Natural sepiolite: Enthalpies of dehydration, dehydroxylation, and formation derived from thermochemical studies

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ABSTRACT

Sepiolite is widely used in various fields due to its unique colloidal-rheological and physicochemical properties. The first experimental thermochemical study of natural sepiolite Mg12Si5O26(OH)2(H2O)2 nH2O from Akkermanovskoe field (Southern Ural, Russia) was performed utilizing the high-temperature heat-flux Tian-Calvet microcalorimeter. X-ray powder diffraction, thermal analysis, and FTIR spectroscopy methods were used to characterize sepiolite. Processes of dehydration, dehydroxylation, and various water types’ removal enthalpies were studied using thermochemical methods. The values of ΔHdehy (298.15 K) of adsorbed, zeolitic, and bound water calculated per 1 mol of released H2O, were as follows: 15 ± 4, 28 ± 8, and 39 ± 15 kJ/mol, respectively. The enthalpy of dehydroxylation of sepiolite was found as 145 ± 14 kJ/mol. Obtained data point at different binding strengths of water in the structure of sepiolite. The enthalpies of formation from the elements ΔHf (298.15 K) were derived by melt solution calorimetry for sepiolite with various content of different water types: −18,773 ± 28 kJ/mol for Mg12Si5O26(OH)2(H2O)2 4H2O and −16,426 ± 21 kJ/mol for Mg12Si5O26(OH)2(H2O)2.

Keywords: Sepiolite, thermochemistry, microcalorimetry, enthalpy of dehydration, enthalpy of dehydroxylation, enthalpy of formation

INTRODUCTION

Sepiolite is a natural nano-structural hydrous magnesium phyllosilicate with theoretical chemical formula Mg12[Si5O26] (OH)2(H2O)2 8H2O. Minerals of the palygorskite-sepiolite group can be typically found in ancient and modern sediments, deep-sea deposits, soils, and crust of weathering of rocks rich in magnesium, however, they do not form large aggregations. They are so-called “special clays” or chain-structure clays. Sepiolite belongs to the mineral group of phyllosilicates, because it contains continuous two-dimensional Si-O tetrahedral sheets. The sepiolite structure can be described as ribbons consisting of 2:1 phyllosilicate structure, one ribbon being linked to the next by inversion of SiO4 tetrahedra along a set of Si-O-Si bonds (Jones and Galan 1988). The important feature of the sepiolite’s structure is the presence of four water types in different crystallographic forms: adsorbed water, zeolitic water, bound water, and constitutional water as hydroxyl groups. Unique structural and physicochemical properties of sepiolite (colloidal-rheological, sorptive, and catalytic), explain its being widely used as catalyst, filler in polymeric and silicate nano-composites, environmental adsorbent, drilling mud additive, molecular sieves etc. Therefore, there is a need to determine the chemical and mineralogical composition of sepiolite clays as well as their physicochemical and thermodynamic parameters. The processes of dehydration and dehydroxylation of sepiolite have been studied previously using different methods of thermal analysis (Nagata et al. 1974; Kiyohiro and Otsuka 1989; Frost and Ding 2003; Giustetto et al. 2011), but their quantitative heat characteristics are not provided in the corresponding literature. Experimental data on the thermodynamic properties of sepiolite are also not available. Results of calorimetric study of the thermodynamic properties of some other layered minerals (saponite, nontronite, and vermiculite) were published recently (Gailhanou et al. 2013). The values of the Gibbs energy of sepiolites of various compositions were estimated using different methods (Tardy and Garrelts 1974; Birsoy 2002), thus, it is difficult to compare them.

The objectives of this work were to study natural sepiolite and the processes of its dehydration and dehydroxylation; to measure the enthalpies of removal of various water types; and to determine the enthalpy of formation of the studied sepiolite using different methods of high-temperature Calvet microcalorimetry.

CHARACTERISTICS OF SAMPLE AND METHODS

Clay sample

The sepiolite sample from the Akkermanovskoe field (Southern Ural, Russia) for our study was taken from the E.A. Fersman Mineralogical Museum of Russian Academy of Sciences (I.I. Ginzburg’s collection). The sample was described as a fibrous dense substance of white color. It had, according to the “wet” chemistry analysis data, the following composition (wt%): 53.59 SiO2, 0.11 Al2O3, 0.26 Fe2O3, 0.16 FeO, 0.13 CaO, 23.88 MgO, 0.16 NiO, 21.44 H2O (Ginzburg and Rukavishnikova 1951). The water content was determined by calcination of the sample at 850 °C for 1 h. The chemical formula calculated on 64 charges has the form Mg11.92Ca0.08Fe2.16Al0.07Si5.38O26(OH)2(H2O)2 9.9H2O and it is close to ideal Mg12Si5O26(OH)2(H2O)2 nH2O. The calculations of the thermodynamic properties