Kinetics of thermal transformation of partially dehydroxylated pyrophyllite

Victor A. Drits,[1] Arkadiusz Derkowski,[2] and Douglas K. McCarty[3,*]

[1]Geological Institute of the Russian Academy of Science, Pyzhevsky per. 7, 119017 Moscow, Russia
[2]Institute of Geological Sciences, Polish Academy of Sciences, Senacka 1, 31-002 Krakow, Poland
[3]Chevron ETC, 3901 Briarpark, Houston, Texas 77063, U.S.A.

Abstract

A multi-cycle heating and cooling thermogravimetric (TG) method was used to study the kinetic behavior of two partially dehydroxylated pyrophyllite samples. In the original state, the S076 sample contains only *trans*-vacant (*tv*) layers, whereas in sample S037 *tv* and *cis*-vacant (*cv*) layers are randomly interstratified. The method consists of consecutive heating cycles (rate 2 °C/min) separated by intervals of cooling to room temperature, with the maximum cycle temperature set (MCT) incrementally higher than in each previous cycle.

The activation energy (E_a) values were calculated for the S037 and S076 samples for all cycles in terms of a homogeneous zero-order reaction with the regression coefficients $r^2 \geq 0.9997$. The S076 sample had E_a values that varied from 40 to 42 kcal/mol within a partial dehydroxylation (D_T) range from 19 to 63%. However, at D_T values <19% and >63% the E_a values are slightly lower at 38–39 kcal/mol and drop below 30 kcal/mol at D_T = 90%. A bimodal distribution of the S037 sample E_a values exists with increasing MCT and D_T. In the first cycles of intense dehydroxylation from *tv* layers the E_a values increase sharply from 34 kcal/mol at D_T = 7% to 45 kcal/mol within the MCT interval from 525 to 575 °C and then decrease to 36–38 kcal/mol at the cycles with MCT = 650–700 °C. In the second portion of cycles corresponding to the dehydroxylation of *cv* layers, the E_a values increase from 36–37 kcal/mol at MCT = 700 °C to 44–46 kcal/mol at MCT = 775 °C. These results show that both *tv* and *cv* layers require exactly the same energy for dehydroxylation and have similar variation of the E_a values with MCT and D_T.

The pyrophyllite particle size distribution is a major factor that is likely responsible for a broad interval of dehydroxylation temperature. This implies that the lower the temperature, the smaller the particles that can be dehydroxylated. Therefore, the activation energy values at the beginning of the reaction are lower than those at higher degrees of dehydroxylation because of the combination of a slow experimental heating rate and thin crystallites, which both contribute to lower temperatures at which the reaction starts.

The decrease in activation energy observed at the end of the dehydroxylation reaction of sample S076, and of the *tv* layer portion of sample S037 is accompanied by an increase in the "induction" temperature interval during which an accumulation of additional thermal energy decreases the activation energy.

The kinetic parameters determined for the samples in this study correspond to a homogeneous reaction and are used to predict a general pattern of the structural transformations of pyrophyllite at different stages during dehydroxylation.

Keywords: Dehydroxylation, pyrophyllite, TGA-DTG, X-ray diffraction, activation energy, *cis*-vacant layers, heating-cooling cycles