

Kinetic behavior of partially dehydroxylated kaolinite

VICTOR A. DRITS^{1,*} AND ARKADIUSZ DERKOWSKI²

¹Geological Institute of the Russian Academy of Science, Pyzhevsky per. 7, 119017 Moscow, Russia

²Institute of Geological Sciences, Polish Academy of Sciences, Senacka 1, 31-002 Krakow, Poland

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 da/dt values that characterize the reaction rate of the dehydroxylated fraction, α , 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 $\ln(da/dt)$ and reciprocal temperature, 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 $\alpha = \alpha_p$ 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 α 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 $f(\alpha)$ is a function of the reaction mechanism in the second step and has the form

$$f(\alpha) = (1 - \alpha)^n / (1 - n)$$

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 , α , 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