

## **Formation of charcoal-montmorillonite complexes during the thermal analysis of organo-montmorillonites, their structures and stabilities**

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Adsorption of organic matter by clay minerals is one of the most widespread reactions in and on the earth, in the environment, agriculture and in various industrial processes. It includes (i) exchange of initially present inorganic cations by organic cations and (ii) accumulation of polar and nonpolar molecules on the surface and inside the interlayer of the mineral. During adsorption, physical or chemical bonds (long- or short-range interactions) are formed between the mineral and the organic matter. The adsorption products are defined as organo-clay complexes. DTA curves of organic substances recorded in oxidizing and inert environments show diagnostic exothermic and endothermic peaks, respectively, associated with combustion, decomposition, dehydration, fusion, vaporization, sublimation and solid-state transitions. Some peaks of organic matter disappear, the temperatures of other peaks shift and their relative intensities change after adsorption by the clay. DTA of organic material or of organo-clay complexes is carried out either in an oxidizing environment (under air or a flow of oxygen) or under a flow of inert gases (nitrogen or argon). In air or under oxygen, the adsorbed organic matter is oxidized, giving rise to significant exothermic peaks. Under an inert atmosphere, weak endothermic peaks attributed to desorption and pyrolysis of the organic matter are obtained. Since the endothermic peaks are very weak, until recently most TA studies of organo-clays were carried out in air. The present study deals with charcoal complexes of smectite clay minerals, to which montmorillonite (MONT), the most common clay mineral used in adsorption studies, belongs. Formation of charcoal-MONT complexes during DTA runs was observed by Bradley and Grim already in 1948 and later confirmed by using combined DTA-TG. In 1988, with the help of EGA in which the evolved gases were analyzed by mass-spectrometry, we described a model for the air-oxidation of the intercalated organic matter. In the first oxidation step at about 250 °C organic hydrogen is oxidized to form H<sub>2</sub>O. Only some carbon and nitrogen are oxidized at this step to form CO<sub>2</sub> and NO<sub>2</sub>, respectively. The rest of carbon and nitrogen are condensed to form intercalated charcoal which is stable to higher temperatures. Since 2002 we studied the thermal analysis of different organo-clays by thermo-IR-spectroscopy and thermo-XRD-analysis supplemented by curve-fitting calculations of the X-ray diffractograms. From basal spacings of the different tactoids which are formed during the thermal treatment, we identified low temperature stable charcoal-MONT (LTSC), in which the charcoal is oxidized at about 400 °C, and high temperature stable charcoal-MONT (HTSC), in which it is oxidized at above 550-750 °C, together with the dehydroxylation of the clay. From basal spacings of the different tactoids of the thermal treated organo-clay two types of HTSC-MONT were identified and were labeled by  $\alpha$  and  $\beta$ . Basal spacings of tactoids of LTSC-MONT ( $\geq 1.3$  nm) allow the presence of intercalated monolayer charcoal. Basal spacings of tactoids of HTSC-a-MONT ( $\geq 1.22$  nm) also allow the presence of intercalated monolayer charcoal which is obtained by the shrinkage of the LTSC-MONT. Basal spacings of tactoids of HTSC-b-MONT ( $\geq 1.15$  nm) require the keying of carbon atoms into the hexagonal holes of the O-plane of the skeleton of the clay mineral. Some organo-MONTs show other intercalated thermal products. For example, during the thermal treatment of urea polymerization occurs and this gives rise to different thermal progression of urea-MONT. Complexes with intercalated bilayer charcoal were also identified.