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THE EFFECT OF REACTION TEMPERATURE AND
TIME ON THE ZEOLITISATION OF NATURAL KAOLINITE

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ABSTRACT

A locally avaliable kaolinite has been decomposed by the hydrothermal technique. Kaolinite activated at 600 ^{o}C was subjected to hydrothermal treatment with NaOH solution in aqueous media for different reaction times at various temperatures. Both kaolinite and the final experimental products after the treatment were characterized by XRD and FT-IR spectra. It has been concluded that calcination at 600 ^{o}C was the key step for the process and, metakaolinite, the calcined product from kaolinite, is a convenient starting material for the hydrothermal treatment. The influence of time and temperature on the reaction products were evaluated in terms of composition of the final products formed in the metakaolinite-alkaline system. Hydrothermal treatment of metakaolinite proved that the reaction products were found to be zeolite NaA and hydroxy sodalite.

KEYWORDS: kaolinite, metakaolinite, hydrothermal treatment, zeolite NaA, hydroxy sodalite.

INTRODUCTION

Kaolinite, having a chemical formula $Al_2O_3.2SiO_2.2H_2O$, is one of the most versatile industrial minerals and is used extensively for many applications. Its structure consists of a single silica tetrahedral sheet and a single alumina octahedral sheet combined to form the unit kaolinite layer [1]. Reactions of kaolinite at elevated temperatures have found many applications. In recent years there has been considerable interest in the use of metakaolinite, obtained by heating kaolinite, as a starting material in zeolite synthesis. If the transformations from kaolinite to zeolites or to feldspathoids involve structural inheritance, it may be reasoned that they would be facilitated by reactions which reduce the coordination of Al from 6 to 4 and result in a network of linked $(Si,Al)O_4$ tetrahedra [2]. Thermal and structural characterization of Brazilian South-Eastern kaolinitic clays were investigated by Souza et al. [3].

Zeolites are crystalline aluminasilicates with uniform pores, channels and cavities. The unique properties of low silica zeolites (zeolites NaA (4A) and NaX) such as ion exchange capacity, sorption and catalytic activity, make them ideal for various industrial applications [4]. Zeolite NaA has been accepted as a better water softening agent in detergent formulations because of its high eco-friendliness, so brightness studies on kaolin based Zeolite NaA has been discussed and investigated [1]. Zeolites have generally been synthesized from sodium alumino silicate gel prepared from various silica and alumina sources. Kaolinite has been reported as an ideal, combined source for silica and alumina for the synthesis of zeolites [5]. Formation of zeolite from the system $Na_2O-Al_2O_3-SiO_2-H_2O$ in alkaline medium (pH> 10) was studied [6]. Novembre et al. [7] investigated the synthesis of zeolitic minerals (Na-X and HS) using natural materials (naturally zeolitised alkaline volcanic rocks and "Tripoli"). Synthesis was conducted at hydrothermal conditions (80 ^{o}C) by use of alkaline silicates ($Na_xSi_yO_z$) and alkaline aluminates ($Na_xAl_yO_z$). They showed that Na-X zeolite synthesis begins after 5 h and reaches its crystallization climax at 18 h, with a broad field of existence (about 500 h) of Na-X phase [7]. Furthermore, coal fly ash was modified to zeolitic materials by hydrothermal treatment at 90 ^{o}C. The zeolite synthesis was studied as a function of the mole ratio of Na_2O/SiO_2 in the reaction mixtures. The results showed that NaP_1 zeolite is obtained when Na_2O/SiO_2 mole ratio was 0.7. Hydroxy sodalite is the dominant zeolite phase in modified fly ash treated with a higher Na_2O concentration solution (Na_2O/SiO_2=1.3) [8]. The synthesis of Zeolite NaA from kaolinite essentially consists of two steps:

i) Thermal pre-activation of the kaolinite to get a dehydroxlated X-ray product called metakaolinite (metakalinisation) and ,

ii) Hydrothermal reaction of metakaolinite with aqueous alkaline solution (Zeolitisation).

It has been reported that the yield of Zeolite NaX produced from metakaolinite is influenced by the firing temperature of the kaolinite precursor. It has been ob-

served that ancillary minerals like quartz and mica present in the kaolinite remain intact during metakaolinisation and further conversion to Zeolite NaA [9]. Zeolite 4A has been recognised as a substitute for sodium tri-polyphosphate (STPP), which is the traditional water softening agent in detergents [1]. A report commissioned from the consulting firm WRc by the European Commission has confirmed that a proposed ban on phosphates in detergents is justified on both environmental and economical grounds. Zeolite A should be used to replace phosphates such as sodium tripolyphosphate (STPP) in detergents. Phosphates in household detergents can contribute around 50% of the bioavailable phosphorus that helps to create toxic algal blooms in waterways [10].

We have previously studied the effects of alkali concentration and solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural kaolinite [11]. In this study we have found the following results;

The higher NaOH concentration results in a higher ratio of hydroxy sodalite formation in the reaction mixture. The product with 4N NaOH consisted of mainly zeolite NaA while hhydroxy sodalite formation increased in the product through 6 and 8N NaOH solutions.

With solid/liquid ratio 1.25g/25ml, 2.50g/25ml and 5.00g/25ml, the product was mainly zeolite NaA, while hydroxy sodalite formation was observed with 7.50g/25ml ratio.

The present paper deals with the reaction of kaolinite with NaOH solutions under hydrothermal conditions. The influence of metakaolinisation temperature, reaction time and temperature have been investigated. All reactions were carried out under hydrothermal conditions and the products obtained at different experimental conditions have been characterized by XRD (X-Ray Powder Diffraction) and FT-IR (Fourier Transform Infra Red Spectroscopy) analyses.

MATERIALS AND METHODS

Raw Material

The kaolinite used was a natural geological sample was obtained from Kalemaden Ltd., Balikesir which is the one of the largest kaolinite processors in Turkey. It was grounded and sieved to 106 μm particle size and analysed by XRF (X-Ray Fluorescence Spectroscopy ARL-9400-XP). The chemical composition of kaolinite is given in Table 1 and the XRD pattern of kaolinite is shown in Figure 1. The XRD analysis indicated that the typical natural clay materials from the ceramic industries in the west of Turkey are mainly composed of kaolinite with muscovite and quartz as impurity. The sodium hydroxide used as main reactant was of Merck grade.

TABLE 1 - Chemical analysis of the kaolinite used.

Component	Weight (%)
SiO_2	48.70
Al_2O_3	36.73
TiO_2	0.33
Fe_2O_3	0.57
CaO	0.32
MgO	0.27
Na_2O	0.01
K_2O	0.88
LoI *	12.59

*: Loss of Ignition

Metakaolinisation

The kaolinite with a particle size of 106 μm was thermally activated in a muffle furnace at 600 °C for 2 h. The metakaolinite formed after calcination was kept in a polyethylene bottle and characterized with FT-IR and TG/DTA (Thermo-Gravimetric/Differential Thermal Analyzer) analyses.
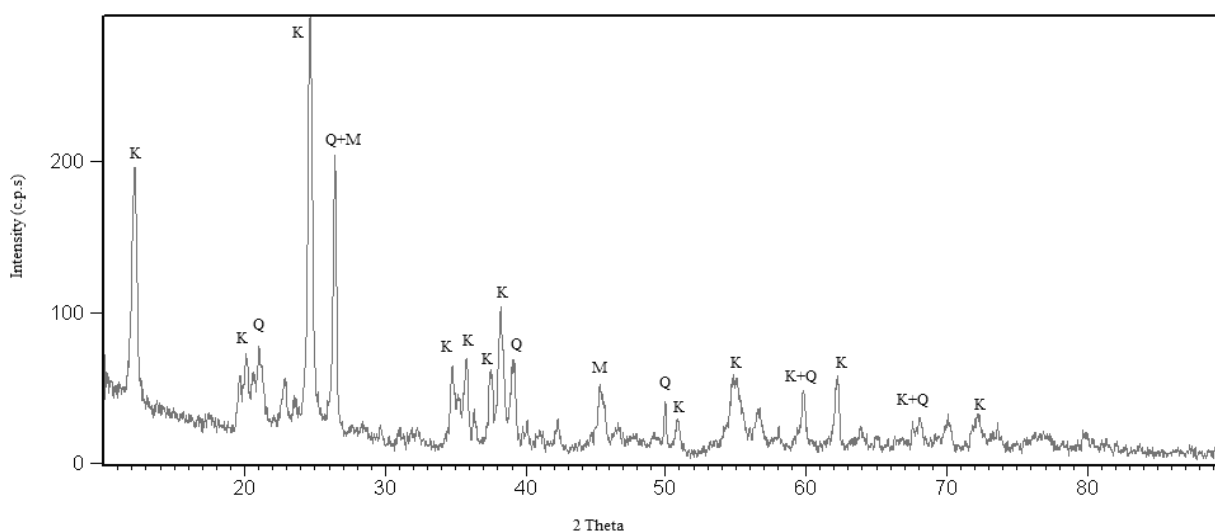

FIGURE 1 - XRD pattern of kaolinite sample (K=Kaolinite, Q=Quartz, M=Muscovite).

Zeolitisation

In order to study the effect of the reaction time and temperature on the products, the calcined kaolinite samples were mixed with 25 mL of 6 M NaOH solutions. Solid:liquid ratio of all samples were 1.25 g/25 mL and, no ageing was carried out. The reaction mixtures (kaolinite + 25 mL of 6M NaOH) were then heat-treated in separate identical sealed bottles in an air oven for 2, 4 and 12 h at 105 $^{\circ}$C to investigate the effect of reaction time. To examine the effect of temperature, the reaction mixtures (kaolinite + 25 mL of 6 M NaOH) have been heat-treated at 105, 95 and 85 $^{\circ}$C for 2 h in a muffle furnace. The reaction parameters are presented in Table 2. The resulting solutions were filtered and washed with distilled water and ethyl alcohol. The products were dried at 105 $^{\circ}$C for 2 h in a drying oven. All final products were encoded as P1 – P5 (P1-P5 as coded for the Product1- Product5) as given in Table 2 and characterized by using XRD and FT-IR techniques.

Characterization

Powder XRD patterns of kaolinite, intermediates and products were recorded on a X'Pert PRO Panalytical diffractometer with CuKα radiation (40kV, 30 mA and λ= 1.5405 Å). The phases were identified from peak positions of products comparing them with the reference data from the ICDD (International Centre for Diffraction Data) database. FTIR spectra were obtained with a Perkin-Elmer BX 2 IR spectrophotometer in a scanning range 4000-400 cm^{-1} using KBr pellets. Thermal analyses were executed with a Perkin-Elmer Diamond TG/DTA instrument.

RESULTS AND DISCUSSION

Thermal Treatment of Kaolinite Sample

The aim of the thermal treatment of kaolinite was to prepare the samples for subsequent hydrothermal treatment of kaolinite in order to convert to zeolite. Although the thermal behaviour of kaolinite has been subjected of several studies it would be useful to discuss briefly the effect of heat treatment on the structure of kaolinite.

Figures 2 and 3 present the DTA/TG curves of the original kaolinite and calcined kaolinite at 600 $^{\circ}$C used in this study, respectively.

With differential thermal analysis (DTA) two endothermic peaks at 120 °C due to the removal of physically adsorbed moisture, and at 550–650 °C due to the loss of structural water and an exothermic peak at 980 °C (first exotherm) related to crystallization of Al–Si spinel phase at the medium scale of temperature were observed.

As discussed in our previous study in detail, in the first step of transformation, kaolinite forms metakaolinite with loss of structural hydroxyl groups during the occurrence of endotherm as noted in DTA. In the second step, metakaolinite decomposes and forms spinel phase generally during heating around the first exothermic peak temperature [11]. However it would be useful and gives a tool for understanding the changes during the heating to discuss the IR spectra and XRD patterns of the products obtained during the reactions.
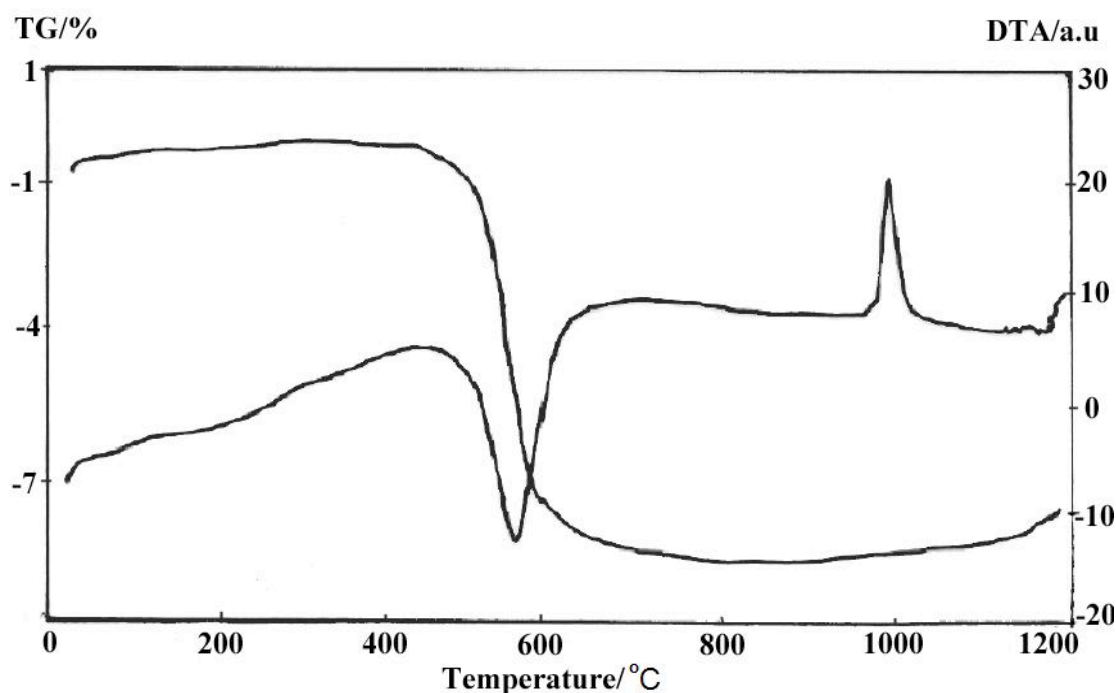

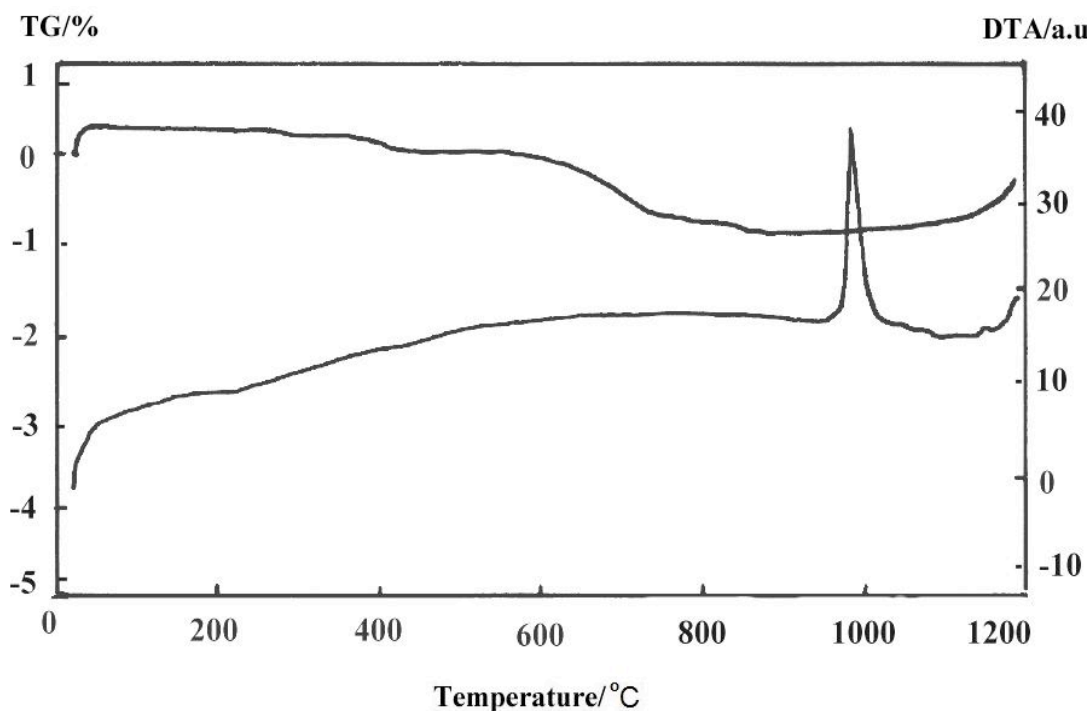**FIGURE 2 - DTA/TG curve of uncalcined kaolinite.**

FIGURE 3 - DTA/TG curve of kaolinite calcined at 600 °C.

Figure 4 presents the IR spectra of the calcined and uncalcined kaolinite. The IR spectra reflect the structural degradation of the clay components and formation of phases during the thermal treatment. In Figure 4, the band located at 3696 and 3621 cm^{-1} is related with the OH$^-$ stretching which has been reported in Mg and Al-enriched dioctahedral smectite [12]. Reported IR data for the dioctahedral smectites show a band near 1030 cm^{-1} due to Si-O stretching vibrations of the tetrahedral layer and bands at 538 and 467 cm^{-1} are due to the Si-O-Al (octahedral) and Si-O-Si bending vibrations, respectively [13]. The weak absorption band at 621 cm^{-1} can be identified as the perpendicular vibration of the octahedral cations (R-O-Si) (R= Al, Mg, Li) where the intensities are weak [14] and the band at 798 cm^{-1} is attributed to Si-O-Si stretching vibration [15].

Some drastic changes were observed for the kaolinite samples calcined temperature at 600 °C in Figure 4-b. The broad band of metakaolinite, located at 798 cm^{-1} was assigned to the Al–O bonds in Al$_2$O$_3$. The vibration band at 1072 cm^{-1} for metakaolinite is due to the Si–O bonds in SiO$_2$. These specific bands confirmed the calcination of kaolinite to metakaolinite phase.

Evaluation of Products

Although the heating temperature for the metakaolinisation was reported to be 900 °C in most studies [9], the experimental results showed that kaolinite is subjected to structural deformations at 600 °C and therefore it is expected to be convenient to use the sample obtained by thermal treating at 600 °C in further experiments of zeolitisation.

Experimental conditions were given in Table 2, in order to observe the effect of reaction time and temperature parameter on the zeolitisation of metakaolinite. The IR spectra of the products which were obtained under different conditions for different reaction times and temperature parameters are shown in Figures 5 and 6.

The range below 1200 cm^{-1} was studied in relation to structural properties of the zeolite framework. The IR spectra of synthesized samples obtained after 2 h reaction times are almost consistent with that of reference zeolite NaA and the literature referred [9].

Band assignments have been given in terms of structure unspecific SiO$_4$, AlO$_4$ vibrations and vibrations of larger entities which are dependent on the actual zeolite structure [16]. In Figure 5 and 6 the broad bands at about 3400 and 1650 cm^{-1} are attributed to zeolitic water [16]. The band of metakaolinite at 1072 cm^{-1} was shifted to 996 cm^{-1} (Figure 5) which could be assigned to anti-symetric stretching of T-O bonds (T: Si or Al) in alumina silicates with zeolite or sodalite structure. Absorptions at 996 and 665 cm^{-1} are the characteristic of the (Si, Al)O$_4$ tetrahedral frameworks of zeolitic structures [2]. The weak band at about 553 cm^{-1} could point to beginning of the crystallization of a zeolite with double rings [8].

At the curve (c) in Figure 5, in the spectral zone 750-650 cm^{-1} there are three well defined bands at 733, 709 and 665 cm^{-1}; they are in good agreement with the bands

at 734, 707 and 664 cm^{-1} for hydroxy sodalite zeolite reported by Flaningen et al. [18]. Absorption at 465 cm^{-1} refers to Si-O-Si bending vibration which is present in the IR spectra for all experimental products. In the sector 500-420 cm^{-1}, related to deformation vibration of T-O-T bond [18] there is evidence of two well defined symmetric bands at 461 and 435 cm^{-1}; they are in consistent with reported values for hydroxy sodalite zeolite at 463 and 435 cm^{-1} [18].

XRD pattern of reference zeolite NaA was given in Figure 7 for comparison of products obtained in the experiments. XRD patterns of P1, P2 and P3 products obtained from experiments at 105 °C with 6 M NaOH solutions for 2, 4 and 12 h, respectively, are given in Figures 8-10. The XRD patterns confirmed the presence of the crystalline phase of zeolite NaA and hydroxy sodalite which was formed in the products, P1, P2 and P3. The positions and relative intensities of the diffraction peaks for products obtained under the conditions given in Table 2 are consistent with the reference data of zeolite NaA (ICDD 39-222) and of hydroxy sodalite (ICDD 11-401) and with XRD pattern of reference zeolite NaA (Figure 7). The quartz which has already been in natural kaolinite is also present in all the products without reacting with any reagents (ICDD 33-1161). When compared the XRD patterns (Figures 8-10), the peak intensities of hydroxy sodalite phase increased with increase in reaction time. For long reaction times (12 h) it was clearly seen that the, zeolite NaA has almost converted to hydroxy sodalite (Figure 10) since the XRD peak intensities of hydroxy sodalite increases in that progress.
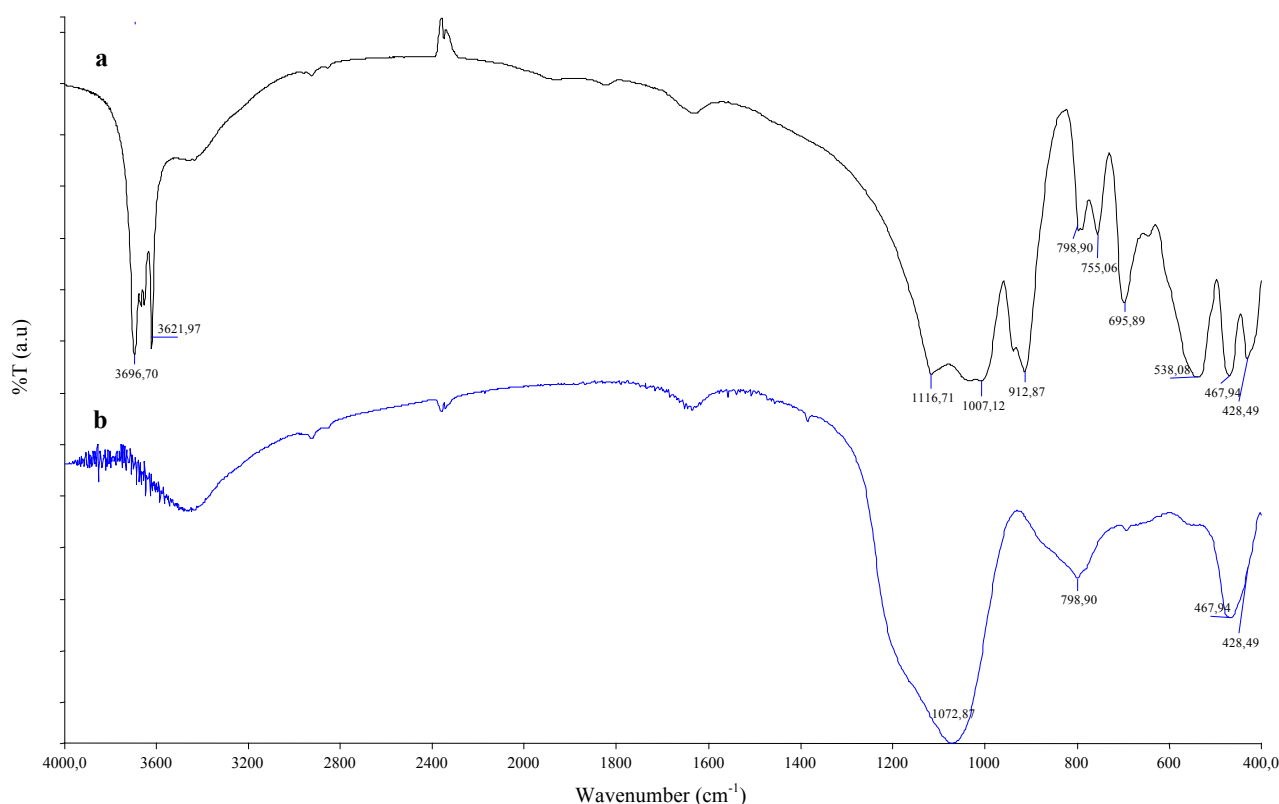

FIGURE 4 - IR Spectra of ; (a) kaolinite uncalcined, (b) kaolinite calcined at 600 ºC.

TABLE 2 - Reaction parameters used for hydrothermal treatment of kaolinite with NaOH solutions.

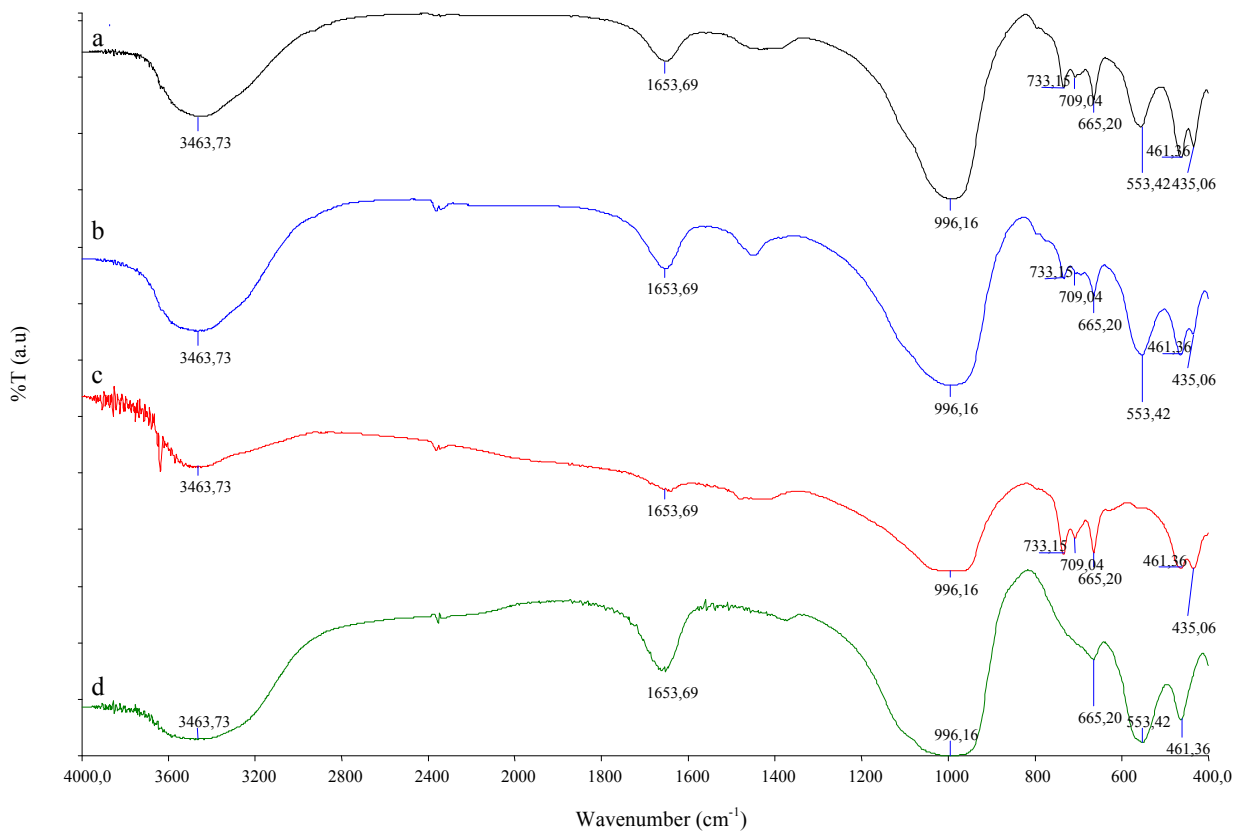| Calcination Temp./Time (°C/h)	NaOH conc. (M)	Reaction Temp.(°C)	Reaction Time (h)	Product Code
600/2	6	105	2	P1
600/2	6	105	4	P2
600/2	6	105	12	P3
600/2	6	95	2	P4
600/2	6	85	2	P5

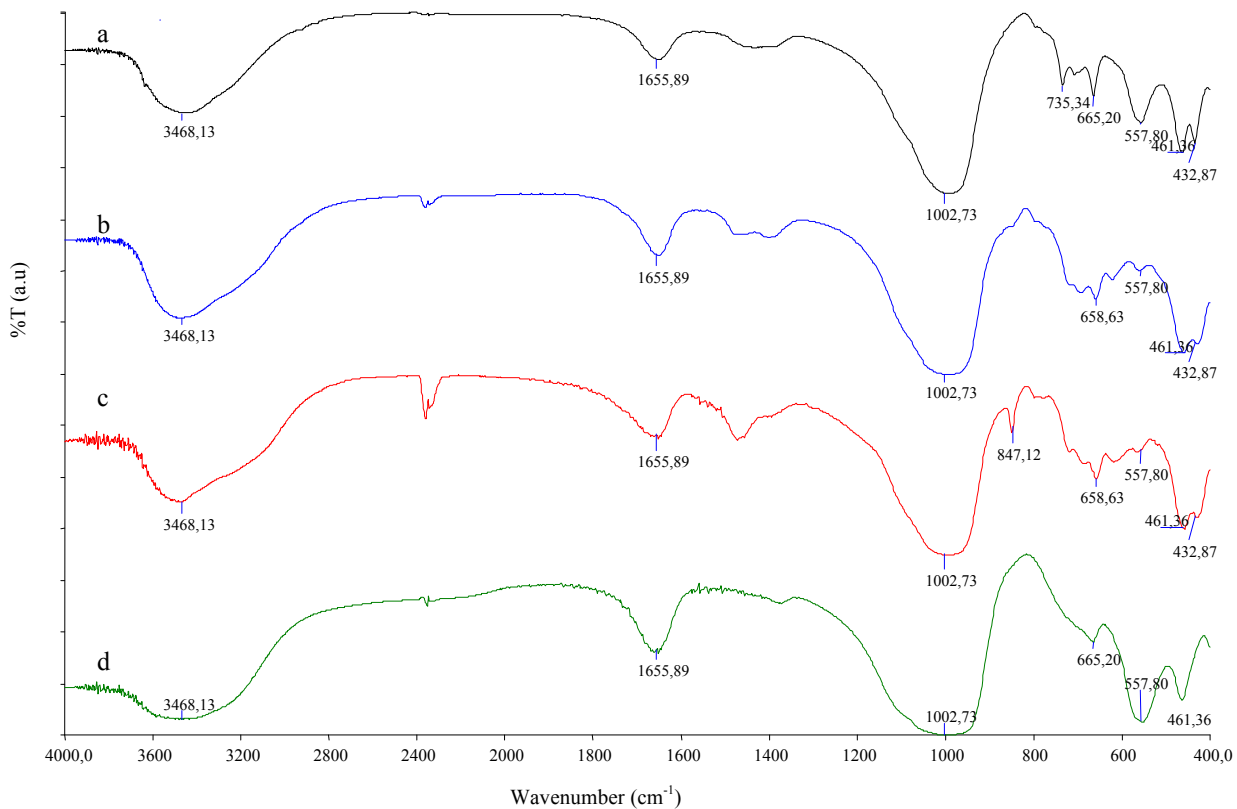**FIGURE 5 - IR Spectra of (a) P1 (b) P2 (c) P3 (d) Reference zeolite NaA.**

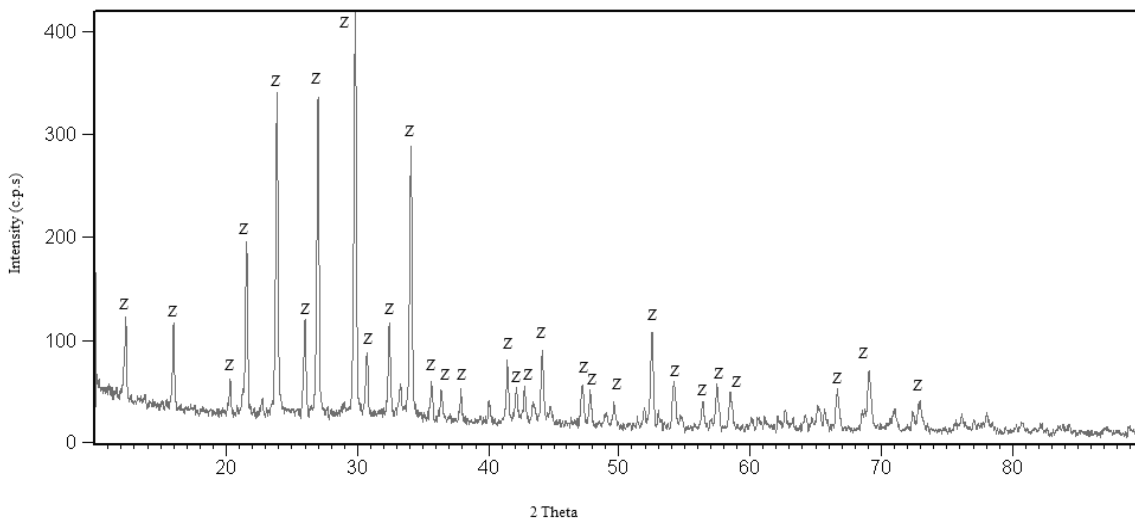**FIGURE 6 - IR spectra of (a) P1, (b) P4, (c) P5, (d) Reference Zeolite NaA.**

FIGURE 7 - XRD pattern of reference Zeolite NaA (Z=Zeolite NaA).
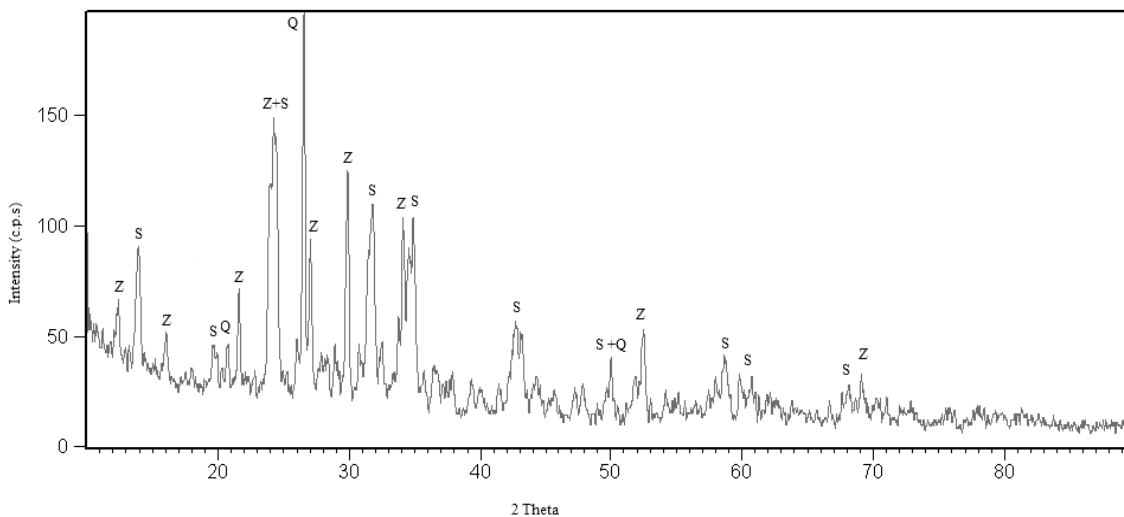

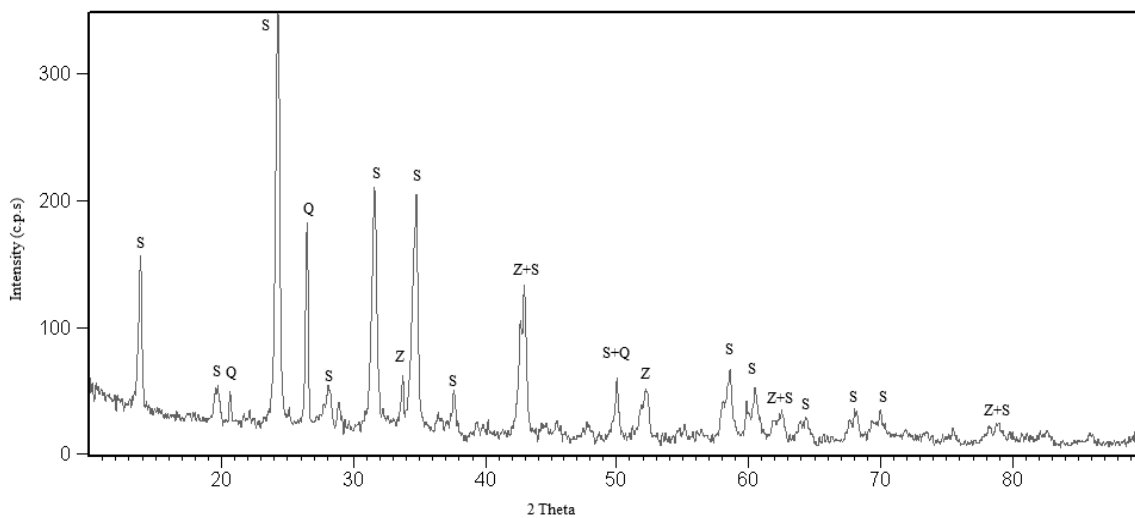**FIGURE 8 - XRD pattern of P1 (Z=Zeolite NaA, S=Hydroxy Sodalite, Q=Quartz).**

FIGURE 9 - XRD pattern of P2 (Z=Zeolite NaA, S=Hydroxy Sodalite, Q=Quartz).
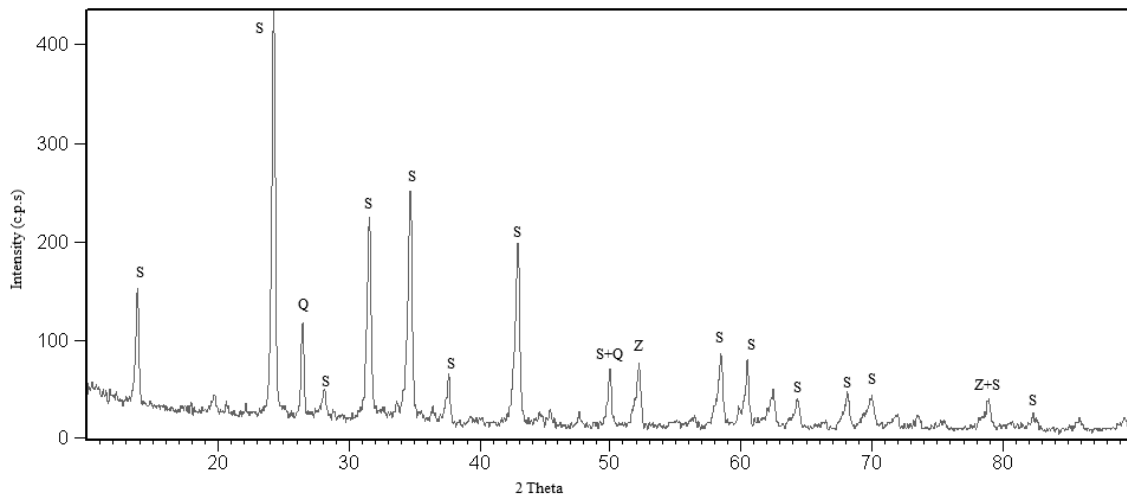
FIGURE 10 - XRD pattern of P3 (Z=Zeolite NaA, S=Hydroxy Sodalite, Q=Quartz).
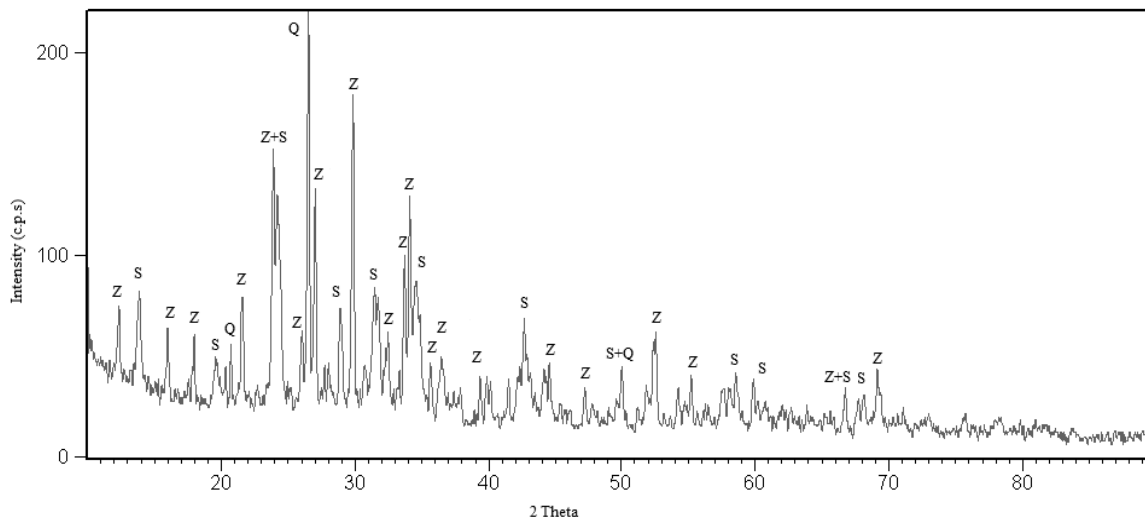

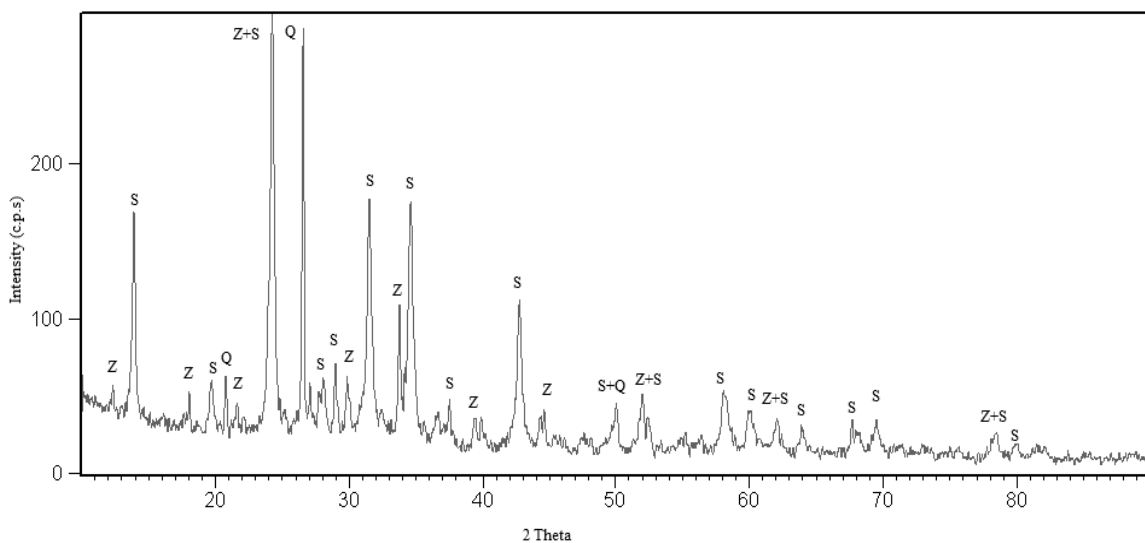**FIGURE 11 - XRD pattern of P4 (Z=Zeolite NaA, S=Hydroxy Sodalite, Q=Quartz).**

FIGURE 12 - XRD pattern of P5 (Z=Zeolite NaA, S=Hydroxy Sodalite, Q=Quartz).

The phases of the products obtained at different temperatures were evaluated with the XRD technique. The XRD patterns of the samples (P1, P4 and P5) (Figures 8, 11 and 12) which are synthesized at 105, 95 and 85 ^{o}C, show that there was no significant changes in the formation of sodalite and zeolite phases for the reactions occured at 105 and 95 ^{o}C. But at 85 ^{o}C it was clearly seen that the sodalite formation increased in great quantity.

CONCLUSIONS

The conclusions after hydrothermal process could be summarized as follows;

i) In order to activate a natural kaolinite, temperature value of 600 ^{o}C seems to be the most convenient one for the calcination of kaolinite before hydrothermal treatment. The activated material called metakaolinite was ready to react with alkaline solutions.

ii) Zeolite NaA can be obtained from kaolinite by hydrothermal method with 6M NaOH solution at 105 ^{o}C for 2, 4 and 12 h. But as the reaction time increases, hydroxy sodalite was observed to form with the zeolite NaA.

When the reaction temperature was decreased from 105 to 85 ^{o}C, the hydroxy sodalite formation was increased. So the hydrthermal reaction temperture 105 ^{o}C should be preferred for the synthesis of zeolite NaA from the natural kaolinite.

ACKNOWLEDGEMENTS

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