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Desorption of stearic acid upon surfactant adsorbed montmorillonite

A thermogravimetric study

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Abstract Thermal analysis and differential thermal analysis offers a novel means of studying the desorption of acids such as stearic acid from clay surfaces. Both adsorption and chemisorption can be distinguished through the differences in the temperature of mass losses. Increased adsorption is achievable by adsorbing onto a surfactant adsorbed montmorillonite. Stearic acid sublimes at 179 °C but when adsorbed upon montmorillonite sublimes at 207 and 248 °C. These mass loss steps are ascribed to the desorption of the stearic acid on the external surfaces of the organoclays and from the de-chemisorption from the surfactant held in the interlayer of the montmorillonite.

Keywords Thermogravimetric analysis · Differential thermogravimetric analysis · Chemisorption · Montmorillonite · Desorption · Stearic acid

Introduction

Mineral phases play an important role in the adsorption and transport of natural organic matter in the aquatic environment. Adsorption of organic matter changes the surface properties of the mineral particles, thus influencing their transport behavior and consequently the fate of pollutants connected to them [1–4]. Therefore, knowledge about the adsorption mechanisms of humic substances, which constitute a major part of natural organic matter, is mandatory for an understanding of contaminant mobility [5]. The focus has been on interactions between long chain organic acids and clays. Čapková et al. [1] applied an anion surfactant such as octadecylamine to intercalate montmorillonite with stearic acid. Recently, we used dodecytrimethyl ammonium bromide (DDTMAB), an ion surfactant modified montmorillonite with stearic acid in aqueous solution successfully.

The use of thermal analysis techniques to study montmorillonitic clays is well known [6]. Some thermoanalytical studies of organo-modified clays have been forthcoming [7–9]. A recent review has demonstrated the applicability of DTA-TG for differentiating between adsorbed and free organic matter and also between ionic and molecular adsorption [8]. This work has shown that the location of the exothermic peaks is diagnostic and serves to show the adsorption of organic molecules on cations. Many of the thermal analytical studies have been applied to nanocomposites involving organoclays [10]. However there have been almost no studies of the thermal stability of organoclays and no studies of the structure of organoclays and certainly no studies of the desorption of adsorbed acids on organoclays. Recently thermal analysis techniques have proven most useful for the study of complex mineral systems [11–17] and materials generated through the modification of surfaces [18–22]. Modification of surfaces through intercalation has also been studied using thermal analysis techniques.

This paper reports the changes in the structure of a calcium montmorillonitic clay with adsorbed organic acids. X-ray diffraction and high resolution thermogravimetric analyses are used to study the changes in the clays basal spacing depending on the adsorption of the stearic acids.

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Experimental

Materials

The montmorillonite used in this study was supplied by the Clay Minerals Society as source clay SWy-2-Na-Montmorillonite (Wyoming) This clay originates from the Newcastle formation, (cretaceous), County of Crook, State of Wyoming, USA. The cation exchange capacity (CEC) is 76.4 meq/100 g (according to the specification of its producer). This clay was cation exchanged with Ca^{2+} to make a calcium montmorillonite.

Preparation of acid adsorption on clay

2.5 g Ca Montrillonite, 4.4 g stearic acid, and 5.3 g dodecytrimethyl ammonium bromide (DDTMAB) surfactant were suspended in 250 ml distilled water. The mixture was heated to- and then maintained at the required reaction temperature, e.g., 80 °C, for 12 h and then allowed to cool down overnight. This cycle was repeated four times. Two additional portions of stearic acid (4.4 g) were added after the first two cycles, so that the overall total was the required amount (13.2 g). In the last cycle the mixture was simply allowed to stir for 9 h without acid addition. The mixture was allowed to cool down slowly to ambient. The solids were recovered by centrifugation, washed once with distilled water, four times with ethanol, and thereafter once with acetone. After each washing the solids were separated from the liquid by centrifugation. The product was allowed to dry at room temperature.

X-ray diffraction

X-Ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Cu K_α radiation (1.54052 Å). Patterns were collected in the range 3 to 90° 2θ with a step size of 0.02° and a rate of 30 s per step. Samples were prepared as a finely pressed powder into aluminium sample holders. The Profile Fitting option of the software uses a model that employs twelve intrinsic parameters to describe the profile, the instrumental aberration and wavelength dependent contributions to the profile.

Thermal analysis

Thermal decomposition of the acid adsorbed on montmorillonite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 2.0 °C/min up to 500 °C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases such as water and carbon dioxide were analyzed.

Results and discussion

X-ray diffraction

Montmorillonite consists of tetrahedral silica layers and octahedral alumina layers, carrying negative charges which must be counterbalanced by exchangeable cations in the interlayers. Such an arrangement results in a basal spacing of around 11.7 Å in a dry air state. This basal spacing is dependent upon the size of the cation be it Na, Ca or Mg and also on the degree of hydration of the cation. If the X-ray diffraction is undertaken in a humid atmosphere then an increase in the expansion of the montmorillonite is expected. This degree of hydration is very dependent on the vapour pressure of water and the temperature.

The XRD patterns of calcium montmorillonite and the organoclays with adsorbed stearic acid before is shown in Fig. 1. The XRD pattern of calcium montmorillonite before and after adsorption stearic acid varied significantly. Calcium montmorillonite exhibited a sharp diffraction peak at 2θ value of 5.92°, while the stearic acid-calcium montmorillonite complexes showed a diffraction peak at 2θ value of 5.25°. This result indicates that the d_{001} spacing of calcium montmorillonite increased from 15.0 to 16.9 Å after adsorption stearic acid, which resulted from carboxylic acid adsorbed onto the surfactant modified calcium montmorillonite. This increase in the basal spacing of

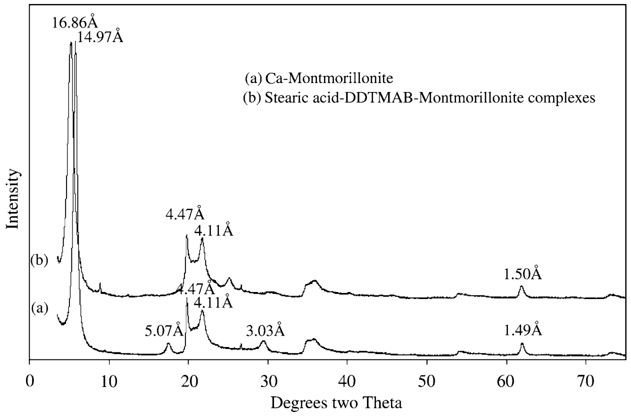

Fig. 1 X-ray diffraction of calcium montmorillonite and stearic acid adsorbed on organoclays

1.9 Å is small and less than the size of the stearic acid even if the molecule was laying flat on the surface of the montmorillonite.

Thermal analysis

In order to study the desorption of stearic acid from the surfactant adsorbed into calcium montmorillonite, it is first necessary to analyze pure stearic acid and surfactant. The thermal analysis of stearic acid is reported in Fig. 2. The TG shows almost a 99.38% mass loss at 175 °C. Some asymmetry on the low temperature side of the DTG peak is observed. The thermal analysis of the surfactant used in this research is reported in Fig. 3. The surfactant is lost at around 201 °C with almost 100% mass loss. The TG and DTG of pure calcium montmorillonite is shown in Fig. 4. For calcium montmorillonites (CM), two mass loss steps are observed centered at temperature ranges between 40 and 120 °C and 450 to 700 °C. The first mass loss step is attributed to dehydration of the montmorillonites. The second mass loss step is due to dehydroxylation of the montmorillonite. The CM shows mass losses at 45 and 121 °C attributed to adsorbed water and water of hydration of the sodium cation in the montmorillonites interlayer. Mass losses of 1.62 and 0.36% are observed for these two dehydration steps. The distinction between the two dehydration steps is accentuated for the CM. The two mass loss steps occur at 51 and 105 °C with mass losses of 2.7 and 1.25%.

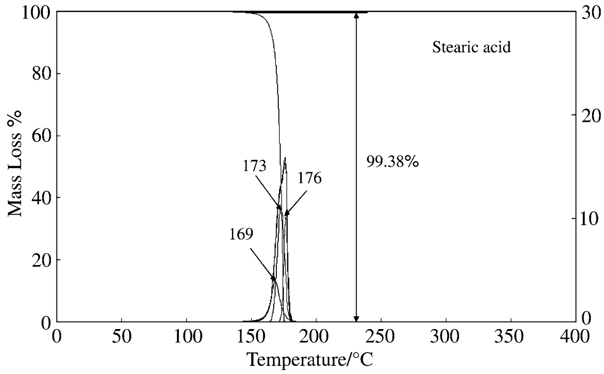

Fig. 2 Thermogravimetric and differential thermogravimetric analysis of stearic acid

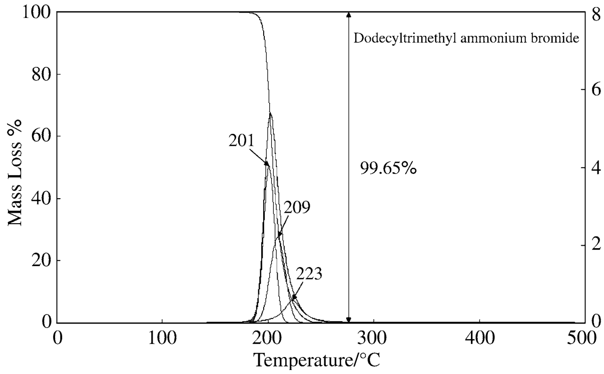

Fig. 3 Thermogravimetric and differential thermogravimetric analysis of dodecyltrimethyl ammonium bromide

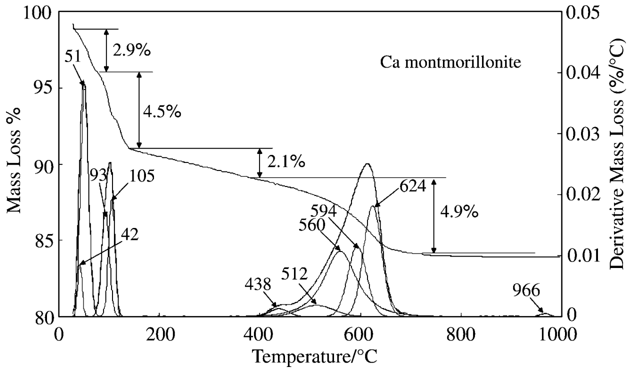

Fig. 4 Thermogravimetric and differential thermogravimetric analysis of calcium montmorillonite

The desorption of stearic acid from the organoclay may be studied through the thermal analysis of the adsorption complex as shown in Fig. 5. A series of small mass losses is observed at 56, 78 and 88 °C and are attributed to water in the montmorillonite interlayer. There is a mass loss of 0.73% for these steps. The DTG peak at 208 °C is in a similar position to that for the pure surfactant and thus is assigned to the mass loss of surfactant adsorbed on the outside surfaces of the montmorillonite. The peak at 208 °C may also be due to the desorption of the stearic acid. Two additional mass loss steps are observed at 248 and 322 °C. These DTG peaks are assigned to the desorption of the stearic acid adsorbed on the surfactant held between the montmorillonite layers. For the DTG peaks at 208, 248, 275 there is a mass loss of 11.74%. The DTG peak at 322 °C is attributed to surfactant adsorbed on the external surfaces of the montmorillonite. The peak at

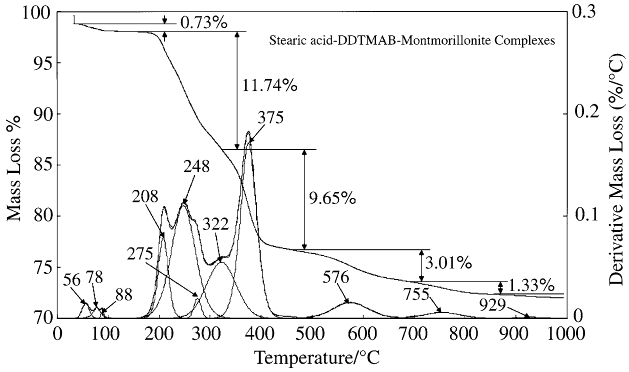

Fig. 5 Thermogravimetric and differential thermogravimetric analysis of stearic acid adsorbed on organoclay

375 °C is assigned to the sublimation of the surfactant. There is a mass loss of 9.65% associated with the loss of surfactant. The DTG step at 576 °C is associated with the dehydroxylation of the montmorillonite. Two higher mass loss steps are observed at 755 and 929 °C. these mass loss steps are attributed to structural rearrangements of the montmorillonite.

Conclusions

The desorption of stearic acid from calcium montmorillonites has been studied using a combination of thermogravimetric analysis and differential thermogravimetric analysis. Stearic acid volatilizes at 179 °C and the surfactant sublimes at around 208 °C. The stearic acid adsorbed on the external surfaces of the montmorillonite at 248 °C. Stearic acid sublimes from the surfactant modified calcium montmorillonites at 322 °C. The surfactant is held in the interlayer of the montmorillonite through electrostatic effects and sublimes from the clay surfaces at 375 °C. This chemisorptions of the stearic acid on the surfactant also effects the dehydroxylation of the montmorillonites which is lowered by the adsorption of the stearic acid. It is proposed that the carboxylic acid (–COOH) part of the stearic acid may penetrate the ditrigonal cavity of the montmorillonite and reacts with the inner hydroxyl group, thus causing a lowering of the dehydroxylation temperature by providing a mechanism for the loss of the OH units.

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