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DIFFERENTIAL THERMAL ANALYSIS OF MONTMORILLONITE

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Abstract

The paper provides an overview of publications on the DTA of montmorillonites (in the temperature range 20–1100°C), starting with the first experiments of Le Chatelier (1887) and ranging up to the present. Consideration is given to the dehydration, dehydroxylation, amorphization and rehydration of montmorillonite (42 references).

Keywords: montmorillonite, thermal analysis

Introduction

Systematic thermoanalytical research on the most common dioctahedral smectite, montmorillonite, started with the well-known work of Le Chatelier in 1887 [1], which demonstrated that, when this clay mineral is heated at constant rate, the first stage involves the endothermic release of water adsorbed on the outer and the inner surfaces. In the second stage, i.e. at about 700°C, a further endothermic effect occurs, which is related to the release of OH groups from the octahedral layer of the three-layered structure. The first endothermic effect is usually attributed to dehydration and the second to dehydroxylation. The third stage in the thermal events is characterized by an endothermic effect followed by an exothermic one. It is now known that these effects are connected with the breakdown of the crystal structure of the dehydrated montmorillonite, and the formation of an X-ray-amorphous product. High-temperature phases may crystallize from such products during the continued elevation of temperature. The problem of the formation and successive disappearance of the high-temperature phases could not be treated by Le Chatelier as his experimental device operated only up to 1100°C.

The thermal changes of montmorillonite in the temperature region 20–1100°C will be discussed in the following.

Dehydration of montmorillonite

For all types of montmorillonites, dehydration is reflected by the first endothermic peak, accompanied by a loss of up to 25 mass %. The shape of the de-

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hydration peak depends on a number of parameters, which may lead to double or triple peaks.

The amount of water adsorbed on a montmorillonite evidently depends on the relative humidity of the external atmosphere, on the nature of the cations occupying exchangeable sites between the layers of the structure skeleton, on the grain diameter distribution of the sample and on the concentration of structure defects.

A number of papers have shown that the dehydration peak is a simple one when the exchangeable sites are occupied by cations with a charge of +1. However, the peak is doubled in the presence of alkaline earth and other +2 cations [2–9]. For a threefold dehydration peak, it is presumed that first the moisture adsorbed on the surface is released, followed by the water molecules bound to the +2 exchanged cations (six molecules per cation) and lastly the molecules bound to the tetrahedral layer of the structure, as a consequence of the high excess of its negative charge [5].

When the exchangeable sites of the structure are occupied by ammonium ions, then, depending on the experimental conditions, their thermal release is manifested by a simple endothermic peak (DTA in inert atmosphere) or is followed by an exothermic effect caused by the oxidation of ammonia [10–12].

The sorption of an organic cation on montmorillonite frequently causes a decrease in hydrophilicity of the mineral surface. Thus, the water adsorbed on the surface is usually released at lower temperature. The successive thermal breakdown of dehydrated organomontmorillonite is a complex process that depends on the mechanism of the pyrolysis of the adsorbed organic molecules [3, 13]. This mechanism is usually different from that of the free sorbate.

Dehydroxylation of montmorillonite

The dehydroxylation of all monoionic forms of the montmorillonites is revealed in the DTA curves (Fig. 1) either by a relatively symmetric endothermic peak with maximum at about 700°C (most frequently 670–710°C) or by two peaks, the first with an extreme at about 550°C and the second one typically at 700°C. Different authors postulate different probable causes of this two-stage dehydroxylation:

- substitution in the tetrahedral and octahedral layers (the role of iron) [14–18];
- defects in the montmorillonite structure [3];
- differences in the mineral particle sizes [19, 20].

The rate of dehydroxylation of montmorillonite and the temperatures at the peak extremes depend both on the nature of the exchangeable cation [18, 21–23] and on the presence of iron ions in the mineral structure [24, 25]. Studies on synthetic montmorillonites have shown that the increase of magne-

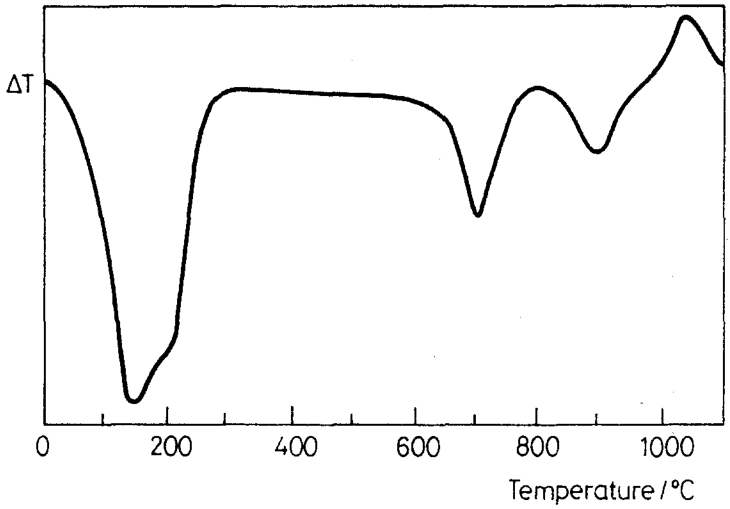

Fig. 1 DTA-curve of Ca-montmorillonite (from locality Stará Kremnička – Jel ovy potok – Slovakia. Derivatograph (MOM Budapest, Hungary): Weight of sample 300 mg, heating rate 15°C min^{-1}, atmosphere air, static

sium in the skeleton structure does not markedly influence the position of the dehydroxylation peak [26].

In his well-known monograph, Mackenzie presumed that montmorillonites with two dehydroxylation peaks are 'abnormal' [3]. This description was first used in that sense by Cole in 1955 [27]. The meaning of this effect remains unclarified [28]. According to Stoch, the montmorillonites originating from the weathering of volcanic ashes give a dehydroxylation peak at 700°C, while those formed by weathering of other minerals (primarily micas) display an additional endothermic peak at 560–600°C [29].

However, a clear discrimination of the dehydration and dehydroxylation of montmorillonites in the TG, DTA and DSC curves is possible only when the exchangeable cation exhibits a low hydration energy, e.g. the Rb- and Cs-montmorillonites. In general, the two processes are mutually superimposed [3, 30].

Amorphization of montmorillonite

Since 1940, it has been known that the third endothermic peak (with maximum usually at 900°C) is related to the breakdown of the crystal structure of the anhydride of montmorillonite and to the formation of an X-ray amorphous product [31]. In spite of the more recent work being focused on clarification of the nature of this endothermic effect, the reason for the absence of this peak for some samples is still unclear. In contrast with the previous endothermic effects, the third endothermic effect is not associated with a change in mass of the samples. We found the first exothermic peak at about 1050°C in the DTA curves (Fig. 1); this is caused by crystallization of the high-temperature phases (from the amorphized product) [3, 32, 33]. The process depends on the chemical composition of the sample, including the type of exchangeable cations. The first review on this topic was that of Grim and Kulbicky in 1957 [34]. This problem is currently frequently treated; at least three of the most contributory articles should be mentioned [35–37].

Rehydration of montmorillonite

The rehydration of montmorillonite under hydrothermal conditions is the theme of special geological research; it is of interest from the point of the changes occurring in clay minerals under natural conditions.

Study of the rehydration of montmorillonites at atmospheric pressure after heating to 100–500°C showed that rehydration and reexpandation ability has upper limit within the interval 350–450°C.

An exception is observed with Li-montmorillonite, where the rehydration ability fades out when heating is effected only to 105–125°C [38]. This effect is caused by the absence of Li^+ in exchangeable positions on the surface of the montmorillonite layers. The mechanism of Li^+ migration and its final distribution in the montmorillonite structure continues to be unclarified [39–42].

The limit of reversible hydration is at about 600°C. Under atmospheric conditions, montmorillonites heated to temperatures exceeding 500–600°C rehydrate only partially and very slowly (hydration requires hundreds of days).

Conclusions

Montmorillonite is the most familiar mineral in the sub-group of dioctahedral smectites and is the one most frequently subjected to thermal studies.

Different samples of montmorillonite yield DTA curves that differ markedly under the same experimental conditions. Because of the variability in the first endothermic peak, it is desirable for measured samples to receive a standard pretreatment to ensure saturation with a known cation (Ca^{2+} or Mg^{2+} are perhaps the most useful) and equilibration at a known relative humidity (e.g. 56% over a saturated solution of calcium nitrate or magnesium nitrate) before measurement. These two pretreatments can be recommended for all dioctahedral smectite samples as they tend to emphasize differences in their behaviour, which will surely predetermine their possible uses.

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