Kinetics of partial dehydroxylation in dioctahedral 2:1 layer clay minerals

VICTOR A. DRITS,1,* ARKADIUSZ DERKOWSKI,2 AND DOUGLAS K. MCCARTY3

1Geological Institute of the Russian Academy of Science, Pyzhevsky per. 7, 119017 Moscow, Russia
2Institute of Geological Sciences, Polish Academy of Sciences, Research Centre in Kraków, Senacka 1, PL-31002 Kraków, Poland
3Chevron ETC, 3901 Briarpark, Houston, Texas 77042, U.S.A.

ABSTRACT

A multi-cycle heating and cooling thermogravimetric (TG) method was used to study the kinetic behavior of partially dehydroxylated illite, aluminocladonite, and dioctahedral smectite samples. The method consists of consecutive heating cycles separated by intervals of cooling to room temperature, with the maximum cycle temperatures (MCTs) set incrementally higher in each consecutive cycle.

In the studied samples, dehydroxylation of each portion of the initial OH groups follows the kinetics of a homogeneous zero-order reaction in each heating cycle. The activation energies (Ea) were calculated in terms of this model for separate heating cycles of each sample with regression coefficients R2 ≥ 0.999. A zero-order reaction determined at each heating cycle indicates that at each stage of partial dehydroxylation, there is no formation of an intermediate phase and the reaction is probably the direct transformation of the original layers into completely dehydroxylated layers.

The Wyoming montmorillonite and illite consisting of cis-vacant (cv) layers had the highest Ea values (53–55 kcal/mol). In the samples consisting of trans-vacant (tv) layers and having almost the same octahedral cation composition the maximum Ea values varied from 45 to 30 kcal/mol and the Ea of each sample in this group are similar over a wide range of the Dτ. For the samples consisting of a mixture of cv and tv illite structures, a bimodal distribution of the Ea values exists with increasing MCT and Dτ. The maximum Ea values for dehydroxylation of the tv and cv illite structures are different.

The activation energies from the tv aluminocladonite and Otay tv montmorillonite samples have similar maximum Ea values (39.4 to 41.8 kcal/mol), but the variation in Ea with Dτ has a skewed bell-like distribution that is probably related to a heterogeneous octahedral cation composition of the 2:1 layers.

The Ea values calculated for the mineral structures in this study are compared with those published and the main factors controlling the Ea variation at different stages of the partial dehydroxylation are discussed.

Keywords: Dehydroxylation, 2:1 layer clay minerals, kinetics, activation energy, thermogravimetry

INTRODUCTION

Rock-forming dioctahedral 2:1 layer clay minerals have various applications in different fields of technology and industry due to their unique physicochemical properties. In particular, the high-temperature transformation of the clay minerals plays an important role in the formation of artificial materials of significant technological and mineralogical interest. For example, these materials are used in the glass, ceramic, and refractory industries as well as in wellbore drilling. Efficient industrial application of clay minerals requires a comprehensive investigation of their structural and kinetic behaviors during different temperature treatments.

The main structural unit of 2:1 phyllosilicates, including clay minerals, is a 2:1 layer that consists of two tetrahedral sheets linked through an octahedral sheet. The octahedral sheet contains three symmetrically independent sites that differ in the arrangement of OH groups and oxygen anions coordinating octahedral cations. In the trans-octahedra the OH groups occupy opposite apices, whereas in the cis-octahedra the OH groups form a shared edge. In dioctahedral 2:1 layers, either trans-octahedra or one of two symmetrically independent cis-octahedra may be vacant, forming trans-vacant (tv) or cis-vacant (cv) layers.

* E-mail: victor.drits@mail.ru

Dioctahedral smectite, illite, and mixed-layer illite-smectite (I-S) may consist of tv or cv layers, or the two layer types may be interstratified in the same crystallite (Tsimpursky and Drits 1984; Zyvagin et al. 1985; Drits et al. 1993, 1995, 1998, 2002; Reynolds and Thomson 1993; Drits and McCarty 1996; McCarty and Reynolds 1995, 2001; Ylagan et al. 2000; Lindgreen et al. 2000; Zviagina et al. 2007; McCarty et al. 2009). The crystal-chemical factors responsible for the distribution of octahedral cations over trans- and cis-sites in dioctahedral 2:1 layer silicates were analyzed in detail by Drits et al. (2006). The structural features, identification, and occurrence of cv 2:1 layer silicates were recently reviewed by Drits and Zviagina (2009).

Structural transformations in dehydroxylated and rehydroxylated dioctahedral smectite and illite depend significantly on their chemical compositions and on the distribution of octahedral cations over trans- and cis-sites (Tsimpursky et al. 1985; Drits et al. 1995, 2011a; Wang and Zhang 1997a, 1997b, 1997c; Emmerich et al. 1999; Drits 2003; Muller et al. 2000a, 2000b; Stackhouse et al. 2004). Formation of dehydroxylates of Al- and Al,Mg-rich tv 2:1 layer clay minerals proceeds in one stage, with each pair of adjacent OH groups forming a H2O molecule that is liberated from the structure. A single residual oxygen atom, Q1, is a product of dehydroxylation of the two OH groups, and it is located at the...