

THERMAL ANALYSIS OF TRIBUTYLAMMONIUM MONTMORILLONITE AND LAPONITE

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Montmorillonite and Laponite loaded with different amounts of tributylammonium cations (TBAH⁺), up to 40 and 30 mmol, respectively, per 100 g clay, were studied by thermo-XRD-analysis. TBAH-smectites heated at 300 and 420°C exhibited basal spacings of 1.30 and 1.24 nm, attributed to smectite tactoids with low- and high-temperature-stable monolayer charcoals, respectively in the interlayers. DTA-EGA and TG of the TBAH-smectites showed four stages of mass loss labeled A, B, C and D. Stage A below 250°C, accompanied by an endothermic DTA peak, resulted from the dehydration of the clay. Mass loss stages B, C and D, at 250–380, 380–605°C and above 605°C, respectively, accompanied by exothermic DTA peaks, were due to three oxidation steps of the organic matter. In mass loss stage B (first oxidation step) mainly organic hydrogen was oxidized to H₂O whereas carbon and nitrogen formed low- and high-temperature-stable charcoals. In stages C and D (second and third oxidation steps) low- and high-temperature-stable charcoals were oxidized, respectively. Dehydroxylation of the smectites occurred together with the second and third oxidation steps. Thermal mass loss at each step was calculated from the TG curves showing that in montmorillonite the percentage of high-temperature-stable charcoal from total charcoal decreased with higher TBAH⁺ loadings of the clay whereas in Laponite this percentage increased with higher loadings of the clay.

Keywords: charcoal-smectite complexes, DTA, EGA, Laponite, montmorillonite, organo-smectites, TG, tributylammonium smectites, XRD

Introduction

Organo-clays prepared by the adsorption of organic amines onto clay minerals are widely used in many sophisticated high-Tec industries and as substrates for pollution purification [1]. Recently these composite-materials have become important for the plastic industry [2]. Most publications on organo-clays deal with their fine structure [e.g. 3] and their organophilic and adsorptive properties [e.g. 4, 5]. Only few papers deal with thermal effects on these materials [e.g. 6–8], in spite of the importance of their thermal behavior in many industrial applications. TG and DTA studies of organo-clays coupled with other thermal methods have been recently reviewed [9, 10].

The present paper describes thermal analyses of TBAH⁺-montmorillonite and -Laponite, where TBAH⁺ is the cation tri-*n*-butylammonium, as a model for the thermal behavior of aliphatic ammonium-smectites. DTA curves of TBAH-montmorillonite and of tributylamine (TBA) adsorbed by Cu-montmorillonite were already recorded in 1963 [10, 11]. In 1992 we described the DSC curves of TBAH-montmorillonite and -Laponite up to 250°C [12]. TBAH-montmorillonite dehydrates in two steps, with two different molar heats of dehydration, whereas TBAH-Laponite dehydrates in one step.

The only step in Laponite and the first step in montmorillonite were attributed to loss of water of the hydrophobic hydration zone (water of zones A_o in the terminology of Yariv [13]). The second dehydration step was specific for montmorillonite and was attributed to non-structured water molecules of zone B_{om}, H-bonded to atoms of the oxygen planes of the clay framework. H-bond formation was attributed to the surface basicity of atoms of the oxygen plane of the smectite framework due to tetrahedral substitution of Al for Si occurring to some extent in montmorillonite from Wyoming but not in Laponite [14].

In the present paper thermo-XRD-analyses, simultaneous DTA-EGA (evolved gas analysis carried out with MS) and TG of TBAH⁺-montmorillonite and -Laponite recorded in air atmosphere are described. In general during thermal treatments of organo-clays in air at above 250°C the adsorbed organic compounds are oxidized into charcoal and water [15]. Carbonization of organic matter in the interlayer of montmorillonite was investigated by graphitizing polymers [16–19]. The black residue obtained at 700°C was a film shape highly stacked structure with small interplanar spacing of 0.337 nm. The formation of such a unique coke was attributed to the peculiar method where the two-dimensional space between the clay lamellae served as a unique field for carbonization.

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In the interlayer charcoal appears in several varieties. Two varieties composed of mono- or multilayer carbon were identified by X-ray of thermal-treated Congo-red-montmorillonite complexes with spacings of 1.10–1.33 and 1.61–2.19 nm, respectively [20]. From spacings of peak components calculated by curve fitting applied on the X-ray diffractograms, two-types of monolayer charcoal were identified. In one type carbons penetrated into the ditrigonal holes of the oxygen plane whereas in the second type there was no penetration [21, 22]. DTA of montmorillonites with different exchangeable cations, loaded with the anionic dye Congo red, showed the formation of two charcoal-varieties with different stabilities. One variety was oxidized in the temperature range 400–600°C and the other in 550–800°C, labeled as low- and high-temperature-stable charcoal, respectively. The surface acidity of the interlayer, determined by the exchangeable metallic cation, affected the type of charcoal formed. With high polarizability-cations the high-temperature-stable charcoal-variety was the main product whereas with cations having a low polarizability the low-temperature-stable variety was the main product [23]. Simultaneous DTA-EGA of Laponite and montmorillonite loaded by aromatic cationic dyes showed that thermal stability of charcoal was higher in the latter [24].

It seems plausible to get a better insight into the different charcoal-smectite complexes as it may open a new field of composite-materials and lead to the synthesis of materials with special properties. In the present study we examined the effects of mineral and loading on the relative amounts of each of the charcoal varieties formed by heating TBAH-smectites. This is determined by TG from the amount of mass loss in the different thermal stages supplemented by thermo-XRD-analysis and DTA-EGA of the samples.

Experimental

Materials

Wyoming bentonite (Na-montmorillonite) was supplied by Ward's National Establishment, Inc., USA. The clay was ground manually and passed through 80-mesh sieve. A 1% aqueous suspension was prepared and after 24 h the clay fraction (particle size <1.5 µm) was separated from the sediment by decantation. The chemical formula of this clay is $[(Al_{3.07}Ti_{0.01}Fe_{0.40}^{III}Mg_{0.49})(Si_{7.79}Al_{0.21})O_{20}(OH)_4]Na_{0.75}$, with about 10% of the octahedral metallic sites isomorphically substituted by Fe [25]. The Wyoming bentonite contained 74, 1, 6.5 and 11.5 mmol exchangeable Na^+ , K^+ , Mg^{2+} and Ca^{2+} per 100 g clay, respectively, determined by atomic absorption in four

extractions with 20 mL of 1.0 M ammonium acetate at pH 7 from a sample of 200 mg of montmorillonite.

Laponite XLG, a synthetic Na-hectorite, described by Neumann and Sansom [26] was kindly donated by Laporte Industries Ltd., UK, and used as received. Its chemical formula is as follows: $[(Mg_{5.1}Li_{0.6}H_{0.6})(Si_8)O_{20}(OH)_4]Na_{0.6}$, indicating the absence of Fe. The cation exchange capacity is 79 mmol per 100 g clay.

Tri-*n*-butylamine (TBA) supplied by Fluka, was used as received. An aqueous 0.2 M solution of TBA was prepared and titrated with HCl 0.2 M, using methyl-orange as indicator. An aqueous 0.1 M solution of the salt tri-*n*-butylammonium chloride was prepared by mixing similar volumes of TBA 0.2 M and HCl 0.2 M aqueous solutions.

Methods

The exchange of Na^+ by $TBAH^+$ was carried out in aqueous suspensions of the smectites. Different amounts of the ammonium chloride salt solutions were added to 1% clay suspensions. To avoid the formation of ammonium-amine associations in the interlayer space [27–30], the clays for the present study, were loaded with up to 30 or 40 mmol $TBAH^+$ per 100 g Laponite or montmorillonite, respectively. With these loadings, only traces of Ca^{2+} were detected in the supernatants, which were beyond the accuracy of the determination, indicating that during the exchange reaction mainly Na^+ was replaced by $TBAH^+$. A Leco Carbon-analyzer determined the carbon content of the samples. Air-dried samples were equilibrated five days in a desiccator under relative humidity of 53% obtained in the presence of a beaker with an aqueous saturated solution and solid crystals of $Mg(NO_3)_2 \cdot 6H_2O$ before the XRD, DTA-EGA, and TG studies.

Thermo-X-ray diffraction analysis

Samples with a preferred orientation were obtained by sedimenting natural non-loaded clays and TBAH-clay complexes from aqueous suspensions on glass slides. After equilibrating the air-dried oriented samples under a relative humidity of 53%, their X-ray patterns were recorded by a Philips Automatic Diffractometer (PW 1710) with a Cu tube anode, before thermal treatment and after heating the samples for two hours at 120, 300 and 420°C. After each thermal treatment the samples were cooled a few minutes in a desiccator over SiO_2 and diffracted at room temperature under ambient atmosphere. Preliminary experiments with samples heated at 420°C showed that reproducible diffractograms were obtained within 24 h, whether or not the samples were kept in the desicca-

tor, in agreement with MacEwan [32] who claimed that the collapse of montmorillonite above 300°C was irreversible.

DTA-EGA experiments

Simultaneous DTA-EGA experiments were performed under a flow of air on a Mettler TA-1 thermal analysis instrument coupled with a Balzer quadrupole mass spectrometer. The thermoanalytical system was described previously [31]. Samples of 20 mg montmorillonite or Laponite, loaded with 40 or 30 mmol TBAH⁺, respectively, were used for each run. The rate of airflow was 1.9 L.p.h. Heating rate was 10°C min⁻¹. Calcined kaolinite was used as a reference material. Total pressure in mass spectrometer was 4·10⁻⁶ mbar. The following atomic masses were used for the gas evolution curves, H₂O, 17 and 18; CO₂, 22 and 44; NO₂, 46; CH₃, 15; C₂H₆, 30.

Thermogravimetry study

Manually pulverized samples of 100–200 mg were used for the TG runs. The instrument was a home-made apparatus [12]. The heating rate was 10°C min⁻¹. All runs were carried out under air.

Results and discussion

Thermo-XRD-analysis

Tactoids or oriented aggregates are clusters of parallel layers held by face-to-face interactions (FF associations). In smectite tactoids water layers and/or layers of the adsorbed organic compounds, separate the silicate layers comprising the interlayer space. According to Bragg's Law, particles obtained from FF associations of similar layers and have similar interlayers are responsible for the X-ray diffraction. Originally the term 'tactoids' was used for particles in colloid solutions and suspensions. In our publications it is also used for solid particles capable to diffract X-rays in powder mixtures.

Thermo-XRD-analysis of organo-smectites is used to determine whether adsorbed organic matter is located inside the interlayer [33]. Oriented samples of unloaded and TBAH-loaded montmorillonite and Laponite, up to 40 and 30 mmol TBAH⁺ per 100 g clay, respectively, were heated at 120, 300 and 420°C and their XRD recorded after each thermal treatment. Representative diffractograms are depicted in Figs 1–4. Before thermal treatment spacings of Na-montmorillonite and -Laponite were 1.27 and 1.45 nm, respectively. Loading increased the basal spacings up to 1.35 and 1.52 nm, respectively.

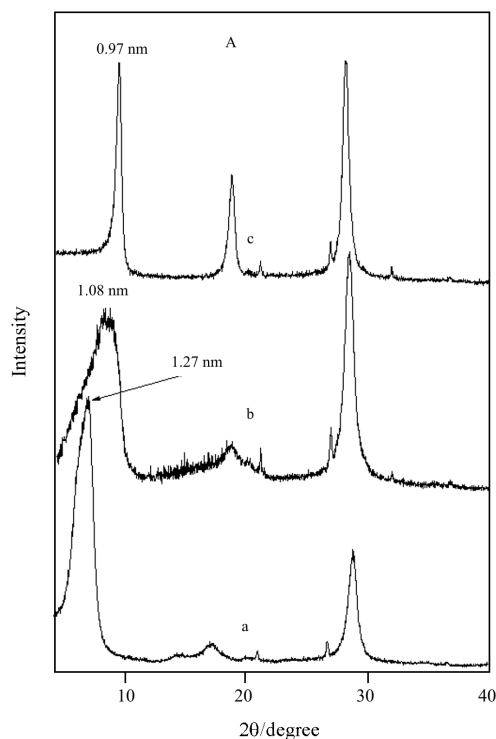


Fig. 1 X-ray diffraction of unloaded montmorillonite, a – unheated sample, b – sample heated 1 h at 300°C and c – at 420°C

After heating at 420°C the unloaded montmorillonite and Laponite collapsed and basal spacings of 0.97 and 1.01 nm, respectively, were recorded. Montmorillonite collapsed already after 2 h at 300°C. Laponite required 420°C for collapsing. In the presence of small amounts of TBAH⁺ (10 mmol per 100 g clay) heating at 420°C, gave a peak at 0.99 nm and a shoulder corresponding to higher spacings. With increasing loadings of TBAH⁺ the shoulder gradually turned into a distinct peak at about 1.24 nm and the 0.99 nm peak disappeared. As shown in the next paragraph the oxidation of the low-temperature-stable charcoal occurs above 380°C and that of the high-temperature-stable charcoal at above 605°C. Consequently, it is assumed that the 1.30 and 1.24 nm spacings obtained at 300 and 420°C, respectively, characterize tactoids with low- and high-temperature-stable charcoal of monolayer carbon in the interlayer space.

Simultaneous DTA-EGA

DTA curves of montmorillonite and Laponite loaded by 40 and 30 mmol TBAH⁺, are shown in Figs 5 and 6, respectively. The H₂O and CO₂ evolution curves, determined by mass-spectroscopy, are also shown. The temperatures of the different thermal reactions are gathered in Table 1. The TA curves of both organo-smectite samples show that the thermal behavior of both organo-clays can be divided into

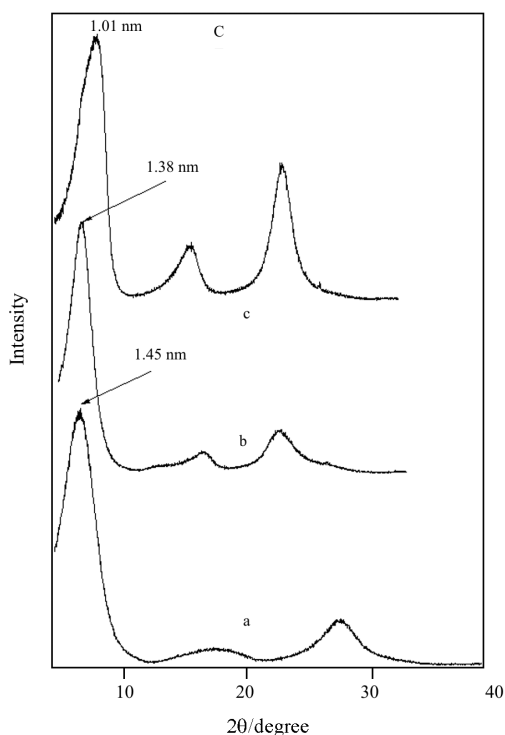


Fig. 2 X-ray diffraction of unloaded Laponite, a – unheated sample, b – sample heated 1 h at 300°C and c – at 420°C

four stages. In the first stage up to 250°C (stage A), the endothermic dehydration of the clay was the major thermal reaction. This resulted in the appearance of a strong DTA endothermic peak at 120°C and a strong peak in the H₂O evolution curves.

At 250°C the oxidation of TBAH⁺ began and all TA curves show a change in the direction of their advance. In the second stage between 250 and 380°C (stage B), the first step of the oxidation of the adsorbed organic matter took place, giving rise to a strong DTA exothermic peak at 320–335°C. The EGA curves show that H₂O was the principal oxidation product, obtained from the oxidation of the hydrogen component of the organic ammonium by air oxygen. Only trace of CO₂ was detected among the evolved gases. At this stage the non-oxidized carbon and nitrogen components of the organic ammonium formed charcoal inside the interlayer.

In the third stage between 380 and 605°C (stage C), the second oxidation step of the adsorbed organic matter took place, accompanied by a medium size DTA exothermic peak at 400–430°C with extension to lower temperatures. According to Yermiyahu *et al.* [23] at this stage the low-temperature-stable charcoal was oxidized by air. According to the evolution curves of both organo-clays CO₂ was the principal product obtained by oxidation of the carbon component of the charcoal. Traces of NO₂ were also detected in the evolved gases. Temperatures of maxi-

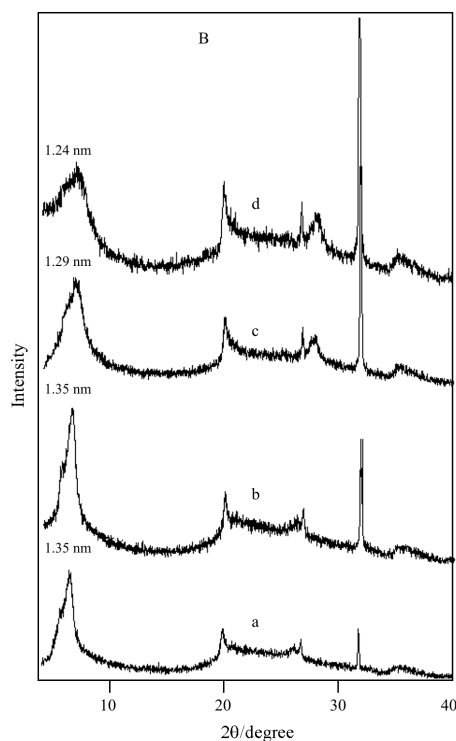


Fig. 3 X-ray diffraction of montmorillonite loaded with 40 mmol TBAH⁺ per 100 g clay, a – unheated sample, b – sample heated 1 h at 120°C c – at 300°C and d – at 420°C

mum evolution of this gas were similar to those of CO₂ (Table 1) but their size in the evolution curves was very small and these curves are not shown in Figs 5 and 6. The H₂O evolution curve showed a small peak at the same temperature where the CO₂ and NO₂ curves showed, indicating that the appearance of water at this step was connected to the oxidation of the low-temperature-stable charcoal, suggesting that this charcoal was composed of H, C and N atoms. It might be possible that at this stage the high-temperature-stable variety was formed from the non-oxidized charcoal.

The thermal reactions of the fourth stage in the thermal analysis curves from 605°C (stage D) are the dehydroxylation of the smectite minerals and the third (last) step of the oxidation of the organic matter. According to Yermiyahu *et al.* [23] the exothermic peaks in this stage represent the oxidation of a high-temperature-stable charcoal. There is a good correlation between the temperatures of the dehydroxylation DTA endothermic peaks and the maxima of the high temperature peaks in the H₂O evolution curves. It is therefore suggested that most water at this stage originated from the dehydroxylation of the clays. The CO₂ and NO₂ evolution curves of TBAH-montmorillonite and -Laponite show that the last oxidation steps of carbon and nitrogen components of charcoal occurred at 690 and 750°C, after the dehydroxylation of both clays.

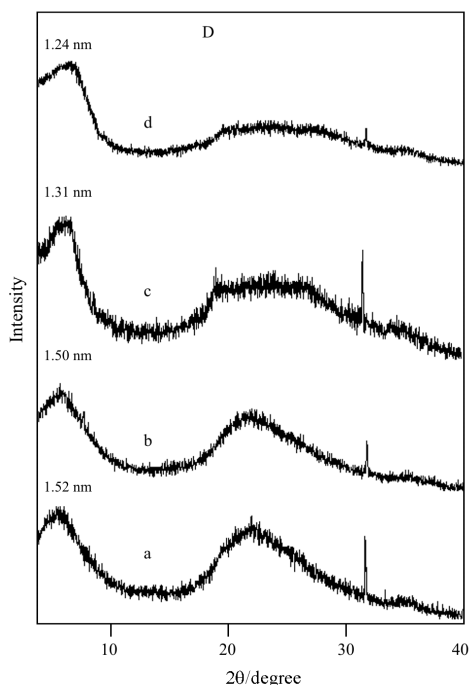


Fig. 4 X-ray diffraction of Laponite loaded with 30 mmol TBAH⁺ per 100 g clay, a – unheated sample, b – sample heated 1 h at 120°C, c – at 300°C and d – at 420°C

The DTA curve of TBAH-montmorillonite showed two exothermic medium size peaks in this stage, at 625 and 720°C, whereas the CO₂ and NO₂ evolution curves showed a single peak at 690°C. Due to the overlapping of this oxidation-exothermic reaction with the dehydroxylation-endothermic of the clay with a maximum at 655°C, the sum of these reactions resulted in two separate exothermic peaks. In the case of Laponite, the principal exothermic peak occurred at 760°C whereas the maximum evolution of CO₂ and NO₂ occurred at 750°C, after the completion

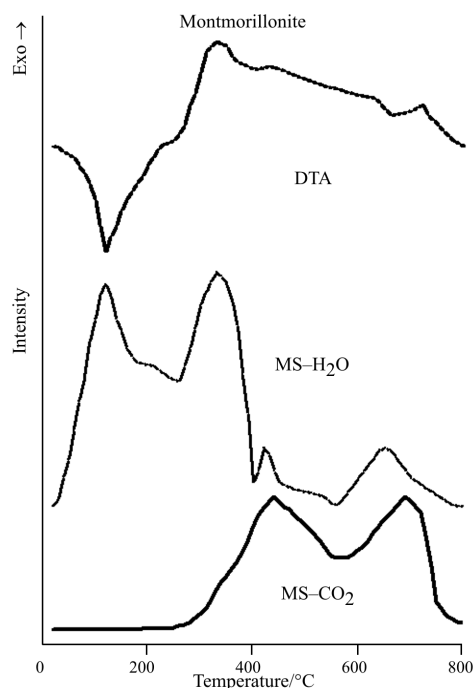


Fig. 5 Simultaneous DTA and thermal evolved gas analysis curves of montmorillonite loaded with 40 mmol TBAH⁺ per 100 g clay. Evolved gases are H₂O and CO₂

of the dehydroxylation-endothermic reaction. It should be noted that at this temperature range the oxidation-exothermic reaction was followed by the exothermic-recrystallization of the dehydroxylated meta-Laponite. In Na-Laponite a sharp exothermic peak of recrystallization at 765°C follows the dehydroxylation endothermic peak at 730°C [34, 35].

Only trace amount of CH₃ and C₂H₆ were detected during the thermal analysis. They were too small to obtain any reliable information on the thermal decomposition and pyrolysis of the organic cat-

Table 1 Endothermic and exothermic peak maxima in the DTA curves of montmorillonite and Laponite loaded with TBAH⁺ (40 and 30 mmol per 100 g air-dried clay, respectively) and peak maxima in the H₂O, CO₂ and NO₂ evolution curves

TBAH-montmorillonite (40 mmol ammonium cation per 100 g clay)							
TA curve	°C						
DTA curve	120 s, endo	335 vs, exo	430 m, exo	625 w, exo	655 w, endo	–	720 m, exo
H ₂ O evolution	120 vvs	330 vs	425 vw	–	655 m	–	–
CO ₂ evolution	–	–	435 vs	–	–	690 vs	–
NO ₂ evolution	–	–	435 w	–	–	690 w	–
TBAH-Laponite (30 mmol ammonium cation per 100 g clay)							
TA curve	°C						
DTA curve	120 s, endo	320 vs, exo	400 m, exo	–	700 m endo	–	760 m, exo
H ₂ O evolution	115 vvs	310 vs	400 vw	–	705 m	–	–
CO ₂ evolution	–	–	400 vs	–	–	750 m	–
NO ₂ evolution	–	–	400 w	–	–	750 w	–

DTA peak; s – strong; m – medium; w – weak; v – very

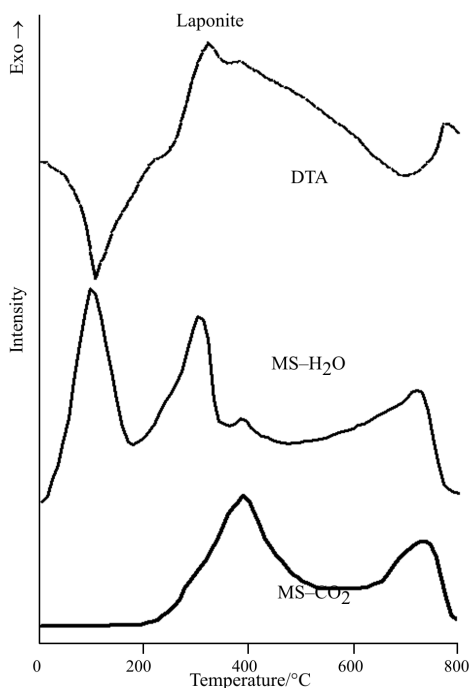


Fig. 6 Simultaneous DTA and thermal evolved gas analysis curves of Laponite loaded with 30 mmol TBAH⁺ per 100 g clay. Evolved gases are H₂O and CO₂

ion. However, it should be mentioned that the thermal analysis was carried out in an oxidizing environment.

Mass loss

TG curves of unloaded montmorillonite and Laponite and of these smectites loaded with 40 and 30 mmol TBAH⁺ per 100 g clay, respectively, are shown in Figs 7 and 8. These smectites with no organic matter showed two stages of mass loss, below and above 380°C. In the first stage dehydration of external and interlayer water occurred. In the latter stage water originated from the dehydroxylation of the clay was evolved.

TG curves of loaded clays showed higher mass loss compared with unloaded clays. There is a good correlation between the TG and DTA-EGA curves, the former show four stages of mass loss. Stage A occurred below 250°C, stages B, C and D in the temperature ranges 250–380, 380–605°C and above 605°C, respectively. Stage A resulted from the dehydration of the clays. The other three stages resulted from the three steps of oxidation of the organic matter, i.e., stage B, evolution of water obtained by the oxidation of organic H, stage C, evolution of CO₂, NO₂ and H₂O obtained by the oxidation of low-temperature-stable charcoal and stage D, evolution of CO₂ and NO₂ obtained by the oxidation of high temperature stable charcoal [15, 23]. TG of unloaded smectites showed that the dehydroxylation of the clay also contributed to mass loss in stages C and D.

In Tables 2 and 3 mass loss (in mass%) are depicted, determined from the TG curves and calculated on the basis of the mass of both clays, unloaded and loaded with increasing amounts of TBAH⁺, calcined at 800°C. According to the tables mass loss in the dehydration stage (up to 380°C) of unloaded montmorillonite and Laponite were 11.0 and 17.8% and in the dehydroxylation stage (380–800°C) 5.7 and 7.3%, respectively.

According to Tables 2 and 3, mass loss below 250°C of the loaded clays was much higher than those of the unloaded clays. Organic ammonium cations may serve as pillars in the interlayer [36] and because of the high basal spacing of TBAH-montmorillonite and TBAH-Laponite (1.35 and 1.52 nm, respectively) compared with the unloaded clays (1.27 and 1.45 nm, respectively), higher amounts of water were adsorbed into the interlayer space during the five equilibration days of the samples at a relative humidity of 53%. It should be noted that the proton in the

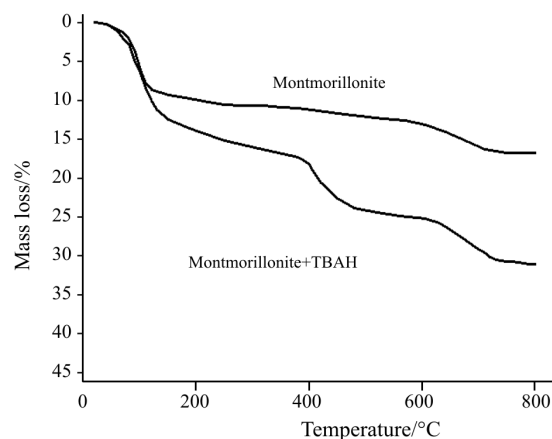


Fig. 7 TG curves of unloaded montmorillonite (upper curve) and of montmorillonite loaded with 40 mmol TBAH⁺ per 100 g clay (lower curve)

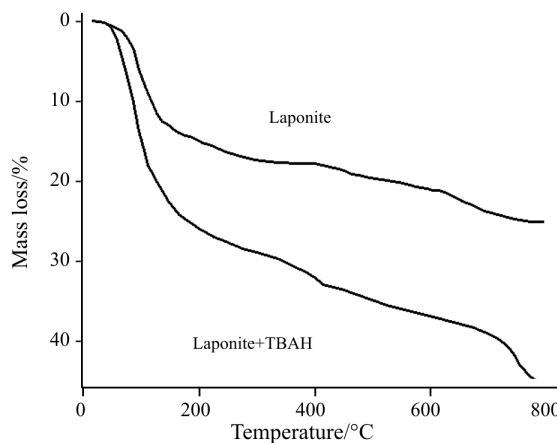


Fig. 8 TG curves of unloaded Laponite XLG (upper curve) and of Laponite loaded with 30 mmol TBAH⁺ per 100 g clay (lower curve)

head group of TBAH⁺ cation (Brønsted acid site) contributes to the hydrophilicity of the interlayer [13, 14].

In the temperature range 205–250°C the mass loss of TBAH⁺-montmorillonite was much higher compared with that of the unloaded clay. Having a relatively large size, TBAH⁺ is a water structure breaker [37]. As a consequence, some of the interlayer water became non-structured (water of zone B_{om}). Due to the tetrahedral substitution in montmorillonite, atoms of its framework oxygen planes are electron-pair donors. Non-structured water molecules formed H-bonds with these atoms and consequently their evolution occurred at higher temperatures compared with that of structured water, which evolved mainly below 205°C [13]. In the case of Laponite the basicity of the framework oxygen plane is weak and

the oxygen atoms do not form H-bonds with non-structured interlayer water molecules of zone B_{om} [14]. Consequently mass loss of organo-Laponite in this temperature range was similar, or even smaller than the loss of the unloaded clay.

Boiling point of TBA is 216.5°C and a small part of mass loss at this temperature might be due to the thermal dissociation of some TBAH⁺ cations to protons and TBA molecules [38] followed by the evolution of free amine. Unfortunately our mass spectrometer was not adapted to detect evolved TBA molecules.

In mass loss stage B at 250–380°C organic H atoms were oxidized to H₂O. Since atomic mass of H is very small, it is difficult to identify this stage in the TG curves shown in Figs 7 and 8. Because of the limited amount of oxygen in air only part of organic C

Table 2 Stages of mass loss (in mass%, calculated on the basis of calcined samples at 800°C) during the thermal treatment of unloaded montmorillonite and of montmorillonite loaded with different amounts of tri-*n*-butylammonium, determined from TG curves

Temp. range/°C	Montmorillonite			
	Unloaded clay	Loaded with tributylammonium cation (mmol TBAH ⁺ per 100 g air-dried clay)		
		10	20	40
0–205	10.0%	18.2%	17.8%	14.0%
205–250	0.5	0.8	1.1	1.1
250–380	0.5	0.8	2.2	2.2
380–405	0.2	0.8	1.1	1.5
405–450	0.5	0.9	2.2	3.7
450–605	1.2	1.5	1.1	2.6
605–680	2.0	3.9	4.5	2.9
680–750	1.8	1.5	2.2	2.2
750–800	0.0	0.0	0.0	0.7
0–800 total mass loss	16.7	28.4	32.2	30.9

Table 3 Stages of mass loss (in mass%, calculated on the basis of calcined samples at 800°C) during the thermal treatment of unloaded Laponite and of Laponite loaded with different amounts of tri-*n*-butylammonium cation, determined from TG curves

Temp. range/°C	Laponite			
	Unloaded clay	Loaded with tributylammonium cation (mmol TBAH ⁺ per 100 g air-dried clay)		
		10	15	30
0–205	14.8%	19.0%	22.7%	26.0%
205–250	1.5	1.1	1.2	1.5
250–380	1.5	1.7	2.0	2.5
380–405	0.0	0.8	0.8	2.5
405–450	0.8	1.8	1.7	1.0
450–605	2.4	1.8	2.4	3.3
605–680	2.1	1.8	0.8	1.5
680–750	1.2	2.6	1.7	3.3
750–800	0.8	0.0	2.5	3.3
0–800 total mass loss	25.1	30.6	35.5	44.9

and N atoms were oxidized at this step to form CO₂ and NO₂ molecules whereas the non-oxidized C, N and to some extent also H atoms, formed charcoal [39–41]. Tables 4 and 5 bring calculated mass loss of organic H in the temperature range 250–380°C by subtracting the mass loss of unloaded samples from that of loaded samples. It should be noted that at this temperature range the calculated percent of oxidized organic H are somewhat not accurate because some interlayer water was evolved together with the oxidation product of H and its amounts changed with the loading. As well, some H atoms were not oxidized at this stage and became incorporated in the charcoal. On the other hand, some CO₂ and NO₂ were evolved at this stage. The calculated percents must therefore be considered only as approximations. However, as we are going to show, these and the following calculations are reliable to demonstrate differences in the thermal behavior between low and high temperature stable charcoals.

In mass loss stages C and D (second and third steps of the oxidation) charcoal was oxidized to CO₂ and NO₂ simultaneously with the dehydroxylation of the smectites. The percentage of mass loss due to dehydroxylation of both clays, calculated on the basis of calcined clay should be independent on the organic matter. With this assumption, percent of charcoal oxidized at each step was calculated by subtracting dehydroxylation mass loss (according to mass loss of unloaded clay) from total mass loss at each tempera-

ture range, on the basis of calcined clay. The calculated mass losses for the different TBAH-clays, with their thermal reactions, are shown in Tables 4 and 5. The theoretical percent of C plus N on the clay, also on the basis of calcined clay, were calculated from the number of mmol TBAH⁺ per 100 g clay, determined from carbon analysis of the samples by a Leco carbon-analyzer, are also shown. A reasonable correlation is obtained between the theoretical calculated percentage of C plus N and the percentage of total charcoal determined from the TG analysis in the temperature range 380–800°C. It should be noted that small discrepancies are due to (1) some thermal dissociation of TBAH⁺ at 205–250°C, (2) some oxidation of C and N at 250–380°C and (3) oxidation of H incorporated in the charcoal. It is also possible that in the presence of intercalated organic matter the evolution of water became more slowly and dehydration continued in stages C and D.

From the calculated results of montmorillonites collected in Table 4 it appears that the percentage of the high temperature stable charcoal from the total charcoal decreased with increasing loading the clay with TBAH⁺. According to Table 5 in the case of Laponite an inverse effect was observed. The percentage of the high temperature stable charcoal from the total charcoal increased with increasing loading the clay with TBAH⁺.

Table 4 Stages of mass loss of organic hydrogen and charcoal (carbon and nitrogen) in mass% during the thermal treatment of montmorillonite loaded with different amounts of tri-*n*-butylammonium cation, calculated on the basis of calcined sample at 800°C, determined from TG curves

Temp. range/%	Evolved organic components	Montmorillonite		
		Loaded with tributylammonium cation (in mmol TBAH ⁺ per 100 g air-dried clay) and theoretical % of C and N calculated on the basis of calcined clay		
		10 2.2% C+N	20 4.7% C+N	40 9.1% C+N
250–380	Organic H	0.3	1.7	1.7
380–405	Low temp. stable charcoal	0.6	0.9	1.3
405–450		0.4	1.7	3.2
450–605		0.3	–0.1	1.4
380–605	Total	1.3	2.5	5.9
	Percent from total charcoal	44.8	46.3	74.7
605–680	High temp. stable charcoal	1.9	2.5	0.9
680–750		–0.3	0.4	0.4
750–800		0.0	0.0	0.7
605–800	Total	1.6	2.9	2.0
	Percent from total charcoal	55.2	53.7	25.3
380–800	Total charcoal	2.9	5.4	7.9

Table 5 Stages of mass loss due to oxidation of organic hydrogen and charcoal (carbon and nitrogen) in mass% during the thermal treatment of Laponite loaded with different amounts of tri-*n*-butylammonium cation, calculated on the basis of calcined sample at 800°C, determined from TG curves

Temp. range/%	Evolved organic components	Laponite		
		Loaded with tributylammonium cation (in mmol TBAH ⁺ per 100 g air-dried clay) and theoretical % of C and N calculated on the basis of calcined clay		
		10 2.3% C+N	15 3.7% C+N	30 8.6% C+N
250–380	Organic H	0.2	0.5	1.0
380–405	Low temp. stable charcoal	0.8	0.8	2.5
405–450		1.0	0.9	0.2
450–605		–0.6	0.0	0.9
380–605	Total	1.2	1.7	3.6
	Percent from total charcoal	80.0	65.4	47.4
605–680	High temp. stable charcoal	–0.3	–1.3	–0.6
680–750		1.4	0.5	2.1
750–800		–0.8	1.7	2.5
605–800	Total	0.3	0.9	4.0
	Percent from total charcoal	20.0	34.6	52.6
380–800	Total charcoal	1.5	2.6	7.6

Conclusions

By heating TBAH-smectites in air at 250–380°C low- and high-temperature-stable charcoals were obtained as a result of partial oxidation. From the EGA curves it was concluded that the charcoals were composed mainly of C with small amounts of N and H. The thermo-XRD-analysis revealed that the charcoal formed during the thermal treatment was located inside the interlayer space. The TG showed that in montmorillonite the percentage of the low temperature stable charcoal from the total charcoal increased with increasing loadings of the clay by TBAH⁺. In the case of Laponite an inverse effect was observed. The percentage of the high temperature stable charcoal increased with higher ammonium loadings. This is probably associated with the differences in the surface acidity of the oxygen plane in the surface of the TOT layers of these two minerals. In montmorillonite atoms of this plane are better electron pair donors than in Laponite, due to the tetrahedral substitution of Al for Si, which does not occur in the latter. Structural iron, which is present in Wyoming bentonite but not in Laponite, may also be responsible for the differences in the behavior of the two smectites. In conclusion, TG seems to be a reliable tool to study the relative amounts of low- and high-temperature-stable charcoals.

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