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Effects of mechanical activation on the non-isothermal kinetics of mullite formation from kaolinite

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Abstract The non-isothermal kinetics of mullite formation from both non-activated and mechanically activated kaolinite have been studied by differential thermal analysis (DTA). Kaolinite was mechanically activated in a planetary mill, while amorphization in the structure was studied by X-ray diffraction analysis. It was established that the mechanical activation especially affected the loss of structural water. The activation energies depending on the conversion for mullite formation have been calculated from the DTA curves by using the non-isothermal method of Coats and Redfern at heating rates of 5, 10, 15, and 20 °C min^{-1}. The mechanical activation and amorphization of the kaolinite brings to the formation of mullite at a lower heating temperature.

Keywords Kaolinite · Mullite · Mechanical activation · Non-isothermal kinetics

Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) is an important ceramic phase in conventional ceramics (such as tableware, construction ceramics, and refractories), advanced high-temperature structural materials, heat exchangers, catalysator convertors, filters, optical devices, and electronic packaging materials. However, mullite suffers from their relatively low fracture toughness which limits their application in industrial use. The conventional route for the preparation of mullite is the solid-state reaction between alumina and silica, which is controlled by diffusion. Mullite formation in this method takes place at a relatively high temperature (>1,500 °C). The mullitization temperature and the morphology of mullite particles depend on the particle size of the initial raw materials and the preparation processes of the precursors before sintering [1, 2].

Kaolinite ($2SiO_2{\cdot}Al_2O_3{\cdot}2H_2O$) is a phyllosilicate that contains a gibbsite octahedral layer and a silicon oxide tetrahedral sheet. This asymmetric structure produces hydrogen bonds with a large cohesive energy between adjacent layers [3]. The material has been widely used in ceramic industries for many years [4–6]. The stoichiometric 3:2 mullite is a thermodynamically stable phase in the SiO_2–Al_2O_3 system. The mullite is thus formed after firing kaolinite at an elevated temperature. Nevertheless, the amount of SiO_2 in kaolinite is much higher than that in mullite; the excess SiO_2 together with the impurities in kaolinite form a glass phase and a cristobalite to accompany the formation of mullite at a temperature higher than 1,000 °C. The cristobalite may also transform to a glass phase as kaolinite is fired above 1,500 °C. The presence of a large amount of the glass phase is detrimental to the mechanical properties of the mullite that is prepared from kaolinite [7].

Mechanical activation of the starting materials is a promising method for the precursor's preparation. Particle size reduction, which increases the contact surfaces between the particles, is the direct consequence of milling. Also, the energy of the system increases and results in a decrease in the reaction temperature [2]. Different processes can remarkably influence the reactivity of the solids. Particularly, the mechanical treatments are important as long as they can help to produce changes in the texture and structure of the solids. In many cases, these alterations in the structure cause certain modifications in the phases that

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formed by thermal treatment of the solids, which were mechanochemically treated [8, 9].

Sugiyama et al. [10] studied the structure in the kaolinite before and after dry grinding and stated that the SiO_4 tetrahedra remain unchanged in the samples of ground kaolinite and the increment of grinding time induced the decrease of oxygen coordination number and the corresponding interatomic distance around aluminum. Miyazaki et al. [11] studied the effect of grinding on the amorphization behavior of kaolinite, using the co-axial double rotating cylinders mill and tumbling mill and reported the different effects of milling types on the amorphization of the samples. Kaolinite powder ground by the ultra-fine mill has a higher chemical activity than that the ground by tumbling mill. Frost et al. [12] activated mechanically kaolinite in a planetary mill and investigated the effects of aging, in the presence of intercelated and adsorbed formadide, and mechanical activation on the rearranging of the kaolinite layers. They reported that the mechanochemical treatment of kaolinite resulted in the dehydroxylation of the kaolinite through point heating and the amount of dehydroxylation increased with grinding time. Vizcayno et al. [13] reported that the milling increased the structural disorder in the kaolinite samples and decreased the peak temperature, symmetry, and width in the thermal behavior of kaolinite, up to 800 °C. Ebadzadeh [14] activated mechanically the mixture of clay and alumina in a planetary ball mill for 30, 50, and 70 h and stated that clay disappeared and alumina and quartz appeared as the only crystalline phases after 30 h milling time.

Sanchez-Soto et al. [15] studied the effects of dry grinding, by using a ball mill, on a natural mixture of aluminum silicates composed of kaolinite, pyrophyllite, and illite. They stated that the grinding produced structural alteration of these silicates, and a decrease in particle size of the original material, producing weight losses (water dehydration and dehydroxylation) at lower temperatures than in unground samples. They also reported that differential thermal analysis (DTA) endothermic effects were shifted to lower temperatures and further grinding produced a breakdown of the crystal structure of the silicates, accompanied by a strong increase of the exothermic DTA effect at 985 °C. Nikaido et al. [16] studied the effects of dry grinding of a mixture composed of kaolinite and aluminum hydroxide in a tumbling ball mill on formation of mullite and reported that about 192 h in grinding time was required to achieve an amorphous state, resulting in the formation of a mullite single phase at relatively low sintering temperature. Ryu [17] activated mechanically the mixture of kaolinite and aluminum trihydroxide and stated that the crystal structure of the mixture was collapsed easily into an amorphous one by planetary ball mill and the grinding treatment was very effective to decrease the thermal decomposition temperature and to obtain direct preparation of mullite at relatively low temperature.

The effects of mechanical activation on the structure and thermal behavior of kaolinite and the crystallization kinetics of mullite from kaolinite were studied in this work.

Experimental methods

Kaolinite was supplied from Çelvit Company, Turkey. The chemical composition of the kaolinite is 52.12% SiO_2, 33.83% Al_2O_3, 0.55% Fe_2O_3, 0.15% CaO, 0.13% K_2O, 0.45% TiO_2, 0.01% Na_2O, and 0.05% MgO with a 12.45% loss on ignition.

Kaolinite was activated mechanically in a planetary ball mill (Fristch Mono Mill Pulverisette 6) under the following conditions: the weight of the sample was 10 g; the weight and diameter of the tungsten carbide (WC) balls were 200 g and 100 mm, respectively; the grinding bowl was 250 mL WC; the grinding times were 0, 1, and 2 h; the speed of the main disk was 600 rpm; and the grinding process was dry.

The X-ray diffraction analysis (XRD) was performed by using a Rigaku Ultima X-ray diffractometer and Cu K_α radiation. A Joel 6060 LV scanning electron microscope (SEM) was used for morphological analysis of the non-activated and activated kaolinite. Mikrotrac S3500 was used for particle size analysis. The degree of amorphization (%A) in the kaolinite structure after mechanical activation was calculated by Eq. 1 [18–20];

$$\%A = \left[1 - \frac{B_o \cdot I_x}{B_x \cdot I_o}\right] \cdot 100, \tag{1}$$

where I_o is the integral intensity of the diffraction peak for non-activated kaolinite, B_o is the background of the diffraction peak for non-activated kaolinite and I_x and B_x are equivalent values for mechanically activated kaolinite.

The activation energies depending on the conversion (α) for mullitization were calculated with the Coats and Redfern equation (see Eq. 2) [21] by using the data in the DTA (TA Instruments SDTQ 600) at heating rates of 5, 10, 15, and 20 °C min^{-1} under an air atmosphere;

$$\ln\left(\beta/T_{\alpha,t}^2\right) = \text{Cons.} - \left(E_\alpha/R \cdot T_{\alpha,t}\right), \tag{2}$$

where β_i is the heating rate, $T_{\alpha,i}$ is the temperature at a given conversion (α), E_α is the activation energy, and R is the gas constant. A plot of $\ln(\beta_i/T_{\alpha,i}^2)$ versus $(1{,}000/T_{\alpha,i})$ corresponding to different conversions α can be obtained by a linear regress of least-square method. The activation energies E_α can be calculated from the slopes of every line.

Results and discussion

Structural changes in activated kaolinite

The XRD of non-activated and activated kaolinite is shown in Fig. 1. By considering the peaks of the non-activated and activated kaolinite, it can clearly be seen that all of the diffraction peaks get shorter and/or disappear after mechanical activation. This is due to amorphization and structural disordering in the kaolinite structure. In the literature [19, 20], it was reported that mechanical activation resulted in amorphization of the mineral particles. Tromans and Meech [22, 23] indicated that mechanical activation resulted in the development of large numbers of dislocations and their associated strain fields, which might lead to an overall decrease in long range lattice periodicity. This may be interpreted as the formation of a metastable "amorphous phase," since line broadening and the disappearance of diffraction peaks takes place in the X-ray patterns after extended milling. It was also reported [24–26] that kaolinite underwent important structural alterations when it is submitted to intensive grinding.

The scanning electron micrographs (SEM) and particle size analysis of the non-activated and activated kaolinite are shown in Fig. 2a–c. The micrograph in Fig. 2a shows that the non-activated kaolinite has micro-size particles. The micro-size particles are composed of individual platelets that conglomerate into larger size particles [3]. After 1 h of mechanical activation the micro-size particles were <3 µm and were agglomerated after 2 h of mechanical activation. D_{10}, D_{50}, and D_{90} sizes corresponding to the particle sizes at the 10, 50, and 90% points on the cumulative distribution for all samples are shown in Table 1. The degree of amorphization in the kaolinite structure as a function of the milling time was calculated by Eq. 1 and was found to be approximately 97% for both 1 and 2 h of activation.

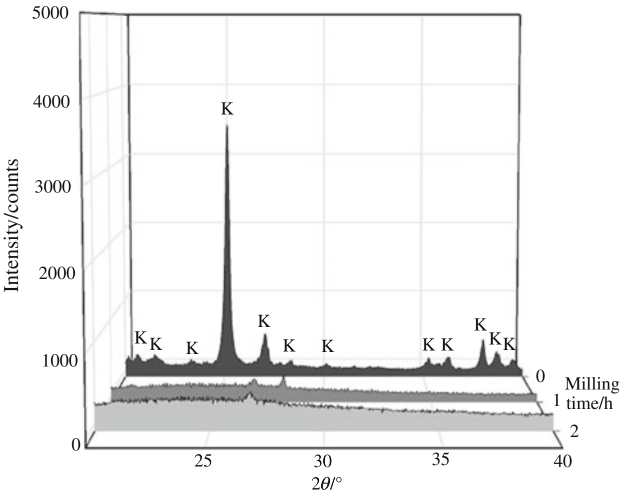

Fig. 1 XRD patterns of non-activated and activated kaolinite [K: Kaolinite]

Thermal behavior of non-activated and activated kaolinite

DTA analyses of non-activated and activated kaolinite are shown in Fig. 3. In the DTA analysis of non-activated kaolinite, an endothermic peak at around 530 °C corresponds to the dehydration of kaolinite. This peak is not present in the activated kaolinite samples, which is probably due to the occurrence of dehydration of kaolinite during mechanical activation. The dehydration and dehydroxylation of mechanochemically activated kaolinite was previously studied by Frost et al. [12] and they stated that the amount of dehydroxylation increased with grinding time. Miller and Oulton [26] also stated that some dehydration occurred even during grinding.

An exothermic peak at around 1,000 °C could be due to the formation of the mullite phase. The mullite formation is lowered to 990 °C after 1 h of mechanical activation. Also, the mullitization temperature after 1 h of mechanical activation is the same as that after 2 h of mechanical activation.

Chakraborty [27] stated that the exothermic peak at ~980 °C was related to the crystallization of the Al–Si spinel phase, weakly crystalline mullite, amorphous aluminosilicate phase, and amorphous silica. Sakizci et al. [28] reported that the exothermic peak at 994 °C was related to the appearance of new crystallization. Kamseu et al. [29] stated that the temperature of crystallization of mullite varied from 973 to 1,001 °C, varying the SiO_2/Al_2O_3 M ratio, the impurities content and the heating rate. In consultation with the reports of Chen et al. [30, 31], when the kaolinite is heated to 1,000 °C, the transformation from kaolinite to mullite occurs according to the following reactions:

$$\mathrm{Al_2O_3\cdot 2SiO_2\cdot 2H_2O\ (kaolin)} \xrightarrow{500-550\,^{\circ}\mathrm{C}} \mathrm{Al_2O_3\cdot 2SiO_2\ (metakaolin) + 2H_2O} \tag{3}$$

$$\mathrm{2[Al_2O_3\cdot 2SiO_2]\ (metakaolin)} \xrightarrow{\approx 950\,^{\circ}\mathrm{C}} \mathrm{Si_3Al_4O_{12}\ (spinel) + SiO_2\ (amorphous)} \tag{4}$$

$$\mathrm{3Si_3Al_4O_{12}\ (spinel)} \xrightarrow{>1{,}000\,^{\circ}\mathrm{C}} \mathrm{2(3Al_2O_3\cdot 2SiO_2)\ (mullite) + 5SiO_2\ (amorphous)} \tag{5}$$

The bulk nucleation is dominant in mullite crystallization and the crystal growth is controlled by diffusion in kaolinite.

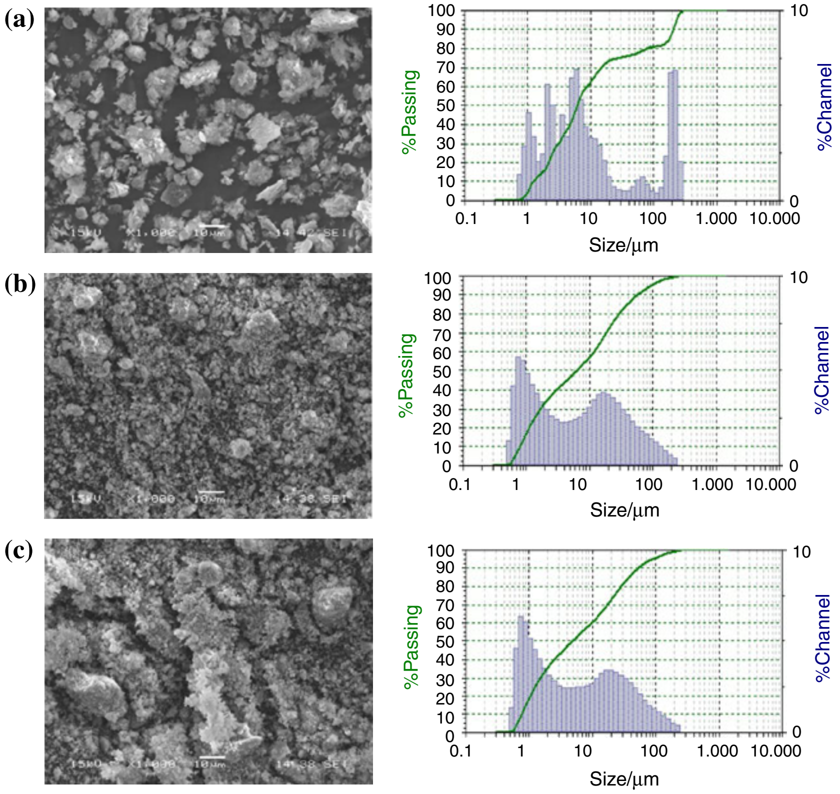

Fig. 2 SEM micrographs and particle size analysis of kaolinite **a** non-activated, **b** activated for 1 h and **c** activated for 2 h

Table 1 D_{10}, D_{50}, and D_{90} particle sizes for the non-activated and activated samples

Samples	D_{10}/µm	D_{50}/µm	D_{90}/µm
Non-activated kaolin	1.5	6.7	223
Activated kaolin/1 h	0.8	5.4	60
Activated kaolin/2 h	0.8	4.8	52

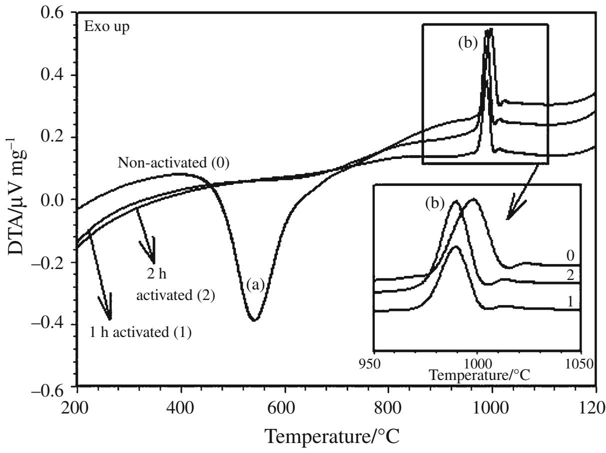

Fig. 3 DTA analysis of non-activated and activated kaolinite

Mullitization kinetics

The DTA curves of non-activated and activated kaolinite (1 h) at different heating rates from 950 to 1,050 °C are shown in Fig. 4a, b. The top temperatures of the exothermic peaks in the DTA of the non-activated kaolinite increased as the heating rate increased, from 987 to 1,004 °C. In this study, the results for both the 1 and 2 h activation are quite similar, thus the activation energy was calculated only for 1 h of activation. The top temperatures of the exothermic peaks in the DTA of the activated kaolinite increased as the heating rate increased from 977 to 1,002 °C.

According to Eq. 2, the plots of $\ln(\beta/T_{\alpha}^{2})$ versus 1,000/T corresponding to different conversions (α) was obtained for non-activated and activated kaolinite. The activation energies (E_{α}) were calculated from the slopes of every line. The α-dependence of the apparent value of E_{α} is shown in Fig. 5. As seen from Fig. 5, there is double-step kinetics in the formation of mullite from kaolinite. With kaolinite in the 950–1,050 °C temperature range, nucleation and crystal growth processes occur simultaneously [32]. The bulk nucleation is dominant in mullite crystallization and the crystal growth is controlled by diffusion in kaolinite [31]. In this study, the energy that was applied to kaolinite first reduced the particle size, the dehydroxylation reaction took place during milling. The activation energy values of the bulk nucleation in mullite crystallization for the non-activated kaolinite were calculated between 928 and 962 kJ/mol. The values in the same step for the activated kaolinite are between 735 and 808 kJ/mol. Also the activation energy values for crystal growth step decreased from 895–343 kJ/mol to

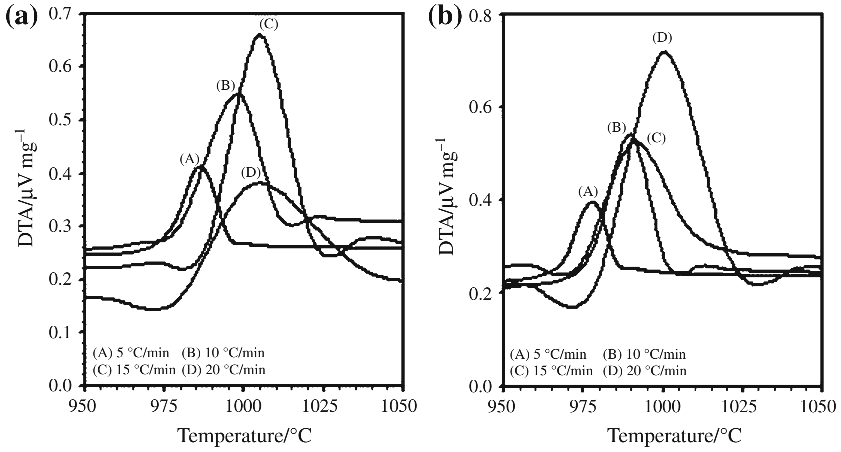

Fig. 4 DTA curves of non-activated (**a**) and activated (**b**) kaolinite measured at different heating rates

694–462 kJ/mol after mechanical activation. The application of high energy milling allows a dramatic change in the structure and surface properties of solids to be induced [19, 20, 33]. Mechanical treatment in a high energy mill generates a stress field within the solids. Stress relaxation can occur via several channels: (1) heat release, (2) development of surface area as a result of brittle fracture of the particles, (3) generation of various sorts of structural defects, and (4) stimulation of chemical reactions within the solids. All of the relaxation channels cause changes in the reactivity of the solid substance that is under treatment, which is why the resulting action is called mechanical activation [34]. The concentration of the mechanically induced defects and their spatial distribution depend on the condition of the energy transfer in the mill. The creation of defects enhances the stored energy in the solids and consequently causes a decrease in the activation barrier for the process and/or subsequent processes [35].

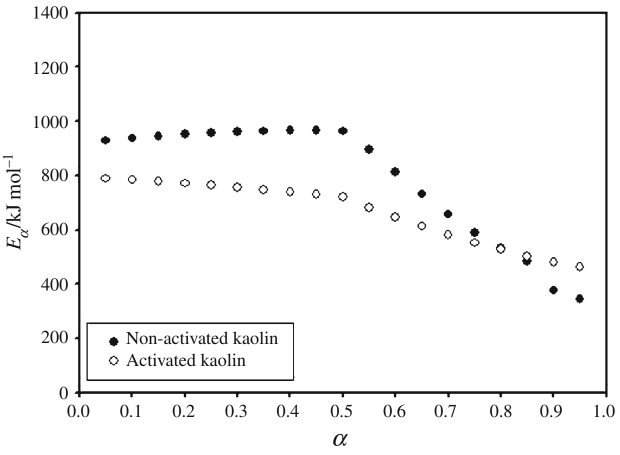

Fig. 5 Variation of activation energy with conversion for mullite formation in the non-activated and activated kaolinite

Conclusions

The effects of mechanical activation on structural changes in kaolinite were studied along with the non-isothermal kinetics of mullite formation from kaolinite by using DTA; the following results were obtained.

(a) The mechanical activation caused amorphization and structural disordering in kaolinite. The degree of amorphization of kaolinite was found to be 97% for both 1 and 2 h of mechanical activation.
(b) The dehydroxylation reaction in kaolinite occurred during milling.
(c) The activation energy values for the bulk nucleation and crystal growth in the mullitization from kaolinite decreased because of the structural disordering and amorphization in the kaolinite structure after mechanical activation.

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