**Kinetic behavior of partially dehydroxylated kaolinite**

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**ABSTRACT**

The multi-cycle heating and cooling thermogravimetric (TG) method was used to study the kinetic behavior of three kaolinite samples: defect-free Keokuk kaolinite, KGa-2 with a very low degree of structural order, and KGa-1 having intermediate structural order. In each cycle, the maximum cycle temperature (MCT) was set to 25 °C higher than the preceding cycle. The TG patterns consist of a set of subsequent DTG maxima representing the portions of OH groups that did not dehydroxylate in previous cycles.

Each stage of partial dehydroxylation consists of two kinetic mechanisms and for each of them the experimental du/dr values that characterize the reaction rate of the dehydroxylated fraction, $a$, within a period of the reaction time, $t$, were computed. One mechanism corresponds to a zero-order reaction that occurs in each cycle and indicates that the reaction is homogeneous and each non-dehydroxylated layer is transformed into metakaolinite layer without formation of intermediate derivatives. For this step of the cycles activation energy, $E_a$, was calculated from the linear relationship between $\ln$($du/dr$) and reciprocal temperature, $1/T$; for KGa-2 kaolinite, the $E_a$ varies from 32.0 to 38.1 kcal/mol; in KGa-1, $E_a$ varies from 37.1 to 40.4 kcal/mol, whereas in Keokuk, $E_a$ varies from 42.7 to 47.5 kcal/mol. The particular variation of the $E_a$ is discussed in terms of structural and morphological features of the samples.

The kinetic mechanism of the second step of reaction corresponds to the temperature range higher than the first step of the same heating cycle. The second step starts from the point where $a = a_f$ that was found to vary between 0.25 and 0.45. The acceleration of the reaction rate of dehydroxylation within this interval decreases with increasing $a$ and $T$, and the mechanism observed for each of the studied samples is independent of its stacking order, average particle size, and particle size distribution. The $f(a)$ is a function of the reaction mechanism in the second step and has the form

$$f(a) = (1 - n)^{1/(1 - n)}$$

where $n$ is an empirical parameter and its value was found from 0.01 to 0.06–0.08 among cycles and samples. The value of $n$ controls the reaction rate slowing or the deviation from the zero-order reaction and increases with increasing metakaolinite content. Using parameters $n$, $a$, and $T$ determined for the second step, $E_a$ values were calculated for the second step of reaction in each heating cycle. For the Keokuk kaolinite, $E_a$ value varies from 31.6 to 37.5 kcal/mol, in KGa-1 $E_a$ is 27.0–35.6 kcal/mol, and in KGa-2 the $E_a$ value varies from 26.3 to 34.9 kcal/mol. A structural model explaining the acceleration rate slowing is discussed.

**Keywords**: Kaolinite, dehydroxylation, reaction kinetics, thermogravimetry, stacking order

**INTRODUCTION**

**Kaolinite structure**

Kaolinite, Al$_2$Si$_2$O$_5$(OH)$_4$, is a common dioctahedral 1:1 layer mineral, forming large and economically valuable deposits. An individual kaolinite layer consists of one alumina octahedral sheet and one silica tetrahedral sheet that are bound to each other via apical oxygen atoms. Strong cohesion of the adjacent layers is formed by hydrogen bonding from OH groups on the basal surface of one layer to oxygen atoms forming a basal surface of the following layer. Three symmetrically independent basal OH groups are referred to as “external” OH groups because they form the outer basal surface of each layer. The fourth (OH) group is referred to as “internal” because it is located within the layer.

The octahedral sheet of the kaolinite layer contains three symmetrically independent sites differing in the arrangement of OH groups and O atoms coordinating to two octahedral Al cations and one vacant octahedron (Brindley and Robinson 1946).

The kaolinite layer has a fixed chemical composition, with well-determined positions of each atom. However, the pattern of stacking of adjacent layers produces a large variation of the kaolinite structure (Brindley et al. 1986; Bailey 1988). According to a model of Bookin et al. (1989), two layer displacement vectors, $t_1$ and $t_2$, related by a pseudomirror plane passing through the kaolinite layer unit cell (Bailey 1988) form defect-free enan-