Thermal behavior of mechanically activated sepiolite

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Abstract: Sepiolite, a complex magnesium silicate mineral, was activated mechanically in a planetary mill and the changes in the mineral structure and thermal behavior of sepiolite were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal analysis (TG-DTA). The results showed that particle size decreased and amorphization in the ore structure was occured with increment of grinding times. The loss of zeolitic water in the structure was actualized during mechanical activation of sepiolite.

Key words: Sepiolite, mechanical activation, thermal behavior.

Introduction

Sepiolite is a natural hydrated magnesium silicate clay mineral and its structural formula can be written as $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4.xH_2O$, (x=6-8) (Mora et al., 2010). Three pyroxene-type chains $(SiO_3)^{2-}$ exist in the structure and oxygen links the chains together so that doubly linked chains occur. This structural formation causes zeolite-like channels (Frost et al., 2003). Octahedral coordinated magnesium locates between the silica sheets (Mora et al., 2010). Water molecules that present in the sepiolite structure have been grouped into zeolitic water, bound water and hydroxyl water (Nagata et al., 1974). From the formula (OH) indicates the hydroxyl group, (OH_2) represent the bound (crystal) water and H_2O shows the zeolitic water (Mora et al., 2010). The surface of this mineral has silanol (Si-O) groups because of the discontinuity of the external silica sheets (Alkan et al., 2005). This formation play important role at the adsorption of organics on the clay surface. Furthermore sepiolites can be used as absorbents for cleaning gas and liquids (Can, 1992) wherefore its zeolitic channels that may be filled with water or organic molecules (Frost et al., 2003). Apart from this new utilization opportunities are constituted by different studies like usage for decolorization of sugar juice (Ünal et al., 1998) sulfur recovery from sour gas or hydrogenation activity on Ni supported on sepiolite (Jung et al., 2004) etc.

Several research that mainly concentrated on calcinations process have been made for explain the water type or transformation and interrelated temperature intervals by means of XRD (Bastida et al., 2006), DTA-TG (Frost et al., 2003) and FT-IR (Mora et al., 2010; Alkan et al., 2005) etc. Grinding process is a very common process in industry (Cornejo et al., 1988) but when mechanical activation process is performed size reduction, surface activation, chemical or decomposition reactions which take place above room temperature, occur simultaneously (Balaz, 2000). For this reason, in this study, the effects of mechanical activation on the structure and thermal behavior of sepiolitic clay were investigated by means of X-ray diffraction (XRD), particle size analysis, scanning electron microscopy (SEM) and thermal analysis (TG/DTA).

Materials and Method

The mechanical activation of sepiolite from Kale Maden (Turkey) was performed in a Planetary Mono Mill Pulverisette 6 under the following conditions: the weight and diameter of tungsten carbide (WC) balls were 200 g and 10 mm respectively; the grinding bowl was 250 mL WC; the grinding times 30 and 60 min; the speed of the main disk was 600 $rev.min^{-1}$; the grinding process was dry. Ball-to-mass ratios during mechanical activation were kept constant at 25.

For comparative study calcination was performed under atmospheric condition at 380, 540 and 580°C for one hour with 10°C/min heating rate. X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and Cu Kα radiation. The degree of amorphization (A) of the mechanically activated sepiolite according to X-ray diffracton results was calculated from equation (1),

$$A = \left(1 - \frac{I_x B_0}{I_0 B_x}\right).100 \qquad (1)$$

where I_0 is the integral intensity of the diffraction peak for the non-activated sepiolite, B_0 is the background of the diffraction peak for the non-activated sepiolite, and I_x and B_x are the equivalent values for the activated sepiolite (Balaz, 2000; Balaz, 2008). A JEOL 6060 LV scanning electron microscope (SEM) was used for morphological analysis of the non-activated and activated samples. DTA was performed using TA Instruments SDTQ 600 at heating rate of 10°C.min^{-1} under atmospheric conditions and Mikrotrac S3500 was used for particle size distribution analysis.

Results and Discussion

Chemical composition of sepiolite which was provided by Kale Maden (Çanakkale/Turkey) was given at Table 1. As seen from the table sepiolite is rich in silicon and magnesium. Lost on ignition value is only 11.74.

Table 1. Chemical composition of sepiolite

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	L.O.I
61.03	7.50	0.20	0.95	1.60	16	0.21	0.48	11.74

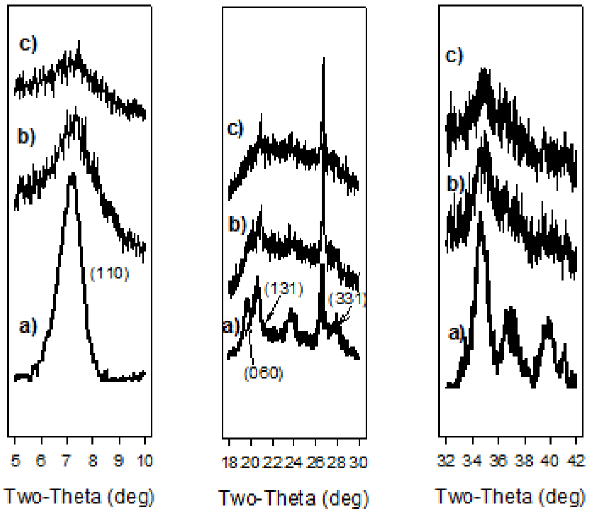


Figure 1. XRD patterns of (a) non-activated sepiolite, (b) activated for 30 min and (c) activated for 60 min

XRD patterns of the mechanically activated sepiolite samples were given in Fig 1. with respect to 5°-10° and 18°-30° and 32°-42° intervals. (110), (060), (131) and (331) reflections were determined at 7,2°,19.7°, 20.6° and 28° respectively for non-activated sepiolite. According to Eq 1, amorphization degree of the peak that found at 7.2° reached 98 percent after 60 min mechanical activation. Amorphization is the situation that peak broadening and decreasing of intensity come along because of the grinding media interaction and material behavior against this media. Particles can be refined at critical size and after this energy accumulation in the volume or at the surface of crystals take place. This occurrence is the beginning of the amorphization. Furthermore because of the interaction local temperatures may be increased (Tunç et al., 2012a; Balaz, 2000; Tunç et al., 2000b). (060) reflection got amorphized approximately 95 percent at 30 min and got lost after this duration. (131) reflection that positioned at 20.6 got amorphized 76 percent after 30 min and stabilized. (331) reflection couldn't be determined for 30 and 60 min activated samples so it can be said that amorphization process took place and finished between 0 and 15 min for this pattern.. Between 32°-42° same amorphization degrees were calculated. According to this values average degrees are 89.9 and 92.3 percentages for 30 and 60 min. respectively. Amorphization degrees for the reflections and average value for mechanically activated sepiolite were given in Fig 2. as graphically. Intensity of the (110) reflection decreased greater than the others in 30 min. After 30 min decreasing behavior of the all peaks are the same. This is the result that originated from first structural ribbons deformation and after atomic structure disruption (Cornejo et al., 1988).

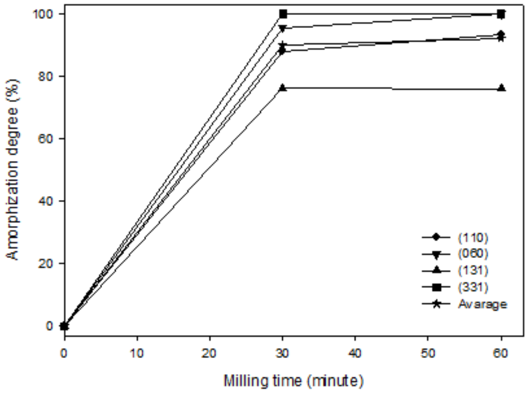


Figure 2. Amorphization degree of mechanically activated sepiolite

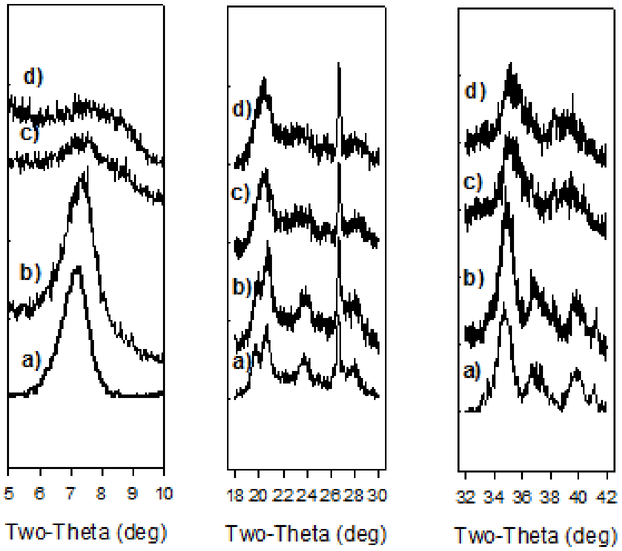


Figure 3. XRD patterns of the a) original sepiolite and calcined at b)380°C c)540°C and d)580°C sepiolite samples

Untreated sepiolite has sharp (110) = 12.1Å reflection that indicate the crystallinity of the sample as shown in Fig. 1 and Fig. 3. (110) diffraction pattern is the interlayer distance in sepiolite (Mora et al., 2010). After calcinig at 380°C, (110) diffraction preserved itself in some degree. But after calcinig at 540°c and 580 °C this peak disappeared and the structure of sepiolite was destroyed as took place in mechanical activation process.

Particle size analysis and SEM microscopy results were given in Table 2 and Fig. 4-6 respectively. Non-activated sepiolite has laminar structure and angled particles can be seen in Fig. 5. Diameter of the ninety percentages of the particles is 270.6 µm. In Fig. 5 and 6 instead of angled particle rounded particles were seen. Mechanically activated samples refined from this dimension to 37.89 and 94.13 for 30 and 60 min. activation duration respectively.

Table 2. Particle size analysis of the samples

Milling Duration (min)	d_{10} (µm)	d_{50}(µm)	d_{90} (µm)
Non-activated	3,660	175,7	270,6
30	0,688	2,834	37,89
60	0,701	3,930	94,13

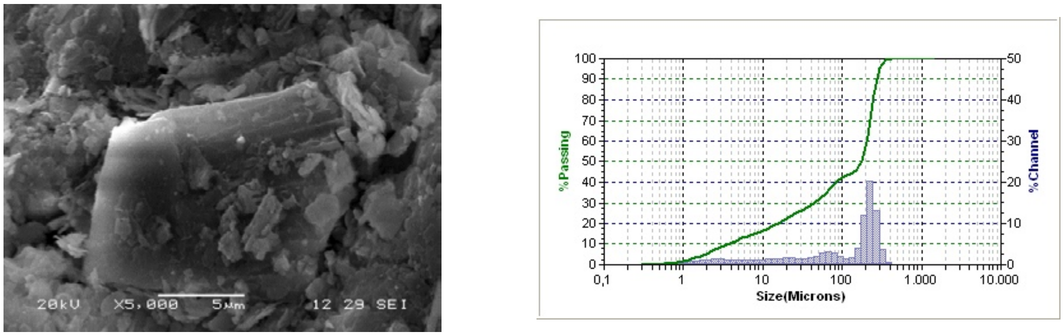
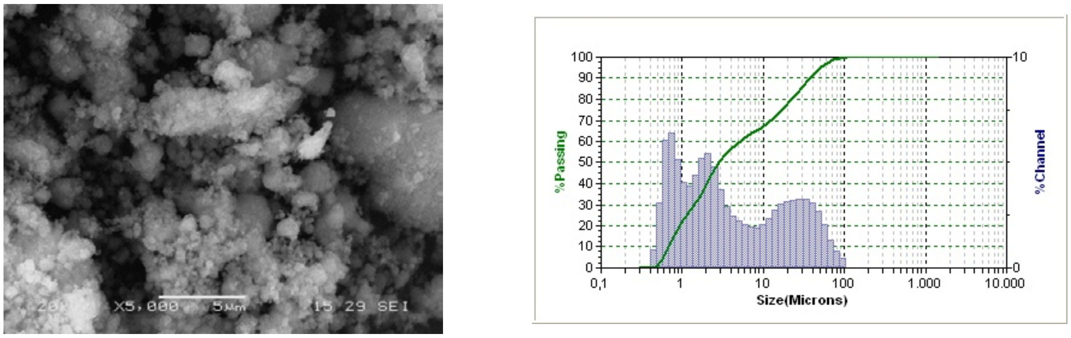


Figure 4. SEM micrograph and particle size analysis of non-activated sepiolite



.**Figure 5.** SEM micrograph and particle size analysis of activated sepiolite for 30 min.

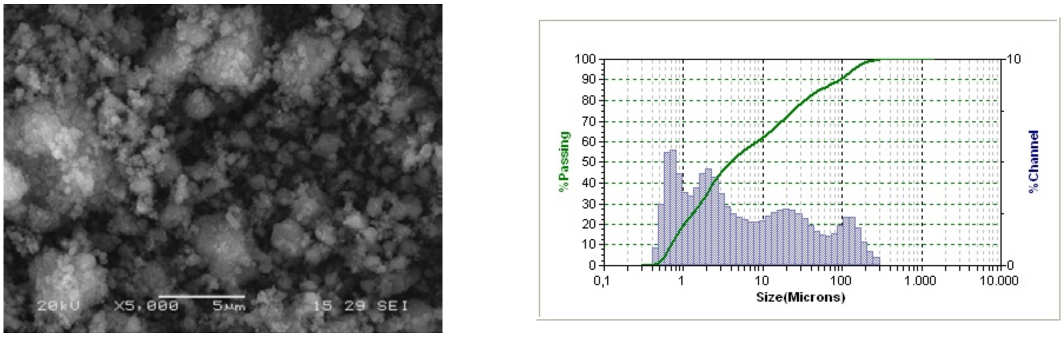


Figure 6. SEM micrograph and particle size analysis of activated sepiolite for 60 min.

The reason of increment in the dimension can be agglomeration that induced by mechanical activation which might be produced new surface area and this area can be more active than the former one (Balaz, 2008).

Thermal analysis of non-activated and activated samples was given in Fig 7. and Fig 8. with respect to thermogravimetric and differantial thermal analysis. Curve of the non-activated sample has four parts that have different slopes. These slopes can characterize the process rapidity (Nagata et al., 1974). Frost and Ding (2003) stated that up to 200C both hygroscopic and zeolitic water were lost. Between 250 and 450°C bound water were lost; more strongly bound water (co-ordinated water) and the hydroxyl units were lost in the temperature range 450-610°C. From these chemical equations theoretical weight loses determined as %11.1, %2.78, % 2.78, % 2.78 for each step respectively (Nagata et al., 1974). From this values and chemical equations step one and two are dehydration and step three and four are the dehydroxylation process (Frost et al., 2003).

Step I $Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4.8H_2O \leftrightarrow Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4 + 8H_2O$
Step II $Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4 \leftrightarrow Mg_8Si_{12}O_{30}(OH)_4(H_2O)_2 + 2H_2O$
Step III $Mg_8Si_{12}O_{30}(OH)_4(H_2O)_2 \rightarrow Mg_8Si_{12}O_{30}(OH)_4 + 2H_2O$
Step IV $Mg_8Si_{12}O_{30}(OH)_4 \rightarrow Mg_8Si_{12}O_{30} + 2H_2O$

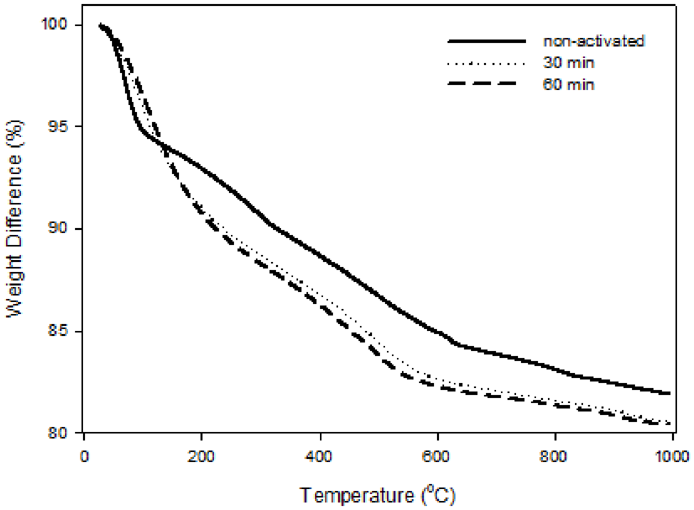


Figure 7. Thermogravimetric analysis of non-activated and activated sepiolite samples

For non-activated and activated sepiolite samples temperature intervals and related weight loses were given in Table 3. As seen from the table for non-activated sepiolite dehydration process did not completed in two steps with regards to hygroscopic and zeolitic water. In step three weight losses originated from residuary zeolitic water and part of the bound water were occurred. Similarly dehydroxylation process came after the loose of zeolitic water and did not completed end of the step four. In spite of non-activated sepiolite, dehydration occurrence finished in step one and dehydroxylation process occurred in step two as shown in Table 1 with regard to weight lost value. Step two and three are the dehydroxylation process for activated samples.

Table 3. Temperature intervals and weight loses for TG curves of the samples

	Step I	WL	Step II	WL	Step III	WL	Step IV	WL
Non-Activated	0-220°C	7.47	220-320°C	2.39	320-660°C	5,94	660-840°C	1.46
30 min.	0-400°C	13.17	400-580°C	3.97	580-1000°C	2.31	-	-
60 min.	0-380°C	13.3	380-560°C	4.07	560-1000°C	2.23	-	-

*WL=Weight Lost (%)

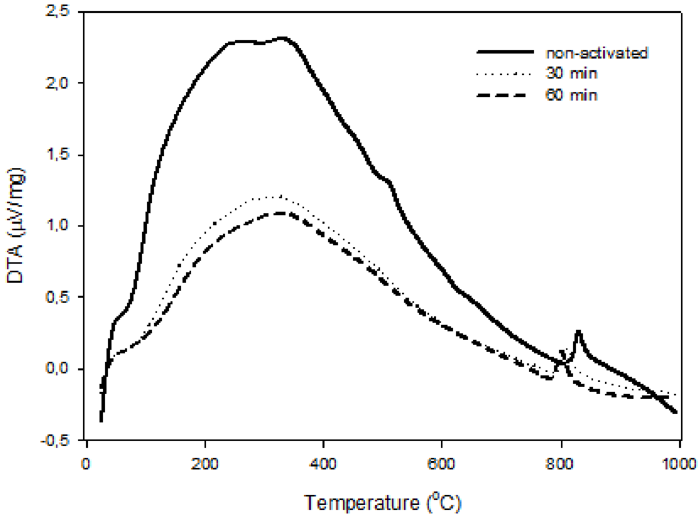


Figure 8. Differantial thermal analysis (DTA) of the samples

The area of the peak is proportional to the quantity of heat absorbed or released during reaction (Seguin, 1973). In Fig. 8 the area of the peaks are different and decreased with increment of milling time. From this result it can be said that with elongated mechanical activation time need of energy for dehydration, dehidraxilation and phase transformation decreased because of the energy accumulation in the volume or at the surface of crystal due to the limit for fragmentation of a partical (Balaz, 2000; Balaz, 2008). As seen from the Table 3 and Fig. 7 for activated sepiolite samples dehydration and dehydroxilation process occurred before of the reference temperatures. Identically transformation in to enstatite occurred at 830°C for non-activated sepiolite, 809°Cfor 30 min activated sepiolite and 801°C for 60 min sepiolite.

Conclusions

With mechanical activation the amorphization occurred in sepiolite structure and the structure was distorted. Dehidration was proceed in one step and dehydroxilation was completed in three steps. Transformation temperature was lowered after mechanical activation. Calcining sepiolite at 540°C gave same results with 60 min of mechanical activation with respect to amorphization that determined via X-ray diffraction analysis.

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