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Thermal Characterization Of Talc: Simplification Brought By CRTA

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ABSTRACT

Controlled transformation rate thermal analysis has been used to study the thermal decomposition of a reference talc sample from Luzenac. The vacuum conditions and low rate of decomposition used in the present study has enabled to understand and quantify the decomposition in terms of the different brucite and talc sheets of the present mineral sample with chlorite impurity.

KEYWORDS

Sample controlled thermal analysis;
Talc;
Chlorite.

INTRODUCTION

Talc is a natural product with properties such as chemical inertness, whiteness, organophilic, sheet-like and hydrophobic. It has equally interesting characteristics of low electrical and high thermal conductivity[1] and is widely used in industry. In cosmetic technology it is used as a cosmetic and a baby powder base, as a cream additive and a filling material for dyestuffs and soaps. Powdered talc is used as an antiphologistic agent and as an adsorbent. In the pharmaceutical industry talc is currently applied as a sliding agent[2]. It improves the friability of the tablet mass, and shows an antistatic and antiadhesive behaviour. In the rubber and paper industries it is used as a filling material. It has also found wide-spread application in ceramics. It is a ceramic/ refractory material and is extensively used for making wall tiles, electrical insulators and ceramic porcelain[3]. From an industrial standpoint therefore, the thermal decomposition behaviour of talc is of considerable interest.

The DTA curve of pure talc, $Mg_3SiO_4O_{10}(OH)_2$, shows one predominant endothermic peak above 900°C which is attributed to the dehydroxylation, yielding enstatite, with the evolution of amorphous silica and chemically combined water.

$$\underset{\text{Talc}}{Mg3(Si_2Os)_2(OH)_2} \longrightarrow \underset{\text{Enstalite}}{3MgSiO_3} + SiO_3 + H_2O$$

However, industrial talc is found in the form of massive foliated or globular aggregates, associated with minor amounts of chlorites, dolomites, calcites, magnesites and quartz[4], in compositions and concentrations which depend on the paragenesis of the mineral.

The influence of these mineral impurities in the mechanical, thermal and electrical behaviour of the talc composite is an important issue consequently; the characterisation of the different talcs is necessary task for the fabrication of talc composites.

The major emphasis of earlier works has been on the structure changes associated with heating talc sample to high temperature, carried out conventional thermoanalytical methods (DTA and TGA with linear heating)[5-30]. The analysed samples originated from locations throughout the world: U.S.S.R[5,6,10,19,23] Germany[16-18], France[20, 26], Spain [28], U.S.A[7, 8, 12], Japan[11], Taiwan[15], Pakistan[21] and India[22]. This fact explains that the descriptions of the thermal decomposition of talc are conflicting.

It must be noted that many factors can have a significant effect on the results obtained by thermoanalytical methods, first the different chemical composition of samples(it must be noted that talc minerals occurring in nature are rarely chemically pure substances) and the type of instrument influences the shape of the thermograms; for this it is problematic to compare the shape of two curves recorded under different experimental conditions (e.g., sample size, geometry of the sample holder, measuring and recording instruments) as well as assured high standardization and reproducible analytical conditions (e.g., furnace atmosphere, particle size of the mineral powder, technique of packing the sample, inert material, and heating rate). Furthermore conventional thermal analysis, which subjects samples to a linear heating rate, can have a major influence on the information content of the TG curve and the nature of the heat treated products.

To minimize as much as possible the influence of these parameters this study uses the method of Controlled transformation Rate Thermal Analysis (CRTA)[31,32]. This method enables a control of the reaction rate allowing a sufficient decrease in the rate to diminish the pressure and temperature gradients within the reaction sample. Rouquerol(1989) has already shown the necessity to control not only the temperature, but also the water vapour pressure above the sample to obtain reproducible results and thus to a more reproducible experiment. The possibility of lowering the rate of transformation at will makes it possible to ensure the sample a more homogeneous temperature. Under these conditions all the grains constituting the sample react at the same time. This results in a better separation of intermediate stages in the thermal decomposition and a greater sensitivity of the detected phenomena.

A previous CRTA study has been carried out by F.Villiéras et al. [33], in which three decomposition steps were highlighted. This study concluded with an estimation of the amount of ferrous iron in the sample. The present investigation using CRTA was undertaken to clarify the dehydroxylation steps of sample of talc. We chose a relatively pure talc; talc de Luzenac which we have taken as a reference. Several intermediate samples were immediately analysed by XRD, FTIR and MEB with the aim to understand the decomposition mechanisms.

EXPERIMENTAL AND METHODS

Samples

The talc sample(A) used in this investigation as reference, was supplied by Talc de Luzenac(France). This sample is composed of two minerals: talc(84%) and chlorite(16%). Both are phyllosilicate-type clays and occur in the form of lamellar, without layer charge. The mineralogical composition, and some physicochemical characteristics of this talc sample (noted A) are presented in TABLE 1.

TGA

TG and DTG measurements were carried out on a commercial apparatus(TA instruments, Q500), under air flow at a rate of 100 mL/min using around 100mg of sample. Experiments were carried under a linear heating rate of 5Kmin^{-1}.

Controlled transformation rate thermal analysis (CRTA)

TABLE 1 : Chemical composition(weight %) of studied talc A sample

Elements	SiO_2	Mg0	Al_2O_3	Fe_2O_3	CaO	P_2O_5	K_2O	TiO_2	MnO	Li_2O	Cr_2O_3	BaO	P.F
% masse	54.83	33.6	2.94	0.87	0.64	0.017	0.005	0.004	0.002	0.001	-	-	6.92

The controlled rate thermal analysis (CRTA) experiments were carried out on an apparatus built in house. On line analysis of the evolved species was carried out using a mass analyser (VG quadrupoles)[32].

The experiments are carried out on 200 mg samples weighed in a silica-cell in 25-1000°C temperature range. Once the equilibrium temperature is reached, the pressure is lowered by using pumping system from 1 bar to the desired value(2×10^{-2} mbar in our case). The pressure is continuously followed using a pirani gauge. The pressure signal produced by the gauge is sent to the furnace-heating controller. The heating of the sample then takes place in such a way as to keep constant at a preset value the vapour pressure generated by the sample[31-32].

X- Ray powder diffraction

Technique using a siemens D 5000 X-ray diffractometer. For powder diffraction we used CuKa1 radiation, (wavelength 1.5406).

Infra-red spectroscopy

FT-IR spectra were recorded in the 4000-400 cm^{-1} range, using an EQUINOX 55 FTIR spectrometer (Bruker). The powder was pressed into KBr pellets.

Scanning electronic microscopy (SEM)

The microstructure of the samples was investigated by using a philips XL 30 scanning electron microscope. The electrical measurements were carried out in the metal-ferroelectric-metal (MFM) configuration where M is gold deposited by thermal evaporation.

RESULT

Conventional thermal analysis: TGA

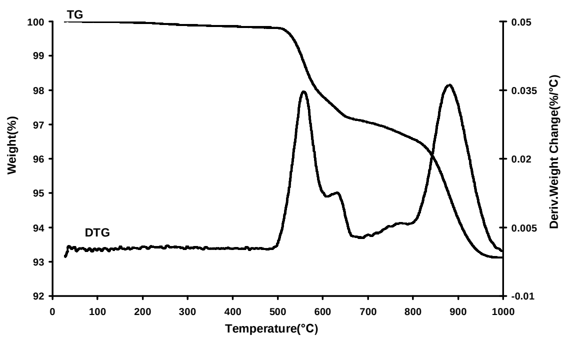

Figure 1: TG-DTG curves of talc (A) under air

TG plots for talc sample(A) are given in figure 1. The curve obtained under air shows a complex decomposition reaction between room temperature and 950°C. Two main decomposition steps are observed. The DTG signal suggests that the first peak can be separated into two, this is not clear from the TG signal.

Controlled rate thermal analysis CRTA

The CRTA curves of talc samples (A) obtained under vapour pressure of 2×10^{-2} mbar are shown in figure 2. The temperature curve 'II' shows the sample temperature variation with time, controlled so as to keep constant the pressure (curve'I'). Thus the time measured for each decomposition step is directly proportional to the weight loss. According to major changes suggested by the form of the temperature curve, as well as the regulation changes that appear in the pressure curve bellow. These methods allow a number of possibilities such as more homogeneous products, limitation of secondary reactions and more meaningful kinetic studies.

The above results show two main steps noted AB and BC. These can be related to the two steps observed in the conventional TG curve(Figure 1). Note that the steps observed in the CRTA curve are not horizontal. Such curve shapes can inform on the limiting kinetic mechanisms and a kinetic study is currently being carried out.

Evolved gas analysis

In order to obtain more information on the thermal

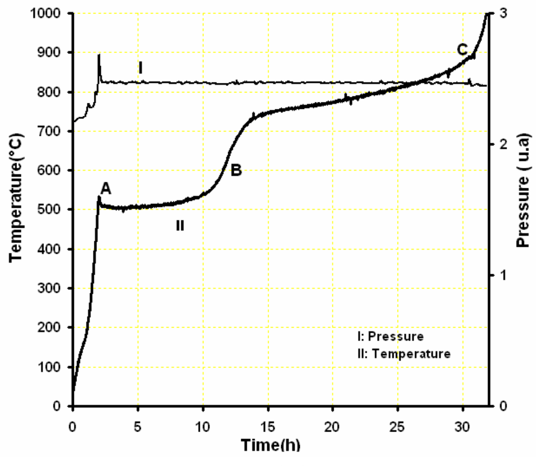

Figure 2: CRTA curve of talc (A) under 2 10^{-2} mbar water vapour pressure

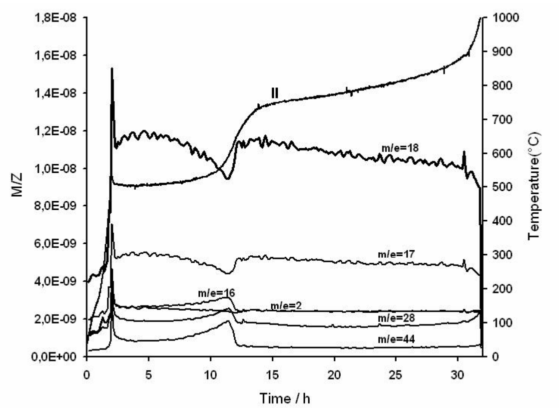

Figure 3: Mass spectrometric analyses of products outgassed from talc sample (A) surface during a controlled thermal analysis

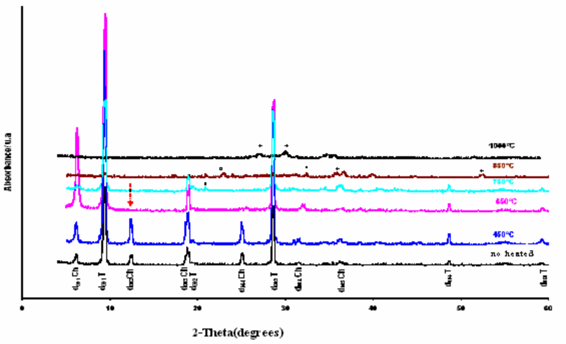

Figure 4: X-ray diffraction patterns of talc (A) and of intermediate products obtained at different temperatures by thermolysis under 2×10^{-2} mbar. T: rays due to talc and Ch ray assigned to chlorite; (($^{\circ}$) forsterite, (+) enstatite)

decomposition of talc samples, a continuous evolved gas analysis was carried out during CRTA. These results are given in figure 3. Between 25 and 1000°C, three phenomena are observed: for temperatures below 200°C, the main products out gassed from the samples surface are in majority physically adsorbed water (mass/charge m/z=18,17,16) and towards the end of the decomposition on can observe a smaller amount of carbon dioxide and/or nitrogen(m/z=28).

The second step at higher temperatures(400-850°C) is again characterised by the loss of water (m/z=18,17,16). The presence of OH groups (peaks m/z=8) until the last step of the thermal transformation of the sample explains the great tendency to agglomeration of the grains at high temperature, shown by SEM microscopy below.

Analysis of intermediates by FTIR, XRD, SEM and BET

To characterize the products obtained at the end of each decomposition step, the CRTA experiment is restarted under identical conditions of rate and pressure; and the reaction was stopped at the temperatures determined from the initial curves: points (a) non-treated, as well as the intermediates treated to (b) 450°C, (c) 650°C, (d) 750°C, (e) 850 and (f) 1000°C. These intermediate products are immediately submitted to IR, X-ray powder diffraction, SEM and BET studies.

Analysis of intermediates by XRD

The X-ray diffraction patterns of untreated compound and the intermediate products are presented in figure 4. The spectra show reflections due to talc as well as impurities such as chlorite. Indeed, a closer analysis of the pattern obtained with the initial sample shows around 16% of chlorite present.

According to the CRTA curves, modifications in the X-ray diffraction patterns (Figure 4) started up to 450°C. It should be noticed that the patterns appearing on the diffractogram of x-rays of the intermediate product at 450°C coincide with those of the initial product.

The diffractogram of the prepared product at 650°C (figure 4), presents a disappearance of the 002 reflection of chlorite and a brutal attenuation of the other basal lines of chlorite; when the intensity of the (001) reflection of chlorite increases, this reveals the deshydroxylation of the brucitic phase of chlorite. [38] However the patterns of talc remain without modification at this temperature.

At 750°C, the reflexions related to chlorite disappeared completely, the patterns of low intensity appear characteristic of the forsterite (($^{\circ}$): forsterite (JCPDS 21-1152), figure 4).In the diffractogram of the isolated product at 850°C one observes the disappearance of the reflexions associated to the talc and the appearance of the new patterns of low intensity, which correspond to the enstatite and the fostérite (($^{\circ}$) and (+), figure 4). However, the X-ray trace is otherwise not very different from that at 1000°C containing broad peaks corresponding to poorly crystalline enstatite(JCPDS 19-0768).

Analysis of intermediates by IR

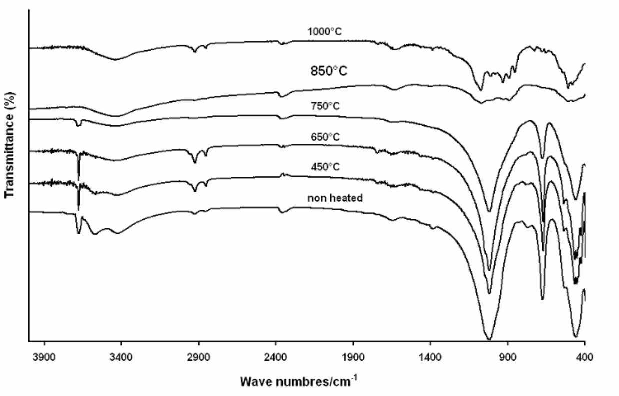

Figure 5: IR spectra of talc (A) and intermediate products obtained at different temperatures (°C) by thermolysis under 2 10^{-2}mbar water vapour pressure.

The IR spectra of untreated compound and the intermediate products are presented in Figure. 5. The infrared spectra of the initial compounds clearly exhibits the presence of talc by the very sharp O-H stretching at 3674cm^{-1}(which is badly overlapped by vibration of talc-like hydroxyl group stretching at 3670cm^{-1}) and the sharp symmetric Si-O-Si stretching at 667cm^{-1}. The asymmetric Si-O-Si stretching is observed at 1004 cm^{-1}.Whereas adsorption bands observed at 3562 and 3411 cm^{-1} correspond to the brucite layer hydroxyl group of chlorite. The appearance of these broad bands is a clear indication of the presence of chlorite in the sample. The absorption bands towards 812 and 727 cm^{-1} are allotted to the mode of vibration of(Si-Al) O-OH. The absorption bands between 401 and 514cm^{-1} are allotted to the bending vibrations of Si-O. Change in the IR spectra appears up to 450°C. The insulated product at 450°C presents practically the same bands IR as the starting product.

At 650°C the 3562 and 3411 cm^{-1} stretching bands of the brucitic hydroxyls of chlorite disappear. The stretching vibration of talc hydroxyls at 3674 cm^{-1}(which is clearly appears at 450°C) disappears completely at 800°C. Whereas in 1500-400 cm^{-1} range; dehydroxylation of the OH groups of interlayer octahedral sheet changes the Si-O stretching bands in the 1051-968 cm^{-1} range into one weak broad band which broadens between 500 and 750°C (figure 5). This could indicate short range disordering in the tetrahedral sheet of the 2:1 layer[38]. This disorganization is further indicated by shoulders near 850 and 750cm^{-1} which could be assigned to the modification of the tetrahedral Al-O environment as the 765cm^{-1} vibration disappears after dehydroxylation. The 699 cm^{-1} band which started to decrease at 750°C, disappears completely at 850°C and the 401-514 cm^{-1} bands are not affected.

The spectrum IR of the product insulated at the end from thermolysis (at 1000°C, figure 5) reveals the bands characteristic of the enstatite[39] .

Analysis of intermediates by SEM

Further, SEM images obtained for the isolated dehydrated salt shows that the crystal morphology was preserved after heat treatment by CRTA up to 700°C (Figure 6a, 6b). This confirms the fact that the loss of the initial water molecules during the first step has little or no effect on the lattice architecture. However SEM images obtained for products isolated at 850 and 1000°C (figures 6c, 6d) shows large cracks on the surface indicating that the loss of the last water molecule degrades the crystal structure.

Analysis of intermediates by BET

Figure 8 presents the adsorption-desorption isotherms of nitrogen at 77K. Each of the isotherms shows type II behaviour indicative of non-porous materials. A negligible amount of hysteresis is observed which may be due to non-rigid interparticle voids. Nevertheless, very few differences are

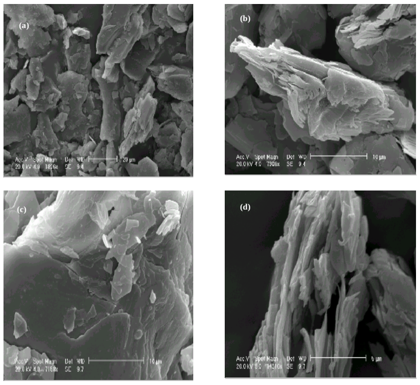

Figure 6: SEM images of talc non heated (a) and heated to 650°C (b), heated to 850°C (c) and heated to 1000°C (d) by CRTA under 210^{-2} mbar water vapour pressure.

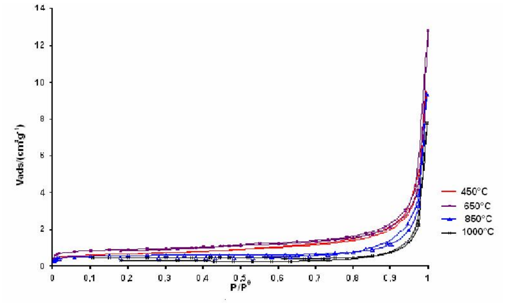

Figure 8. Nitrogen isotherms obtained at 77 K on intermediate samples isolated at 450°C, 650°C; 850°C and 1000°C. The curves are each offset for clearer comparison

observed between the unheated sample and the intermediate products at 550, 650; 850°C and 1000°C which all have similar BET surface areas: 2.37, 2.55; 2.62 and 2.74 (±0.2) m^2g^{-1}.

DISCUSSION AND CONCLUSIONS

According to these above CRTA results, the decomposition steps, noted on the CRTA curves correspond to the complete deshydroxylation of talc sample (A), in this case the gas composition above the sample does not greatly change, the vapour pressure is kept in a state of quasi-equilibrium: its rate of production during the dehydration is maintained constantly equal to its rate of elimination which is it self kept constant with time. Under these conditions, the length of each dehydration step varies proportionally with the mass of water lost. The CRTA curve thus obtained is thus analogue to a thermogravimetric curve.

The CRTA curves of sample(A)(Figure 2)exhibits two decomposition steps are clearly separated occurring between 500-630°C(I) and 630-1000°C (II) respectively.

According to the result of the characterisation of intermediate sample by FTIR, XRD, SEM and BET, the first decomposition step, having the minor length, can be attributed to the removal of the hydroxyl group from brucite layer of chlorite also the second step can be attributed to the loss of water talc and chlorite.

To explain this result it was necessary to take a closer look at the structure of both minerals (talc/chlorite) and also the arrangement of the hydroxyl groups.

Both talc and chlorite are trioctahedric minerals with sheet structure and theoretical formula $Mg_3SiO_4O_{10}(OH)_2$ and $(Mg_{6-x-y}Fe_yAl_x)(Si_{4-x}Al_x)O_{10}(OH)_8$, respectively. The elemental layer of talc is composed of an octahedral plane of brucite (Mg $(OH)_2$ with therefore only one type of –OH site confined between two external tetrahedral silicate sheets[34,35]. Chlorite, however is composed of alternating talc (containing two hydroxyl (OH) groups separated by a bridging oxygen) and brucite layers (containing six hydroxyl (OH) groups arranged next to each other)[34-37].

Thus talc logically can produce only water from two different –OH groups. During the heating of the mineral, water is liberated in distinct steps due to differences in bonding energy. The CRTA conditions used in the present study seem only to highlight two types of OH groups as would be expected from a simple study of the talc sample here. This would seem to be in contradiction with the conventional TG analysis and certainly in contradiction with previous studies[33]. This is certainly due to a difference in sample origins and maybe to experimental conditions. Indeed, CRTA under the present vacuum allows not only for a low reaction rate but also for the possibility to evacuate gas species as they are formed. This avoids any possibility of secondary reactions.

Nevertheless a closer inspection of the relative length of the two steps in the CRTA curve shows a 1:2 ratio for parts I and II respectively. The chemical and XRD analysis of the initial product indicated a chlorite content of 16%.

The CRTA curve thus reflects this percentage and 1:2 ratio perfectly :

- The first step is due to loss of water from the brucite sheets in chlorite. Thus 16%×6(OH groups per brucite sheet(i.e. 96), and,
- The second step is due to water loss from the talc layers in chlorite and in the talc itself (i.e. 16×2 -OH groups in chlorite in addition to 84%×2 -OH groups in the talc(i.e. a total of 200).

This study thus shows the possibility to characterise, via CRTA, a mineral talc sample in terms of talc decomposition and the quantification of impurities such as chlorite. Further work will use this initial reference sample to quantify samples of other origins.

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