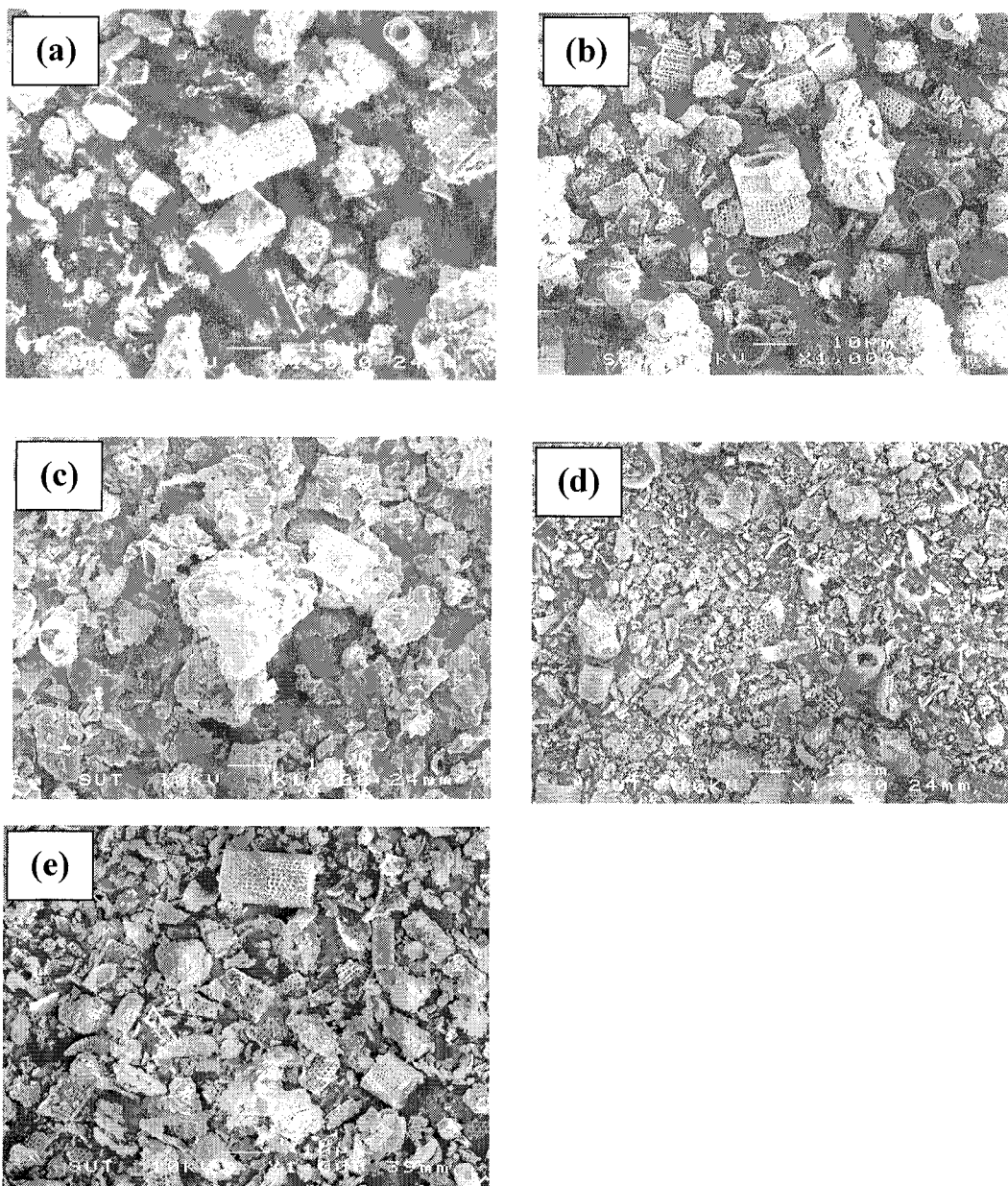
Figure 1. SEM with 10 kV and 1000 magnification of (a) D (b) D-C(900) (c) D-C(1100) (d)D-H$_2$SO$_4$ and (e) D-H$_2$SO$_4$-C(1100), respectively.

Table 1. The chemical compositions of starting diatomite materials determined by

XRF.

Diatomite starting material	Chemical content (% weight)							
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	MnO	TiO_2
D	71.90	14.60	5.78	1.95	0.17	0.69	0.01	0.51
D-C(900)	76.34	15.43	6.08	1.96	0.17	0.75	0.01	0.53
D-C(1100)	76.73	15.48	6.18	1.92	0.17	0.75	0.01	0.52
D-H_2SO_4	93.56	3.63	0.53	0.80	0.00	0.16	0.00	0.46
D-H_2SO_4-C(1100)	94.42	3.68	0.50	0.68	0.00	0.14	0.00	0.43
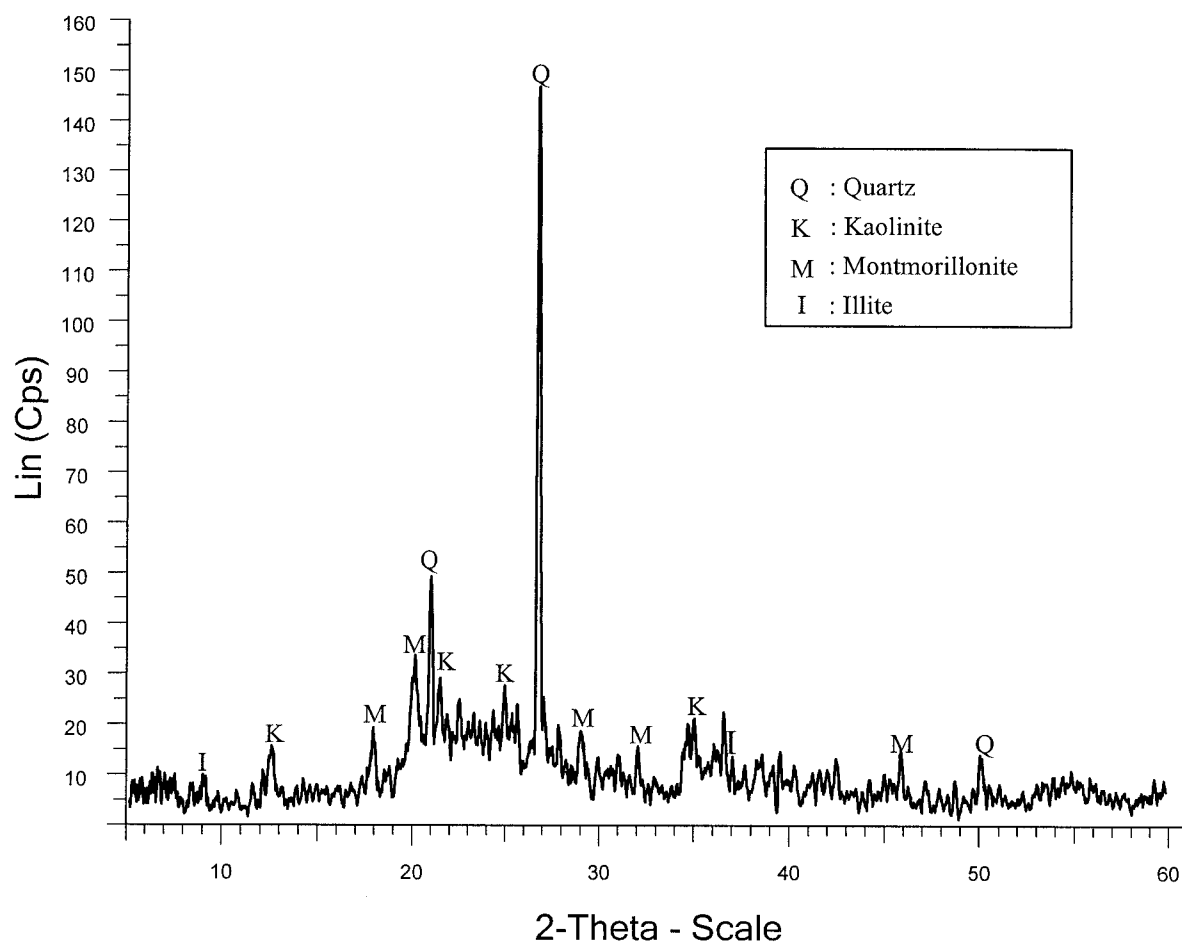
Figure 2. XRD pattern of the natural raw diatomite compared with the stand pattern

from JCPDS database.
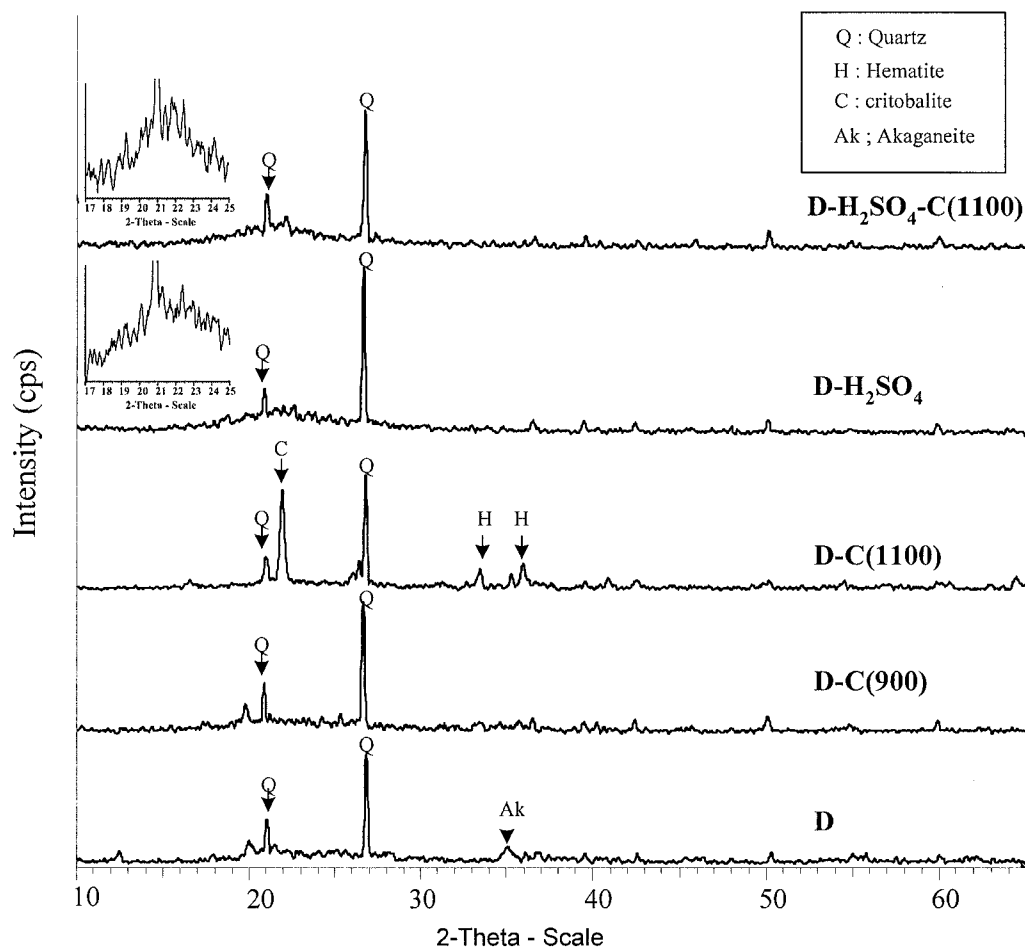
Figure 3. XRD pattern starting materials of (a) D (b) D-C(900) (c) D-C(1100) (d)D-H_2SO_4 and (e) D-H_2SO_4-C(1100), respectively.
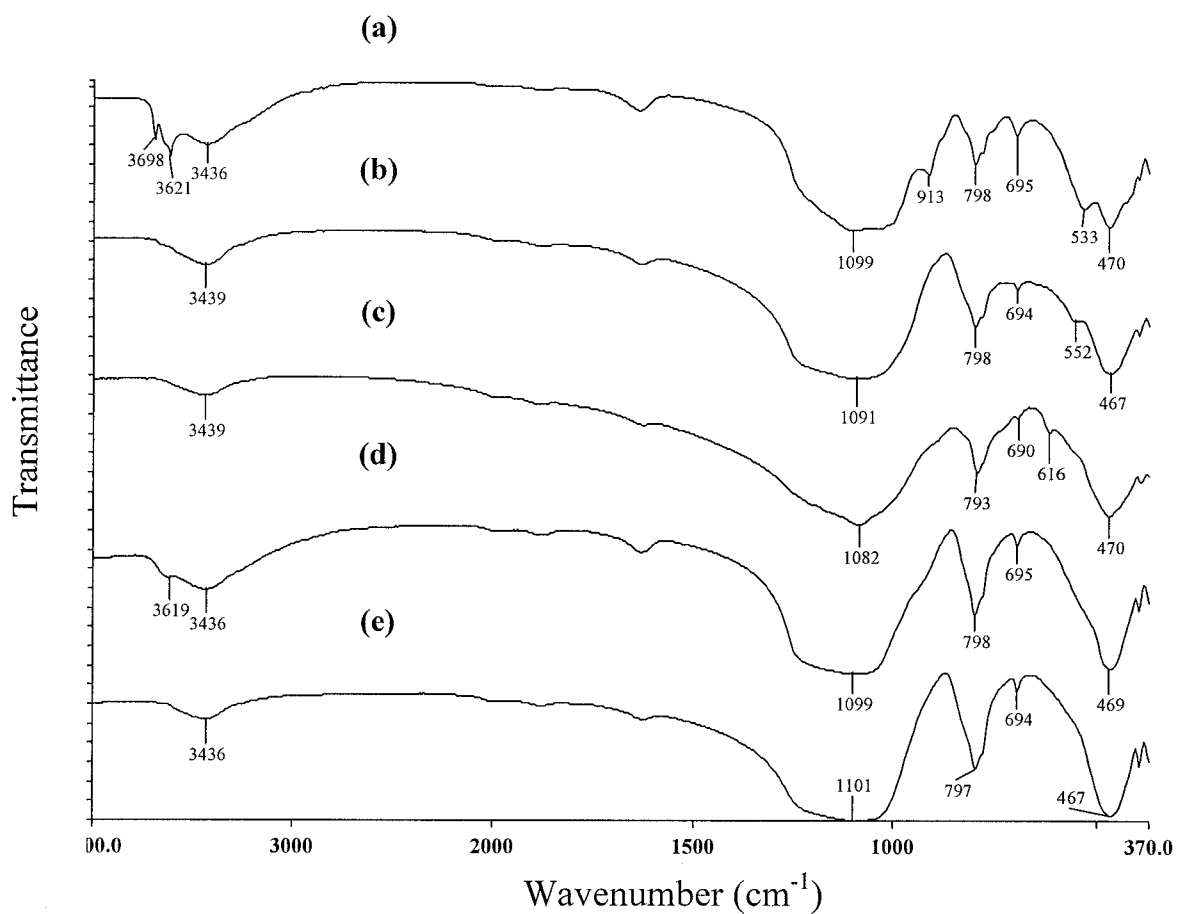
Figure 4. IR spectra starting materials of (a) D (b) D-C(900) (c) D-C(1100) (d)D-H₂SO₄ and (e) D-H₂SO₄-C(1100), respectively.
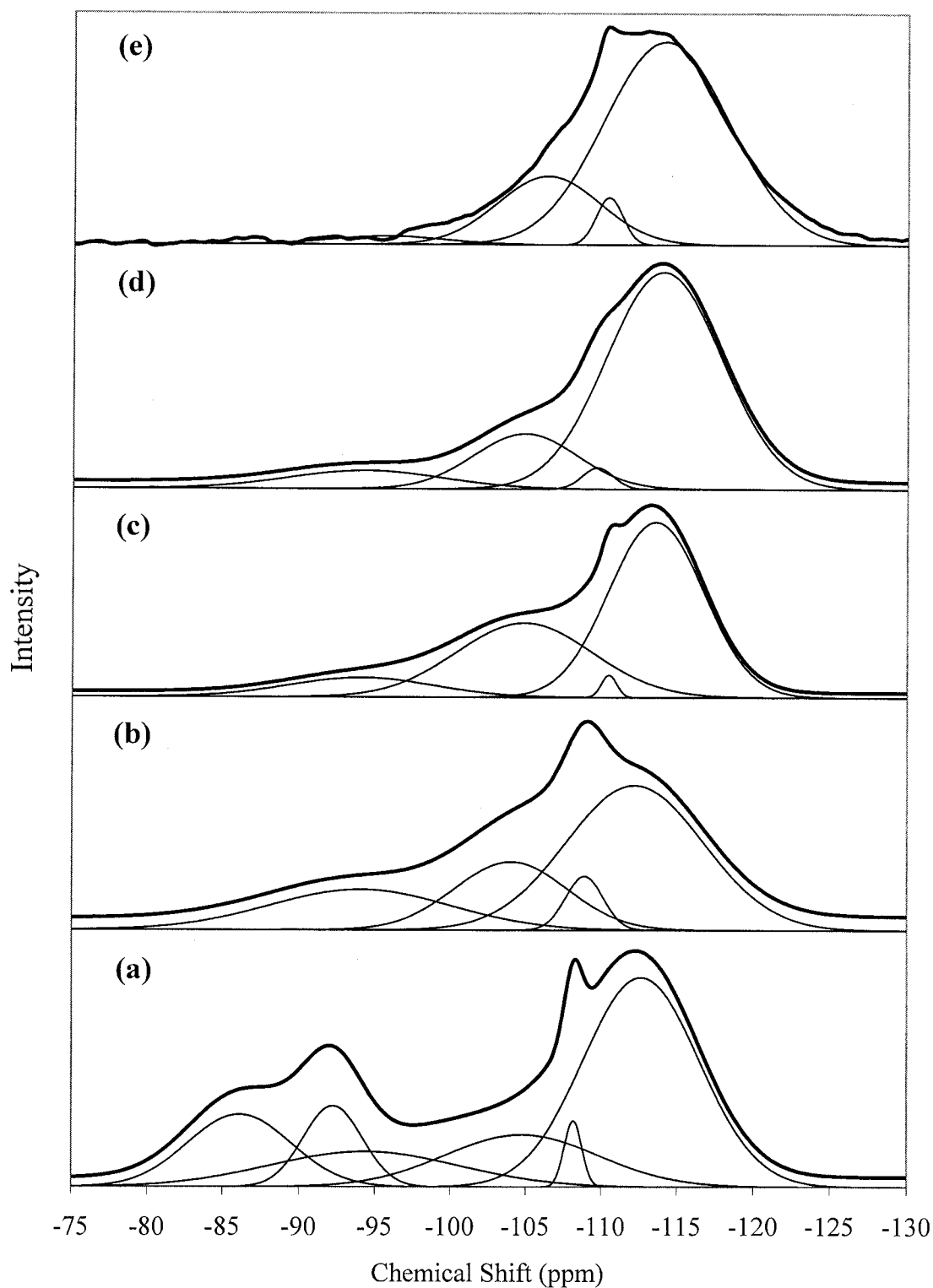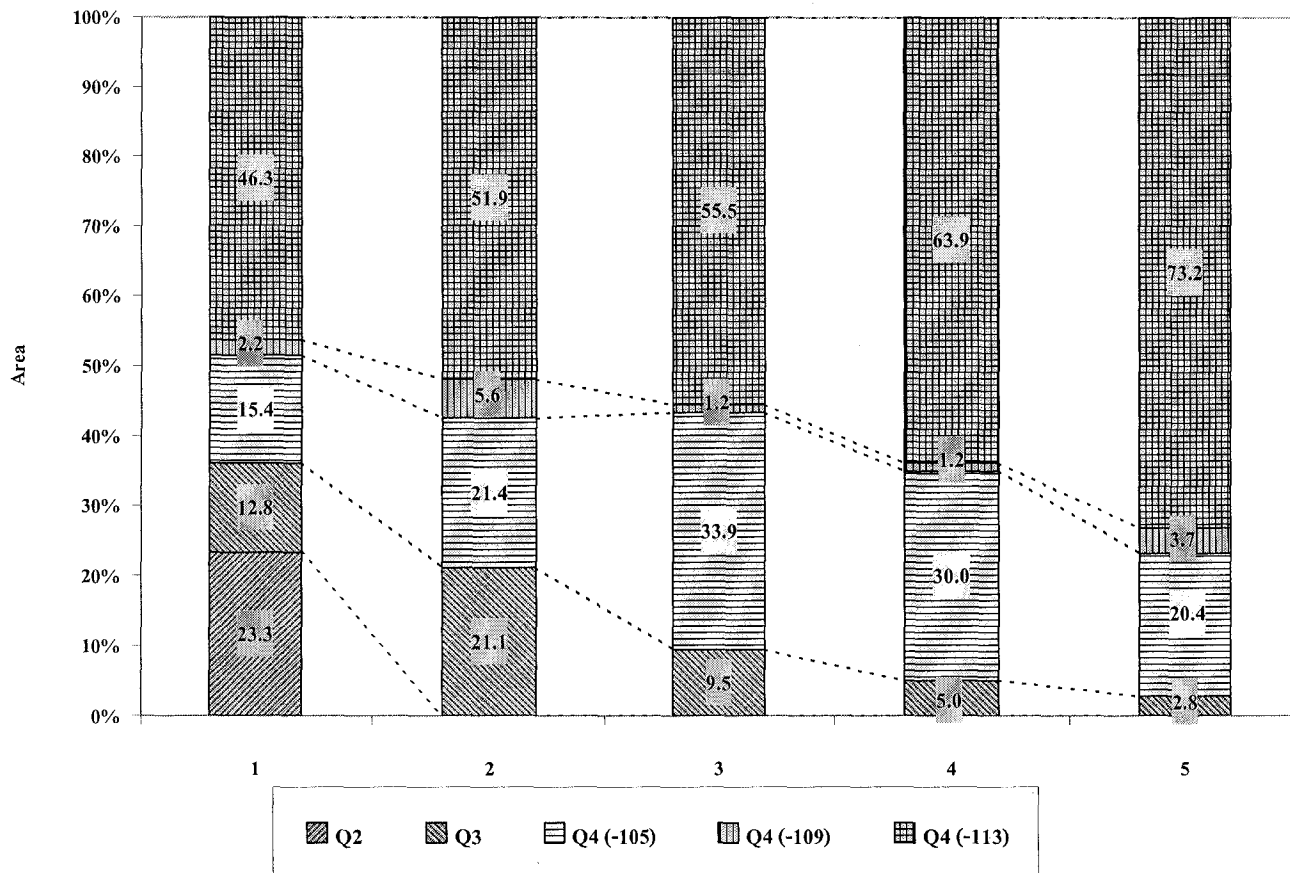
Figure 5. Experimental and simulated MAS ^{29}Si-NMR spectra (arbitrary Intensity

unit) starting materials of (a) D (b) D-C(900) (c) D-C(1100) (d)D-H_2SO_4 and (e) D-

H_2SO_4-C(1100), respectively.

Figure 6. The percent of Q^2, Q^3, Q^4 from simulation of the ^{29}Si MAS NMR spectra

of starting materials; (1) D (2) D-C(900) (3) D-C(1100) (4) D-H$_2$SO$_4$ and (5) D-

H$_2$SO$_4$-C(1100).
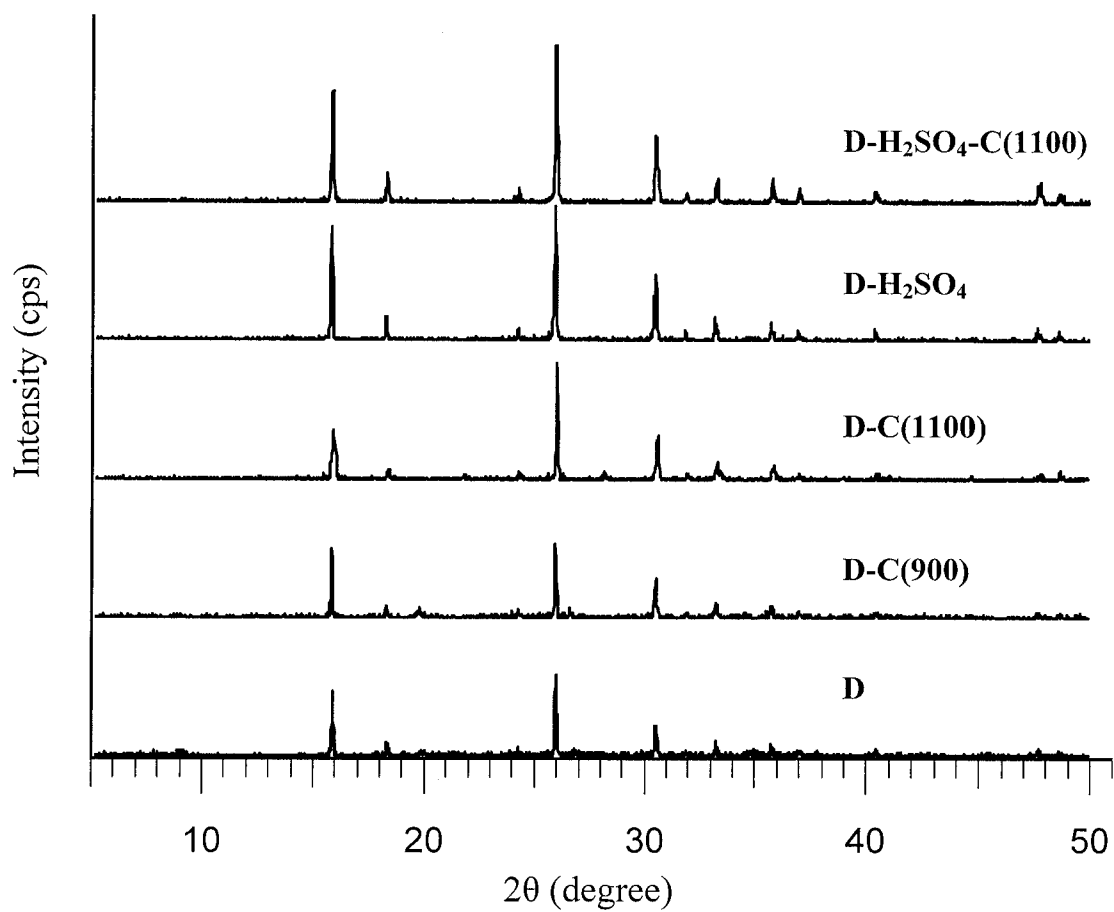
Figure 7. Analcime XRD intensity obtained from the reaction of each starting

materials activated at 140 °C with 10 % NaOH concentration, S/L=1/10 for 72 hours.
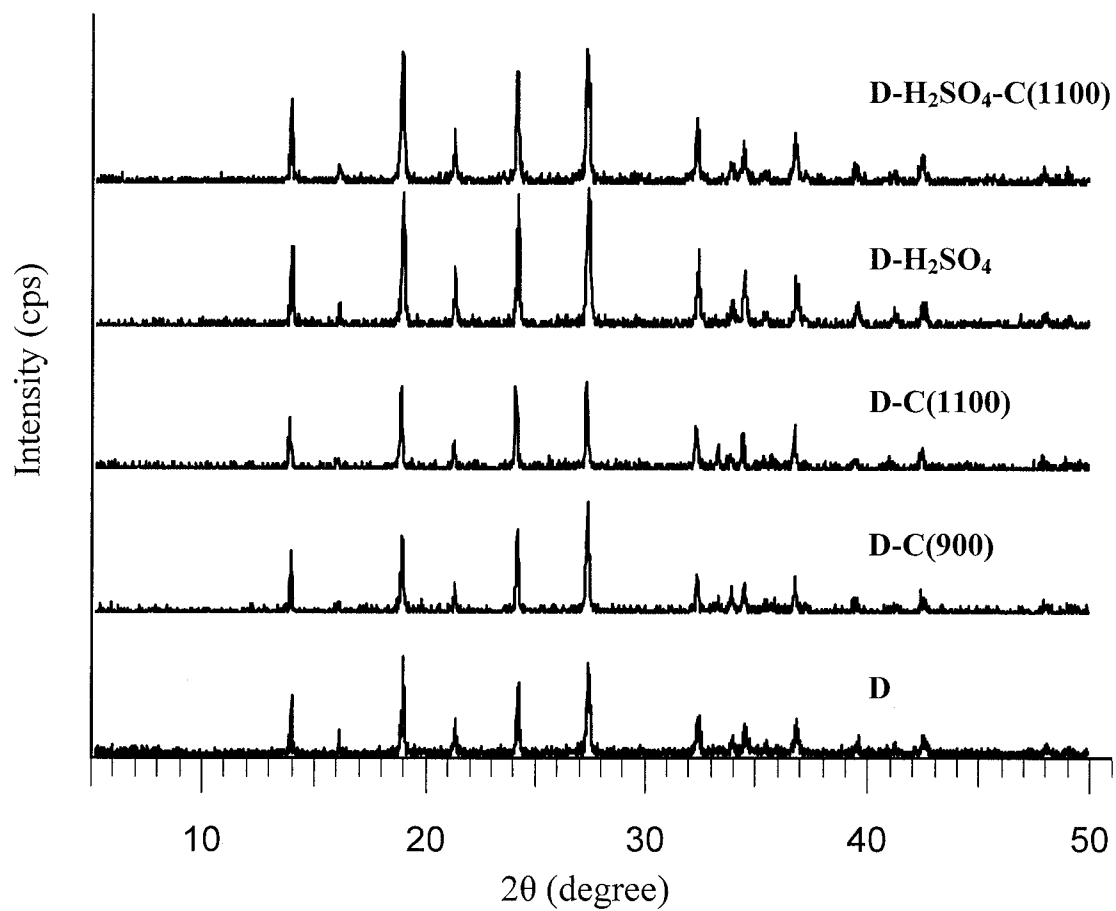
Figure 8. Cancrinite XRD intensity obtained from the reaction of each starting

materials activated at 180 °C with 20 % NaOH concentration, S/L=1/10 for 120 hours.
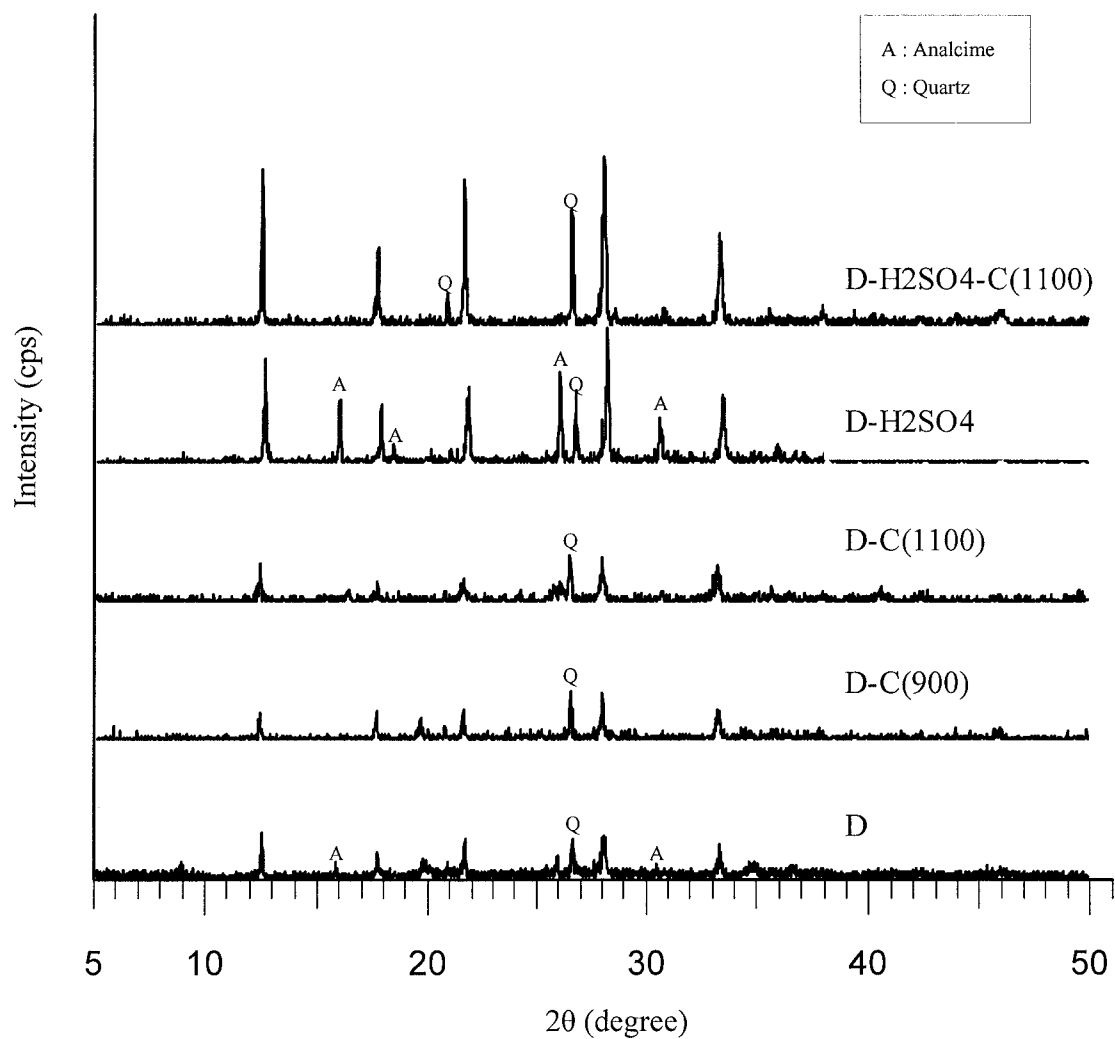
Figure 9. Na-P1 XRD intensity obtained from the reaction of each starting materials activated at 100 °C with 10 % NaOH concentration, S/L=1/10 for 72 hours and analcime mixed phase.
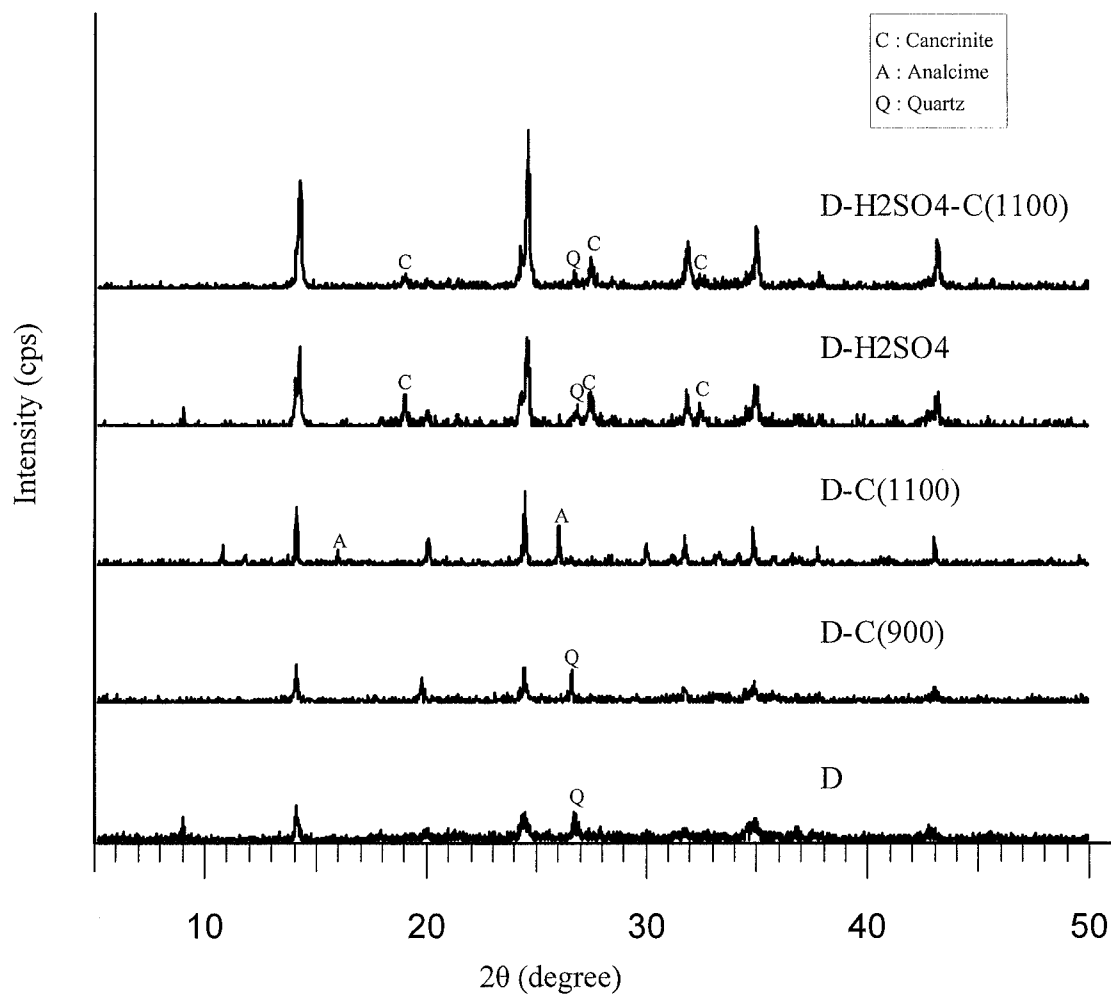
Figure 10. Hydroxysodalite XRD intensity obtained from the reaction of each starting

materials activated at 100 °C with 30 % NaOH concentration, S/L=1/10 for 120 hours
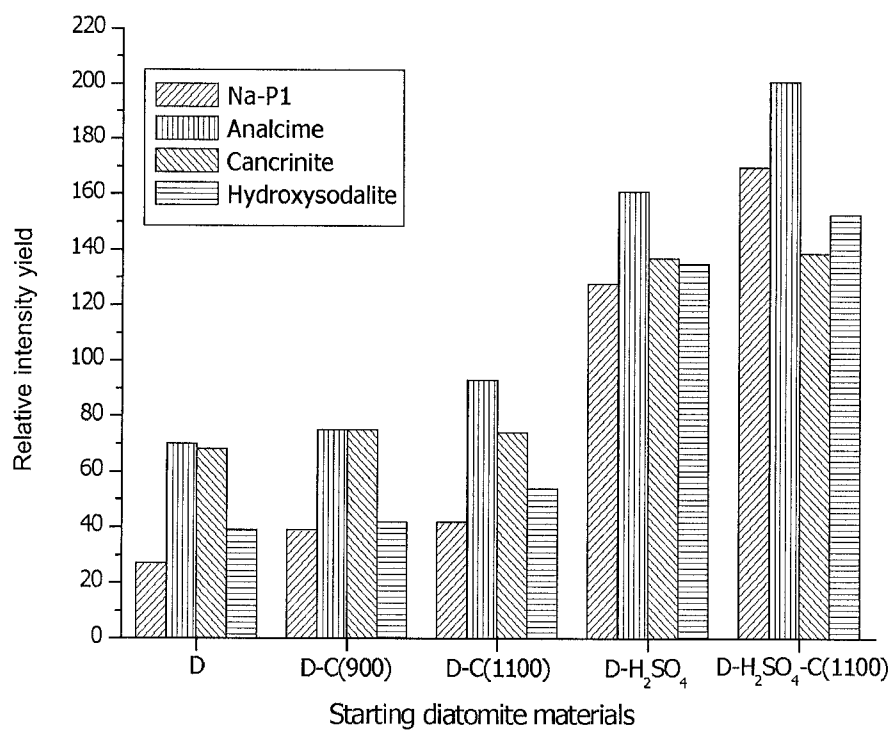
and other zeolitic mixed phases.

Figure 11. XRD intensity sodium zeolite yields obtained from the different starting diatomite materials.