

2016 - Volume: 17 Number: 5

Page: 823 - 829

DOI: 10.18038/aubtda.279851

Received: 18 May 2016   Revised: 28 October 2016   Accepted: 07 November 2016

---

## INVESTIGATION OF THE INFLUENCE OF HEAT TREATMENT ON THE STRUCTURAL PROPERTIES OF ILLITE-RICH CLAY MINERAL USING FT-IR, $^{29}\text{Si}$ MAS NMR, TG AND DTA METHODS

Burcu ERDOĞAN ALVER<sup>1</sup>, Gökhan DİKMEN<sup>2</sup>, Özgür ALVER<sup>1,\*</sup>

<sup>1</sup> Department of Physics, Science Faculty, Anadolu University, 26470, Eskişehir, Turkey

<sup>2</sup> Central Research Laboratory, Eskişehir Osmangazi University, Eskişehir, Turkey

### ABSTRACT

In the production and development of building materials, fired clays are the center of major interest. They particularly play an important role in the building industry. Henceforth, in order to analyze the effect of heat treatment on illite-rich natural clay samples from Turkey, they were exposed to heat at various temperatures between 350-650 °C. The results of the heat treatment on the structure of the samples were followed by Fourier transform infrared (FT-IR), solid state magic angle spinning nuclear magnetic resonance (MAS NMR) thermogravimetric (TG) and differential thermal (DTA) analyses techniques and all the findings were explained and discussed in brief.

**Keywords:** DTA, ILLITE, FT-IR,  $^{29}\text{Si}$  MAS NMR, TG

---

### 1. INTRODUCTION

Illite is a micaceous clay mineral which was named by Grim et al. [1]. The structure is a 2:1 layer in which the interlayers are bonded together with a potassium atom. The largest charge deficiency is in the tetrahedral sheet rather than in the octahedral sheet [2]. Thus, potassium bonds the layers in a fixed position so that water and other polar compounds cannot readily enter the interlayer position and also the potassium ion is not readily exchangeable. For this reason, the illite group has non-expanding lattice [2]. Its composition is quite variable and strongly dependent on their origin.

Illite is one of the major component of clays used in the manufacture of extruded and other bricks, portland and other cements, concrete blocks and structural concrete, refractories and in traditional ceramic industry for the production of cooking pots, plates, tiles and bricks [3]. Highway surfacing, ceramic tiles, and ceramics and glass are other important uses. Illite enhances the plasticity of the porcelain mass and generates a superior end product by filling the gaps in the kaolin [4]. Use in cosmetics requires a light-coloured illite with minimal iron oxide suggested that illite could also serve as a less expensive substitute for feldspar in ceramics [5]. For this reason, the understanding of its high temperature transformations is of great importance for the knowledge of the structural and properties of fired ceramic products [6]. There are numerous studies regarding the properties of thermally treated illites [7-17]. However, there has not been enough study in literature about the heat treatment of illite type clay minerals from Turkey [18-19]. Therefore, the objective of the present study is to investigate the influence of the heating on the structural and spectroscopic properties of the illite-rich clay mineral from Tokat region for possible applications in civil engineering and ceramic industry.

---

\*Corresponding Author: [ozguralver@anadolu.edu.tr](mailto:ozguralver@anadolu.edu.tr)

## 2. EXPERIMENTAL

### 2.1. Materials and Methods

Natural illite-rich clay sample was obtained from Tokat region of Turkey. The samples were finely powdered before the application and sieved to pass through a  $< 125 \mu\text{m}$  sieve. The quantitative XRD analysis demonstrated that the C0 sample is mainly constituted by illite (50-55 %) with minor contents of opal-CT (15-20 %), feldspar (5-10 %), zeolite (5-10 %), calcite (10-15 %). Samples were labeled as C0 (untreated), C1 (350 °C), C2 (450 °C), C3 (550 °C) and C4 (650 °C) were put in a kiln for 2 h before the measurements. The temperature of the oven was set at 350-650 °C before the insertion of the samples.

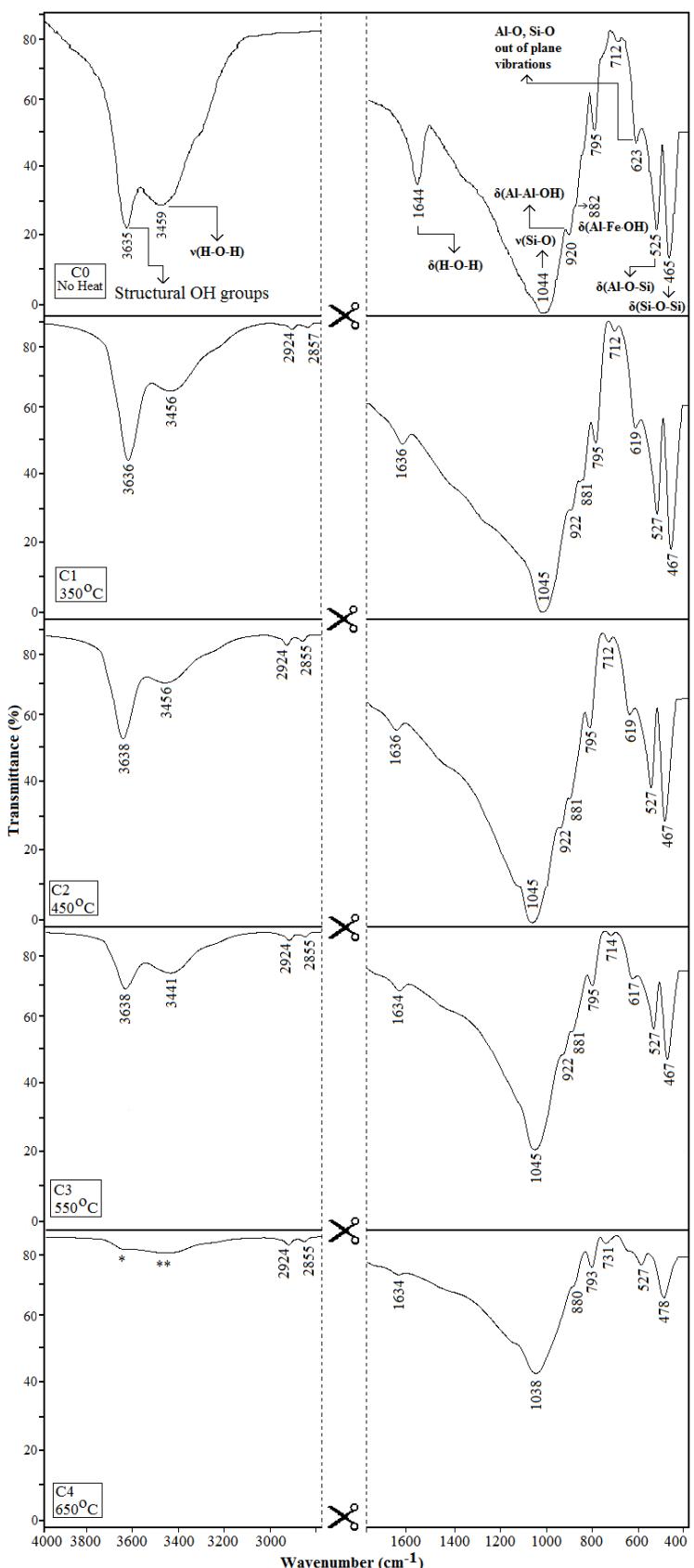
### 2.2. Instrumentation

Bruker Avance 300 spectrometer operating at 59.59 MHz for  $^{29}\text{Si}$  was used for to obtain the solid state spectra. Finely powdered samples were pack into Zirconium oxide rotor with a 4 mm diameter and it was used to acquire the NMR spectra of  $^{29}\text{Si}$ . Spinning rate was kept at 7 kHz during the NMR measurements and data collection was carried out under MAS technique and spectra gathered with 3000 scans for  $^{29}\text{Si}$  MAS NMR. External references TMS (for  $^{29}\text{Si}$ ) was used for chemical shift assignment. Infrared spectra of the illite-rich samples were recorded ( $4000\text{--}400 \text{ cm}^{-1}$ ) with Bruker Tensor 27 spectrometer at a resolution of  $4 \text{ cm}^{-1}$  using KBr pellet technique. Simultaneous TG/DTA experiments were carried out using a Setsys Evolution Setaram thermal analyzer employing ca. 45 mg of sample material in each run. The powdered samples were loaded into an alumina pan and all experiments were performed at a heating rate of 10 °C/min over the temperature range 30–1000 °C.

## 3. RESULTS AND DISCUSSION

### 3.1. FT-IR Studies

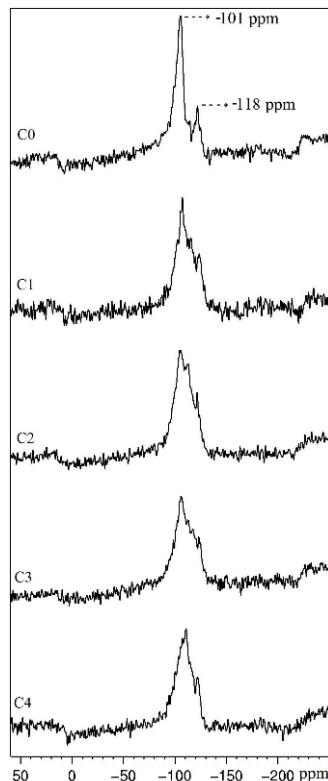
FT-IR spectra, vibrational wavenumbers and identifications of these wavenumbers for C0-C4 samples are shown in Figure 1. The absorption bands at around 3638, 3636, 3635  $\text{cm}^{-1}$  and broad adsorption bands between 3459-3441  $\text{cm}^{-1}$  and as well as the bands marked with asterisks (Figure 1, C4) are because of stretching vibrations of structural OH groups and overlapping of both antisymmetric and symmetric stretching vibrations of water molecules. In Figure 1, for sample C4 the mentioned bands can not be assigned to a specific wavenumber since they were much broadened upon the heat treatment. Vibrational bending modes of water molecules appeared at 1644, 1636 and 1634  $\text{cm}^{-1}$  as expected. Because of Si-O stretching vibrations, FT-IR spectra of C0-C4 samples indicate an intense and broad band at around 1038-1045  $\text{cm}^{-1}$ . The bands at 922, 920, 882, 881, 880  $\text{cm}^{-1}$  are in the hydroxyl bending region. 922 and 920  $\text{cm}^{-1}$  are due to Al-Al-OH bending vibrations. Al-Mg-OH bending vibrations appear around 840  $\text{cm}^{-1}$  [20] but it is not present instead the bands at 880-882  $\text{cm}^{-1}$  exist as a result of Al-Fe-OH bendings which is an indication of low Mg content in the octahedral sheets. Si-O stretching vibrations of SiO<sub>2</sub> impurities appeared around 795-793  $\text{cm}^{-1}$  as expected. The bands around 617-623  $\text{cm}^{-1}$  are due to Al-O and Si-O out of plane vibrations. Bands at 527-525  $\text{cm}^{-1}$  are contributed to Al-O-Si bending vibrations, while bands at 465-478  $\text{cm}^{-1}$  contributed Si-O-Si bending vibrations.



**Figure 1.** FT-IR spectra of C0–C4

### 3.2. $^{29}\text{Si}$ MAS NMR Studies

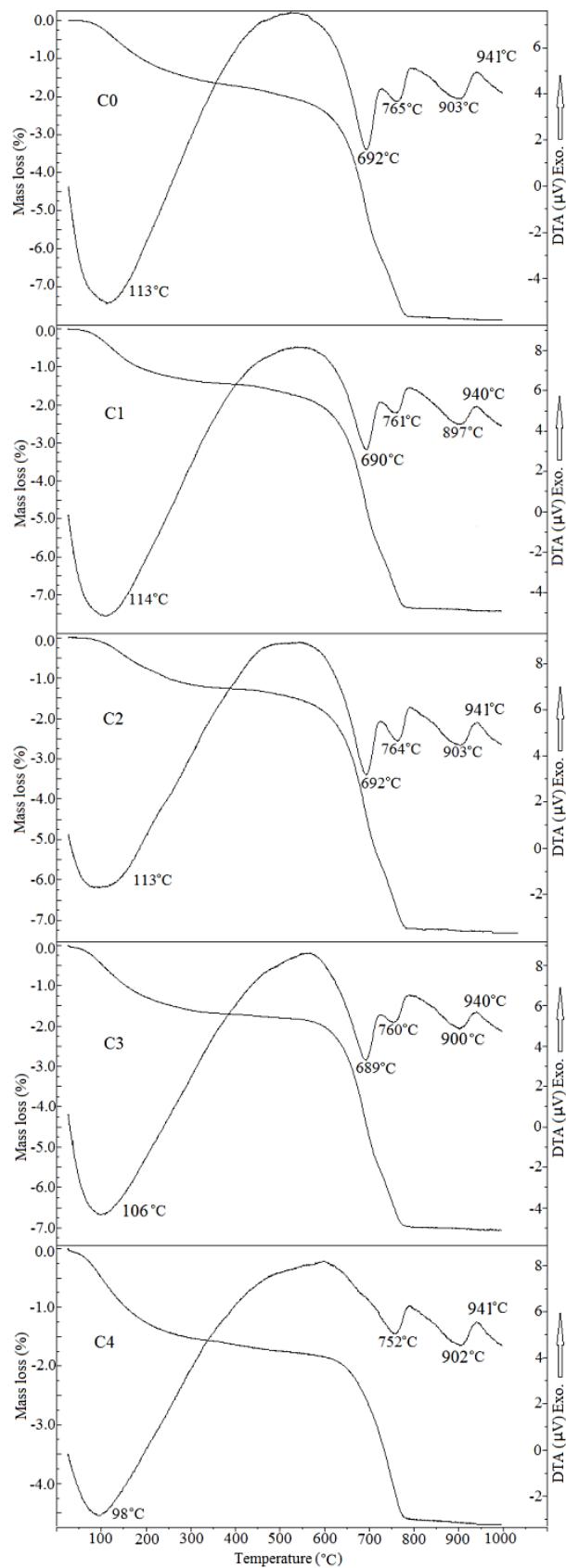
The  $^{29}\text{Si}$  MAS NMR spectra of the untreated and heat treated illite-rich samples were measured to investigate the structural changes by which temperature activation leaded with examining the local structure around the Si atoms.  $^{29}\text{Si}$  MAS NMR spectra of C0 and C4 are given for comparison in Figure 2. The peaks appeared at about  $-101\text{ ppm}$  is due to  $\text{SiO}_4$  groups crosslinked in the tetrahedral sheets with no aluminum in the neighboring tetrahedral [21] and the smaller peak at about  $-118\text{ ppm}$  correspond to three-dimensional silica generally shown as Q4(OAl) [22-23].



**Figure 2.**  $^{29}\text{Si}$  MAS NMR spectra of C0–C4

### 3.3. Thermal Analysis

Illite is one of the most widely used clay component in ceramic industry. For this reason, changes of the illite-rich clay mineral by dehydration and dehydroxylation arising from increasing of temperature were investigated using TG and DTA analysis for the temperature range of  $30\text{--}1000\text{ }^{\circ}\text{C}$  (Figure 3). In the DTA curves of C0-C4 samples, the first and dominant endothermic peaks temperature ranging from  $98\text{ to }114\text{ }^{\circ}\text{C}$  were associated with the dehydration of physically adsorbed water and the water molecules bound to exchangeable cations. The second endothermic peaks at about  $690\text{ }^{\circ}\text{C}$  were due to the loss of the hydroxyl groups. Presence of other mineral components in the illite-rich sample is clearly reflected by endothermic peaks at about  $765\text{ }^{\circ}\text{C}$  associated with the decomposition of calcite [24]. From TG/DTA curves, the peak temperatures are mainly influenced with the number and types of mixed components [25]. Finally, low intense endothermic peaks at temperature ranging from  $897$  to  $903\text{ }^{\circ}\text{C}$  and exothermic peaks at around  $940\text{ }^{\circ}\text{C}$  appeared to be related to the phase transformations and collapse of the clay structure [26]. The TG curves of C0-C4 samples, the first mass losses ( $< 200\text{ }^{\circ}\text{C}$ ) were in the range of  $0.75\text{--}1.28\text{ }\%$ . The second mass losses ( $2.62\text{--}4.66\text{ }\%$ ) started at around  $650\text{ }^{\circ}\text{C}$  and decreased gradually up to  $900\text{ }^{\circ}\text{C}$ . TG data shows that C0 has the greatest mass loss ( $7.89\text{ }\%$ ) in the temperature interval  $30\text{--}1000\text{ }^{\circ}\text{C}$  compared to those of the thermally treated forms.



**Figure 3.** TG-DTA curves of C0–C4

The relative mass losses of heat treated forms decrease with the increasing treatment of temperature, as expected. The DTA curve of C4 show the presence of a small endothermic shoulder at about 650 °C indicating the almost complete dehydroxylation of illite rich sample and the endothermic peak at about 750 °C was associated with the decomposition of calcite. Experimental results of thermal analysis before and after heat treatment of illite are in agreement with literature [6, 7, 27].

#### 4. CONCLUSIONS

In this study, the effect of heat treatment on the structural properties of illite-rich samples with different temperatures were examined using FT-IR,  $^{29}\text{Si}$  MAS NMR, TG and DTA techniques. Heat treatment at 650 °C for 2 h is almost enough to complete the dehydroxylation process but still a certain amount residue is present indicated with asterisks and vibrational bending modes of water molecules (Figure 1). As the samples heated the peak at -101 ppm in  $^{29}\text{Si}$  MAS NMR still present at 650 °C indicating that tetrahedral Si structure is not fully collapsed but line shape of  $^{29}\text{Si}$  signal severely distorted evidence of local changes in the investigated illite samples. Even after 650 °C heat treatment, as can be seen from FT-IR spectra and DTA results dehydroxylation of illite-rich clay mineral was not fully completed.

#### REFERENCES

- [1] Grim RE, Bray RH, Bradley WF. The mica and argillaceous sediments. Am Mineral 1937; 22: 813–829.
- [2] Murray HH. Applied Clay Mineralogy: Occurrences, Processing, and Application of Kaolins, Bentonites, Palygorskite-sepiolite, and Common Clays, Elsevier, Amsterdam, 2007.
- [3] Ferrari S, Gualtieri AF. The use of illitic clays in the production of stoneware tile ceramics. Appl Clay Sci 2006; 32: 73–81.
- [4] Adamis Z, Williams RB. Bentonite, kaolin and selected clay minerals, Environmental health criteria; 231, Geneva: World Health Organization, 2005.
- [5] Fan CM, Aw PC. Processing of illite powder in Bidor, Perak: a study of the process and potential use of illite clay. Warta Geol 1988; 15(1); 37.
- [6] Gualtieri AF, Ferrari S. Kinetics of illite dehydroxylation. Phys Chem Miner 2006; 33: 490-501.
- [7] Gaudette HE, Eades JL, Grim RE. The Nature of Illite, Clays Clay Miner 1964; 13: 33-48.
- [8] Murad E, Wagner U. The Thermal Behaviour of An Fe-Rich Illite. Clay Miner 1996; 31: 45-52.
- [9] Aras A. The change of phase composition in kaolinite- and illite-rich clay-based ceramic bodies. Appl Clay Sci 2004; 24: 3-4, 257-269.
- [10] Carroll DL, Kemp TF, Bastow TJ, Smith ME. Solid-state NMR characterisation of the thermal transformation of a Hungarian white illite. Solid State Nucl Magn Reson 2005; 28: 1, 31-43.
- [11] Jiang T, Li G, Qiu G, Fan XH, Huang ZC. Thermal activation and alkali dissolution of silicon from illite. Appl Clay Sci 2008; 40: 1-4, 81-89.
- [12] Buchwald A, Hohmann M, Posern K, Brendler E. The suitability of thermally activated illite/smectite clay as raw material for geopolymers binders. Appl Clay Sci 2009; 46(3): 300-304.

- [13] Fernandez R, Martirena F, Scrivener KL. The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite, *Cem Concr Res* 2011; 41(1): 113-122.
- [14] Landoulsi O, Megliche A, Calvet R, Espitalier F, Ferreira JMF, Mgaidi1 A. Effects of Heating and Acid Activation on the Structure and Surface Properties of a Kaolinite-illite-smectite Clayey Mixture. *TOMPJ* 2013; 6: 13-20.
- [15] Bennour A, Mahmoudi S, Srasra E, Boussen S, Htira N. Composition, firing behavior and ceramic properties of the Sejnene clays (Northwest Tunisia). *Appl Clay Sci* 2015;115: 30-38.
- [16] Garg N, Skibsted J. Pozzolanic reactivity of a calcined interstratified illite/smectite (70/30) clay. *Cem Concr Res* 2016; 79: 101-111.
- [17] Kubliha M, Trnovcova V, Ondruska J, Stubna I, Bosak O, Kaljuvee T, Bacik P. DC conductivity of illitic clay after various firing. *J Ther Anal Calorim* 2016; 124: 1, 81-86.
- [18] Turak F, Afsar M. Adsorption of oil-grease from oil-in water dispersions on different thermal activated clay minerals. *Rev Anal Chem* 2007; 26: 1, 13-22.
- [19] Colak M, Ozkan I. Sintering properties of the Bornova shale (Turkey) and its application in the production of red fired ceramics. *Ind Ceram* 2011; 31(3): 209-215.
- [20] Andrejkovicova S, Madejova J, Czimerova A, Galko I, Dohrmann R, Komadel P. Mineralogy and chemistry of Fe-rich bentonite from the Lieskovec deposit (Central Slovakia). *Geol Carpath* 2006; 57(5): 371-378.
- [21] Benharrats N, Belbachir M, Legrand AP, D'Espinose de la Caillerie JB.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR study of the zeolitization of kaolin by alkali leaching. *Clay Miner* 2003; 38: 49-61.
- [22] Breen C, Madejovà J, Komadel P. Characterisation of moderately acid-treated, size-fractionated montmorillonites using IR and MAS NMR spectroscopy and thermal analysis. *J Mater Chem* 1995; 5: 469-474.
- [23] Thompson JG.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  Nuclear Magnetic Resonance Spectroscopy of 2:1. *Clay Miner* 1984; 19: 229-236.
- [24] Rodriguez-Navarro C, Ruiz-Agudo E, Luque A, Rodriguez-Navarro AB, Ortega-Huertas M, Thermal decomposition of calcite: Mechanisms of formation and textural evolution of CaO nanocrystals. *Am Mineral* 2009; 94: 578–593.
- [25] Cebulak S, Langier-Kuñiarowa A. Some remarks on the methodology of thermal analysis of clay minerals. *J Ther Anal Calorim* 1998; 53: 375-381.
- [26] Grim RE, Rowland RA. Differential thermal analyses of clay minerals and other hydrous materials. *Am Mineralogist* 1942; 27(746-61): 801-818.
- [27] Vaculikova L, Plevova E. Identification of Clay Minerals and Micas in Sedimentary Rocks. *Acta Geodyn Geomater* 2005; 2(138); 167-175.