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QUALITATIVE AND QUANTITATIVE CHARACTERIZATION OF BRAZILIAN NATURAL AND ORGANOPHILIC CLAYS BY THERMAL ANALYSIS

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Differential thermal analysis (DTA) was the first thermal analysis technique used to qualitatively characterize natural clays and respective curves has been used since more than 60 years as their 'fingerprint'. With the development of microprocessed equipments in the last decades, derivative thermogravimetric (DTG) curves also may be used for this purpose in some cases, which also may allow a quantitative characterization of clay components. TG and DTG curves are more indicated than DTA or DSC curves to identify and to better analyze the several decomposition steps of natural or synthetic organoclays. These questions are discussed in applications developed to characterize Brazilian kaolinitic clays, bentonites and organophilic clays.

Keywords: *clays, DTA, DTG, organophilic clays*

íIntroduction

Differential thermal analysis (DTA) was the first thermal analysis technique, which was used to characterize and to qualitatively distinguish natural clays with a same chemical composition but with different molecular structures [1] and usually their DTA curves are considered as their 'fingerprint'. One of the main reasons is due to the fact that the dehydroxylation temperature range of a clay and respective kinetics depends on the characteristics of its molecular and interlayer structure and how the hydroxyl groups are linked to it and not on their content in total composition.

Actually in 1887, Le Chatelier was the first to publish heating curves of clays, using a photographic recording of the reflection of a galvanometer mirror, which was activated by a thermocouple in the sample and only in 1899, clays and silicate minerals characterization was done from the difference between a sample and reference temperature [2].

Any physical, physicochemical and/or chemical transformation occurs with a thermal effect, which causes a difference between the sample and reference temperature. Thus, the respective endo- or exothermic peaks shown in DTA curves are a very practical way to identify transformations with or without mass loss and have been used as one of the main tools for qualitative clay characterization [3, 4].

For mass changing systems, in the last century, at the beginning of classic thermogravimetric studies in the 50's, when derivative thermogravimetric (DTG) curves were not even used [5], it was much easier to visualize different mass loss steps from respective DTA peaks than from respective TG curves, mainly for overlapped events [6]. This is very probably one of the reasons why DTA curves have been so much used also to study other materials and their thermal properties [7]. Since the last three decades, with the development of microprocessed equipments, DTG curves can be automatically obtained by software, from respective thermogravimetric (TG) curves. This allows one to use DTG peaks alternatively to DTA ones for clay characterization.

When natural or synthetic clay contains organic matter, it may present simultaneous endo- and exothermic mass loss transformations during thermal analysis [8]. In these cases, DTA peaks may not allow one to properly analyze all the steps with mass loss, because they actually represent the difference of the simultaneous different types of thermal effects, as also occurs in the case of differential scanning calorimetry (DSC) peaks, which have similar characteristics.

Organoclays thermal analysis still presents some questions to be solved [9]. To contribute for this purpose, as will be shown in the present paper, DTG curves, in some cases, are more indicated than DTA or DSC curves to identify and to better analyze the several decomposition steps of natural organoclays and/or synthetic organophilic clays. As DTG curves represent the total mass loss rate during all the occurrence of the endo- and exothermic decompositions, they allow a better evaluation of these simultaneous transformations from respective DTG peaks.

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Experimental

The present paper discusses practical aspects of the use of DTA and DTG curves in the characterization of some Brazilian natural and organophilic clays, showing specific characteristics of the application of each technique and how qualitative and quantitative clay component analysis may be done by their separate and/or simultaneous use.

When only one mass changing transformation occurs, the consumed or generated heat flux dq/dt, in an infinitesimal period of time dt, can be expressed by Eq. (1):

$$\mathrm{d}q/\mathrm{d}t=\mathrm{d}m/\mathrm{d}t(\Delta H) \tag{1}$$

where dm/dt=mass changing rate of the sample, ΔH=transformation enthalpy change per unit mass of reactant.

As the DTA signal is proportional to dq/dt and the respective DTG signal is equal to dm/dt, the module of the DTA signal will be proportional to the module of DTG signal. As a consequence, the correspondent DTA and DTG peaks of the transformation will have similar shapes. When simultaneous mass changing transformations occur, corresponding overlapped DTA and DTG peaks will present similar behavior only when the simultaneous events have the same type of heat effect.

Unless stated differently, the thermal analyses were performed in simultaneous TG/DTA TA Instruments equipment, model SDT2960 from room temperature to 1000°C. 100 mL min^{-1} of air was used as the purge gas, with a heating rate of 10°C min^{-1}.

Results and discussion

Figure 1 shows the TG, DTG and DTA curves of commercial clay from Paraiba State, Brazil, which is mainly composed by kaolinite and montmorrilonite [10]. The overlapped endothermic peaks occurring up to 200°C correspond to the release of adsorbed water from the clay pores and from the interlayer space. The DTA or DTG peaks from 200 to 350°C are due to the dehydration of hydrated iron oxides present in the clay, which are followed by the kaolinite and montmorrilonite dehydroxylation peaks, which occurs up to 750°C. As all these events are endothermic and respective DTA and DTG peaks present very similar shapes. Between 850 and 950°C there is no mass loss and the collapse of the mineral structure, followed by a little mullite crystallization [3], can only be seen from the respective DTA endo-exothermic peaks.

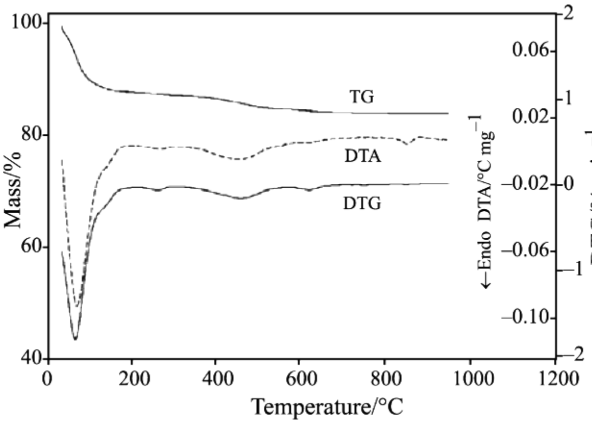

Fig. 1 TG, DTG and DTA curves of clay mainly composed by kaolinite and montmorillonite

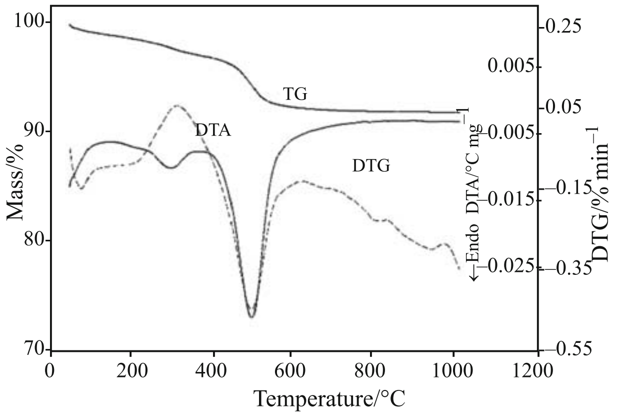

Fig. 2 TG, DTG and DTA curves of a plastic kaolinitic clay

Figure 2 shows the TG, DTG and DTA of a plastic kaolinitic clay from Rio de Janeiro State, which is used for red ceramics production [11]. After the initial dehydration step, which ends at 150°C, the organic matter present in the clay begins to decompose and from 250 to 350°C, an exothermic DTA peak characterizes combustion of the released gases.

Actually the beginning of the mass loss step, during which pyrolysis of the natural organic matter occurs, is much better identified from the DTG curve. As this thermally decomposition proceeds, the respective maximum mass loss rate indicated by the DTG peak occurs at a lower temperature than that of maximum exothermic effect shown by the DTA peak. This last peak represents the resulting thermal effect of the endothermic organic decomposition with the much higher exothermal effect promoted by the combustion of the evolved gases, which occurs at higher temperatures. When kaolinite dehydroxylation occurs from 400 to 650°C, it is practically the main endothermic mass loss transformation in this temperature range. As in this case the mass loss rate is dependent on the effective heat flux received by the sample, DTG and DTA peaks present similar shapes. Residual mineral structure collapses from 750 to 800°C and mullite crystallization occurs from 950 to 1000°C. Respective DTA peaks identify these events.

Kaolinite content estimation from TG/DTG curves

When kaolinite dehydroxylation does not overlap with other mass loss transformations and respective limits can be well defined from DTG curve, its content may be estimated from respective TG curve. Figure 3 shows a simultaneous TG/DTA analysis of clay from Pará State, which has high kaolinite content.

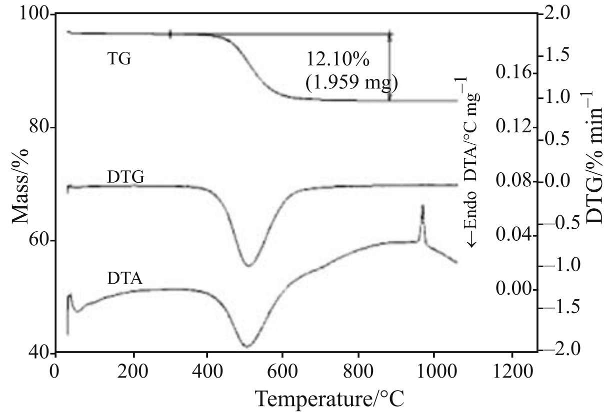

Fig. 3 TG, DTG and DTA curves of clay with high kaolinite content

DTA curve of Fig. 3 shows a broad endothermic kaolinite dehydroxylation peak and, as the mineral has a high purity degree, a sharp exothermic mullite crystallization peak occurs at 980°C. The DTG curve presents a better baseline than that of DTA curve. Based on the DTG peak limits of kaolinite dehydroxylation, a mass loss of 12.10% occurs in TG curve, and meta-kaolin is formed [3] according to Eq. (2):

$$\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \rightarrow \underset{\text{meta-kaolin}}{Al_2Si_2O_3+2H_2O} \tag{2}$$

As the stoichiometrical mass loss due to water release during this reaction is 13.94%, the estimated kaolinite content in the clay is 12.10(100)/13.94= 86.8 mass%.

Quartz and organics qualitative identification from DTA curves

Figure 4 shows a DTA curve of a sample of sand mainly composed by SiO_2. At 573°C, the sharp endothermic peak is characteristic of the crystalline transformation from alpha to beta quartz [12].

Figure 5 shows the TG, DTG and DTA curves of another kaolinitic clay from Rio de Janeiro State, which contains, as minor components, organic material, quartz and gibbsite. Comparing DTG and DTA curves, the respective peaks up to 250°C, present similar behavior and refer to the loss of adsorbed and interlayer water and to gibbsite dehydration.

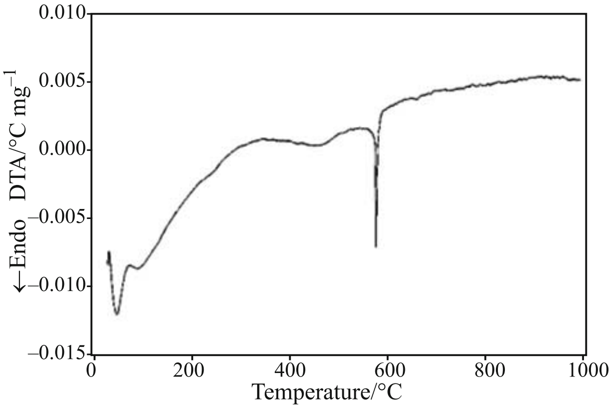

Fig. 4 DTA curve of a sample of sand

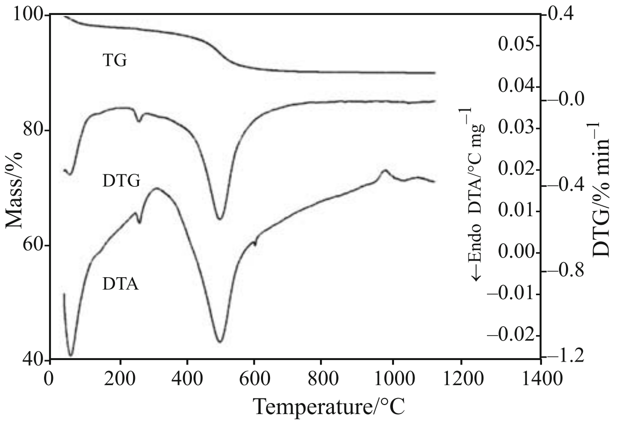

Fig. 5 TG, DTG and DTA curve of kaolinitic clay with quartz, gibbsite and organic matter, as minor components

However, it can be seen from DTA curve that, between the endothermic gibbsite dehydration and kaolinite dehydroxylation peaks, there is a little exothermic DTA peak, with a maximum at 300°C, characteristics of organics burnout. This event cannot be seen in the DTG curve because it is occurring with other more significant overlapped mass loss events. The little endothermic peak at 573°C, due to its crystalline phase transformation, identifies the presence of quartz.

Figure 6 shows the analysis of two kaolinitic clays from Paraná State, which were sampled from a same deposit. Clay B appears in dark colored veins in the reserve, mainly composed by clay A, which is light colored. As shown in clay B DTA curve, the presence of a significant exothermic peak between 250 and 400°C, which does not occur in the case of clay A, indicates that the color of clay B is due to the burnout of a carbonaceous material, not present in the other clay. Respective DTG peaks in Fig. 5 indicate that the gibbsite content of both clays is almost the same, but clay B presents a higher kaolinite content, due to a higher dehydroxylation DTG peak area.

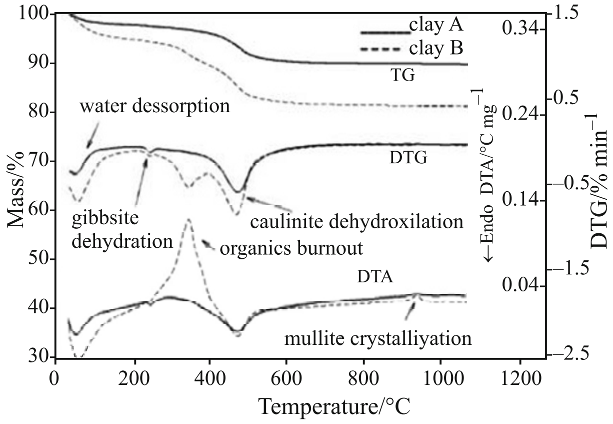

Fig. 6 TG, DTG and DTA curves of two kaolinitic clays sampled from a same deposit

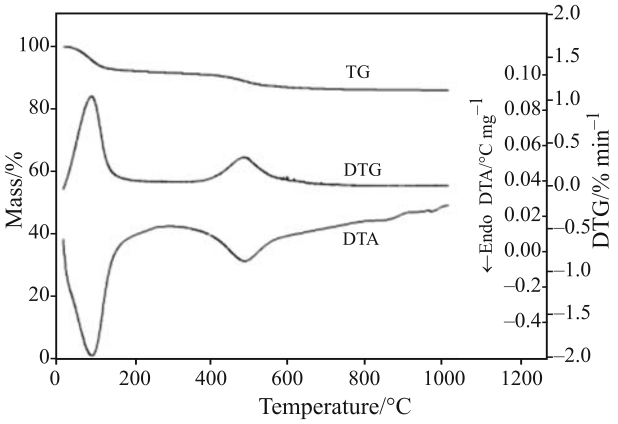

Fig. 7 TG, DTG and DTA curves of the VCNa sodium bentonite

A special care has to be taken in these cases of simultaneous organics burnout with mineral component dehydration or dehydroxylation steps to avoid erroneous interpretation when only DTA peak area compared. In the present case, as the endothermic DTA dehydroxylation peak area of clay B is little lower than the area of correspondent peak of clay A, this would apparently indicate that the kaolinite content of clay B would be lower than that of clay A. Differently from the sum of mass loss effects that are shown in respective DTG curves, DTA patterns show the difference among all simultaneous endothermic and exothermic effects. In the case of clay B, a part of the higher endothermic effect, which actually occurs during its higher kaolinite content dehydroxylation, is neutralized by a part of the opposite exothermic effect of the organics burnout. Thus in this case, DTA peak area cannot be used as a parameter to evaluate kaolinite content.

Characterization of organophilic bentonites

Organophilic clays are obtained from natural clays by replacing the metallic ions initially present in the clay interlayer space by organic ammonium cations [9]. When the original clay has many metallic ions, they are usually first exchanged to a same ion such as sodium, by reaction with an inorganic sodium salt and then, this sodium clay is reacted with a quaternary organic ammonium chloride or bromide to exchange the sodium ions to organic ammonium ions [8].

Figure 7 shows respectively the TG, DTG and DTA curves of a sodium bentonite (VCNa) obtained from a natural smectitic clay from Paraiba State, which was used to obtain a cetyl-trimethyl ammonium bentonite (VCO), which respective TG, DTG and DTA curves are shown in Fig. 8. DTG curves were inverted in both cases, for a better comparison with DTA curves in the following discussion and the same was done in next figures.

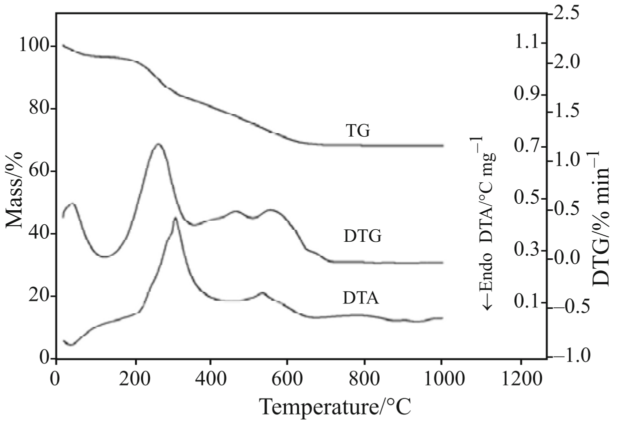

Fig. 8 TG, DTG and DTA curves of the VCO organophilic bentonite

As shown in Fig. 7, during VCNa sample analysis, the release of adsorbed and interlayer water up to 200°C and the following dehydroxylation step, which ends at 750°C, are endothermic. Thus, the shape of DTA and DTG peaks of these events are very similar, as occurred in case shown in Fig. 1. In this case, either DTA or DTG peaks can allow a correct interpretation of mass loss steps.

However in the case of VCO sample, a significantly different DTG and DTA peak behavior occurs after the first step of water desorption, which ends at 150°C. At this temperature, a new mass loss step begins, identified by the beginning of a second DTG peak, but from 150 to 200°C, respective thermal effect is not so apparent on the DTA curve. The maximum of the second exothermic DTA peak occurs at a much higher temperature than that of the maximum of the second DTG peak. Besides this fact, after 400°C, there is only one apparent exothermal significant DTA peak, while in the case of the DTG curve there are more two main DTG peaks. These and other different behavior of DTG and DTA curves usually occur with organophilic clay thermal analysis and are of

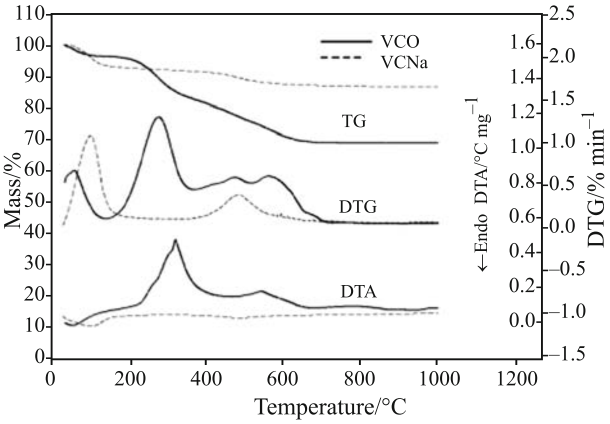

Fig. 9 TG, DTG and DTA curves of VCO and VCNa clays

complex interpretation [9]. However, some of these questions may be solved if DTG and DTA curves of organophilic clays are compared with those of the clay from which they were formed, as shown in Fig. 9. This applies to the present case, in the temperature range where the organic matter is thermally decomposed and burned.

On the basis of TG and DTG curve patterns shown in Fig. 9, which represent the cumulative effect of all mass loss steps of respective samples, the following can be deduced:

- VCO organophilic clay presents less adsorbed water than VCNa clay.
- The pyrolysis of the organic ammonium ion, which is in the VCO interlayer space, begins at 150°C as indicated from respective DTG peak.
- The beginning of organic matter pyrolysis is endothermic and as it proceeds, combustion of the evolved gases with air is exothermic [8]. As DTA curve represents the difference between endo-exothermic effects, only after 200°C, a clear resultant exothermic effect begins, indicated by the respective DTA peak, and the highest exothermic effect of the combustion of evolved gases only occurs at higher temperatures. This explains the different DTG and DTA peak behavior, respective maximum peak temperatures at 268 and 312°C and the different temperature ranges of occurrence.
- Comparing VCNa and VCO DTG curves, the third DTG peak of VCO clay, with a maximum at 465°C, is due to the dehydroxylation of the mineral structure. In the case of VCNa, the maximum of the dehydroxylation DTG peak occurs at 475°C. This fact is due to the higher interlayer distance in VCO case, which was increased by the insertion of the organic ammonium ions, and to the additional energy evolved in reacting media from the organics burnout.
- It is important to note that within the VCO dehydroxylation temperature range, there is a 'depression' on its DTA curve, due to the endothermic effect of the dehydroxilation on the exothermic behavior of the simultaneous organics combustion. This also indicates that the energy evolved from the continuous combustion process is higher than the energy consumed by dehydroxylation.
- The third DTG peak indicates that, the residual charcoal, which is formed during the organophilic clay thermal oxidation [13], decomposes continuously with a maximum mass loss rate at 554°C.
- A second maximum on DTA curve of VCO clay occurs at 537°C. As decomposition enthalpy as well as respective calorific power changes with the composition of the residual carbonaceous material [14], non-necessarily the resulting thermal effect is directly dependent on the mass loss rate. This explains why DTG and DTA maxima for this complementary combustion step after dehydroxylation do not present same maximum temperatures.

Quantitative determination of sorbed material by TG and DTG

The quantitative determination of the organic matter adsorbed by a natural or synthetic clay has been done by chemical or instrumental analysis techniques other than thermal analysis techniques [8, 13, 15–19]. From the previous discussions, it can be concluded that DTG peaks are more indicated than DTA peaks for a better understanding and evaluation of the thermal decomposition steps of organophilic clays or natural clays that contain organic matter. The same applies to the characterization of organophilic clays with organic sorbed materials. As a consequence, using TG and DTG analysis, a method for quantitative determination of the adsorbed organic matter was developed. The following example refers to an application of the method to organophilic clays used as adsorbents of organic contaminants dissolved in wastewater.

Figure 10 shows the thermal analysis curves of VCO clay after phenol adsorption from an aqueous solution (VCOph). These analyses were performed in TA instruments simultaneous TG/DTA/DSC equipment model Q600, at the same operating conditions than VCO sample. As can be seen, the patterns of TG, DTG and DTA curves of VCOph clay are similar to those of VCO clay. As DSC signal represents the heat flux (dq/dt) consumed or generated by the sample and DTA signal is proportional to the heat flux, DSC curves patterns are very similar to those of respective DTA curve.

Actually DSC peaks allow new quantitative information on the enthalpies of the resultant thermal effects. However, for the same reasons which apply to DTA peaks, they can not contribute to a better analysis of all the mass loss events that occur during natural

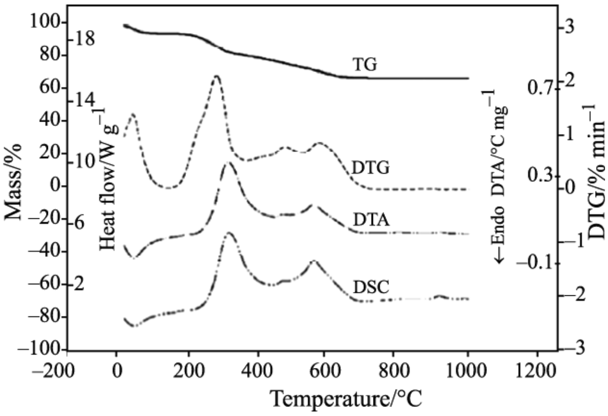

Fig. 10 TG, DTG, DTA and DSC curves of VCOph clay

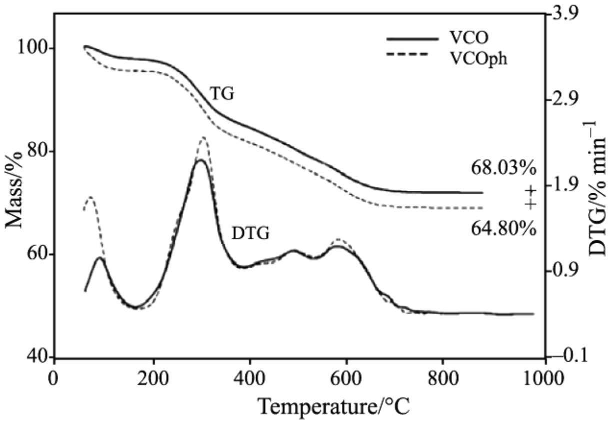

Fig. 11 TG and DTG curves of VCO and VCOph clays on initial mass basis

or synthetic organoclay thermal decomposition, as DTG peaks do.

Figure 11 shows the TG and DTG curves of VCO and VCOph samples. These and all the previous figures show thermal analysis curves on respective initial sample mass basis, which are obtained by default by the equipment data analysis software. From TG curves it can be seen that VCOph clay shows a higher adsorbed water content than VCO, which could be the cause of the higher total mass loss and lower residual calcined mass%. However, the first and third VCOph heights of DTG peaks after 150°C are higher than respective VCO DTG peaks. This indicates that an additional product, which can only be the sorbed phenol, is being simultaneously decomposed with the organic ammonium, from the interlayer space of the mineral matrix.

Thus, after desorption of respective adsorbed water, VCO and VCOph mass losses are due to the release of the organic ammonium radical and of the water evolved from dehydroxylation. In the case of VCOph sample, there is an additional mass loss due to simultaneous phenol thermal decomposition. Apparently the phenol adsorbed mass percent could be calculated from the difference of respective dried and calcined masses. But this cannot be done, because dried VCO and VCOph samples have different chemical compositions.

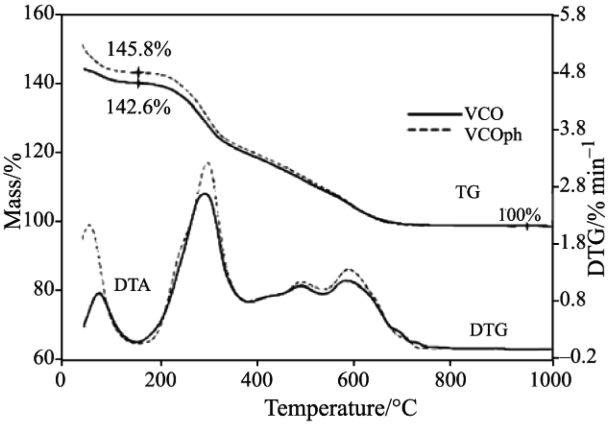

Fig. 12 TG and DTG curves of VCO and VCOph clays on calcined mass basis

However, after respective total organics burnout, when dehydroxylation also has occurred, calcined VCO and VCOph mineral residues have the same chemical composition and on this basis the different samples can be properly compared. Figure 12 shows the TG and DTG curves of VCO and VCOph samples, plotted on respective calcined mass basis. From these TG curves, it is more evident that the mass loss of adsorbed phenol occurs during practically all the thermal decomposition of dried VCOph. As shown, after respective adsorbed water release, the total mass losses are 45.8 and 42.6 mass% on calcined mass basis. Thus, the adsorbed phenol mass content represents 3.2% of VCO calcined mass.

The previous example shows how from thermogravimetric analysis the organic adsorbed matter on calcined mass basis can be determined. By using the ratio between the calcined and initial mass of the adsorbent, the adsorptive capacity can be obtained on initial adsorbent mass basis, as usually used in adsorption studies. From Fig. 11, VCO calcined mass is 68.03% of its initial mass. Thus, the adsorbed phenol represents actually 3.2 (68.03/100)=2.2% of the initial VCO mass. This means that 22 mg of phenol were adsorbed per each gram of VCO clay.

Conclusions

- DTA has been used since more than 60 years to qualitatively characterize natural clays as their ‘fingerprint’. With the development of microprocessed equipments in the last decades, DTG curves also may be used for this purpose, which also may allow a quantitative characterization of clay components.

- However, due to the characteristics of respective measurement systems, there are some limitations of each thermal analysis technique when used to characterize natural or synthetic clays and organoclays. The discussion of these specific characteristics and how qualitative and quantitative component analysis may be done by their separate and/or simultaneous use were the objectives of the present paper.
- When simultaneous decomposition transformations occur, DTA, DSC and DTG curves have similar patterns only when a same type of thermal effect occurs for all transformations. In this case, DTG, DSC or DTA peaks can be used alternatively for clay characterization.
- Only DTA and/or DSC peaks allow one to analyze structural phase transformations without mass loss, which may also be used to identify the presence of some components.
- DTG peaks are more indicated than DTA or DSC peaks for a better understanding and complete evaluation of the thermal decomposition steps of organophilic clays or natural clays with organic matter. As a consequence, TG and DTG analysis in air allows a quantitative determination of the organic matter sorbed by organophilic clays, as an alternative to other procedures used for this purpose.

Acknowledgements

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