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Thermal decomposition of the calcium salts of several carboxylic acids

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Abstract

A systematic study of thermal decomposition of the calcium salts of eight carboxylic acids, using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), is presented. Synthesized calcium salts of carboxylic acids with 3–13 carbon atoms in the aliphatic chain exist as monohydrates that transform into anhydrous salts at about 110 °C, changing their structures and diminishing their crystallinity. Beginning at temperatures between 160 and 315 °C, the salts decompose, forming carbonates as final solid products. From a qualitative point of view, the studied salts show a thermal stability that exponentially decreases with the aliphatic chain length growth. In the temperature interval between dehydration and decomposition, some of the samples suffer a recrystallization process, while others melt. The conclusions possible from thermal analysis were confirmed by monitoring the changes in salt crystallinity with temperature and the appearance of new phases by X-ray powder diffraction (XRD). Infrared (IR) spectroscopy also suggests these conclusions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thermal analysis; Calcium salts of carboxylic acids; Powder diffraction; Infrared spectroscopy

1. Introduction

The cooking of corn grains in an alkaline solution of calcium hydroxide, followed by steeping for about 14 h and thorough washing in water to obtain, after grounding the treated maize, a pasty bulk (*masa*) is a common way of obtaining a variety of corn products, such as flat cakes (*tortillas*) in Mexico and other central American countries. This process, known as *nixtamalization*, brings to corn a high content of calcium and new taste and rheological properties. It has been found that the main form of interaction of calcium with corn components is the formation of salts of carboxylic acids through saponification of grain lipids [1]. It is believed that these salts are responsible for the elasticity of the obtained bulk and for the resistance of these products to spoilage. Calcium salts of aliphatic carboxylic acids have not been systematically studied. However, some of them have been investigated in connection with their uses. The use of calcium salts such as calcium propionate as preservatives is well known in the food industry. The thermal

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behavior of this compound has been reported [2,3]. Calcium stearate has been studied by XRD and thermal analysis [4,5] in relation to its use in the soap and lubricant industry. Salts of carboxylic acids with 12–18 carbon atoms in the aliphatic chain have been studied thermally in connection with their presence in human gallstone [6].

In a previous work, it was established that the calcium salt monohydrates of carboxylic acids with 3–6 carbon atoms in the chain have the same type of crystalline cell. This cell has monoclinic symmetry described by the $P2_1/a$ space group, the monoclinic axis lineally grows with the growing of the number of carbon atoms in the aliphatic chain [7,8].

In this work, a systematic thermal study of nine different calcium salts was conducted. This study can be useful not only for understanding processes that take place during the processing of the most consumed food in countries such as Mexico, Guatemala, etc. but can also provide some understanding of the nature of the thermal decomposition of the calcium salts of carboxylic acids.

2. Experimental

Calcium salts of propionic, butyric, valeric, caproic, heptanoic, caprylic, decanoic, lauric and tridecanoic acids (3, 4, 5, 6, 7, 8, 10, 12 and 13 carbon atoms in the chain, respectively) were synthesized mixing calcium hydroxide powder with an excess of the liquid acids in an agate mortar. In the case of solid acids, the synthesis was made putting the acids in distilled water at 85 °C and adding an aqueous solution of calcium hydroxide while stirring with a magnetic stirrer. In both cases, the obtained insoluble mixtures were washed in distilled water, filtered and dried in air at room temperature. Afterwards, the powders were washed repeatedly in chloroform and again dried at room temperature. All the reagents were analytical grade Sigma products. The purity of the obtained samples was checked by IR spectroscopy and X-ray powder diffraction.

From now on the synthesized samples are referred to as propionic-Ca (C3), butyric-Ca (C4), valeric-Ca (C5), caproic-Ca (C6), heptanoic-Ca (C7), caprylic-Ca (C8), decanoic-Ca (C10), lauric-Ca (C12) and tridecanoic-Ca (C13), respectively.

For observing the samples under a scanning electron microscope (SEM) (JEOL 35M), they were coated with gold using the sputtering technique.

Thermogravimetric analysis (TGA) was performed with a DuPont Instruments 1600 thermobalance. The weight of the samples was in the range 10–20 mg.

The differential scanning calorimetry (DSC) measurements were made with a Perkin-Elmer-Pyris-1 calorimeter calibrated with indium. Both TGA and DSC measurements were carried out from room temperature up to 350 °C, at the rate of 10 $^\circ\mathrm{C\ min^{-1}}$ in air.

The XRD powder patterns were obtained using a Siemens D5000 diffractometer and Cu Kα radiation at 40 kV and 30 mA. The registrations were performed in the 2–50° 2θ range, measuring 15 s per point every 0.01° 2θ.

Using the EVA software distributed with the Siemens diffractometer, the background and the Kα2 lines were subtracted from the measured patterns.

Infrared (IR) spectra were obtained using a Brucker Equinox FT-IR spectrometer. The samples were prepared in KBr disks.

The thermal treatment of some of the samples was conducted in a North Atlantic oven with temperature control.

3. Results and discussion

Samples of calcium carboxylates consist of white waxy powders that are stable in air. Under the SEM, it could be seen that they represent elongated plates of size that vary from one sample to another. In Fig. 1, the microstructure of sample C8 is presented. There the platelet shape of the crystallites is clearly evident, the platelet faces are parallel to the (1 0 0) plane [8,9]. The rest of the samples exhibit similar microstructures of thin lamellae.

Fig. 2 shows the TGA curves for the nine samples. In all the cases, at about 110–120 °C occurs a transition that can be linked to the loss of water of crystallization. The temperatures of dehydration T_1 are presented in the second column of Table 1. From the weight lost in TGA, it was established that the samples were actually monohydrates of the corresponding calcium salts of the carboxylic acids.

After the samples had lost water, their weights remain constant for a temperature range that varies

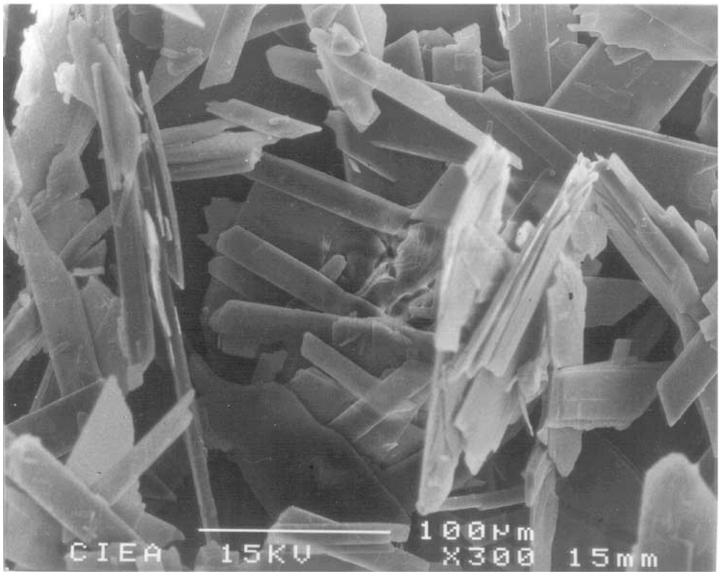

Fig. 1. SEM micrograph of sample C8 showing the platelet shape of the crystallites. The platelet faces are parallel to the (1 0 0) plane.

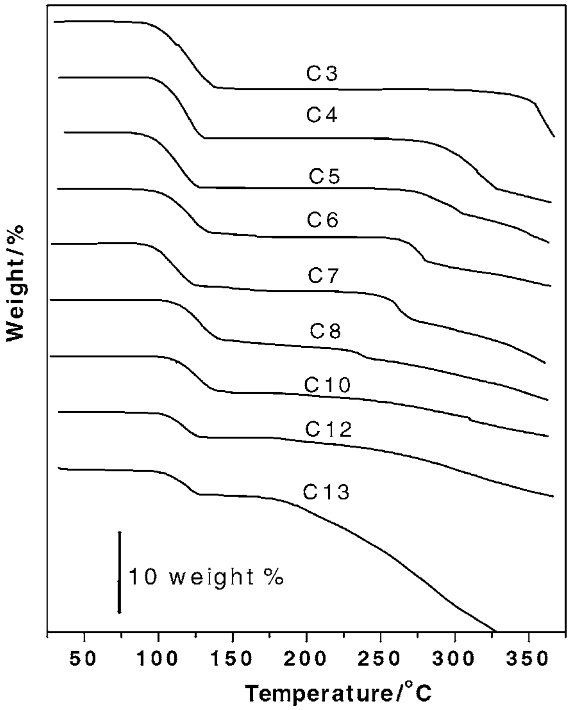

Fig. 2. Thermograms for the decomposition of nine calcium carboxylates. The first transition at about 100 °C corresponds to the dehydration. The second weight loss is associated to decomposition. The samples were heated at a rate of 10° $\min^{-1}$ in dry air.

from sample to sample. Afterwards, samples begin losing weight again, reflecting the decomposition of the anhydrous salts. With an increase in the aliphatic chain length of the salts, the temperature at which the decomposition begins diminishes. For calcium tridecanoate the decomposition starts immediately after the sample has lost the water. The third column of Table 1 shows the temperature T_2 that corresponds to the start of the decomposition for each sample. In Fig. 3, this temperature is plotted against the number of carbon atoms in the chain. This curve shows that the temperature at which the decomposition begins exponentially decreases with the growth of the chain length,

Table 1
Temperature (°C) of dehydration T_1 and onset temperature T_2 for decomposition of selected calcium carboxylates

Sample	T_1	T_2
C3	113.3	312
C4	119.8	274
C5	116.9	255
C6	116.9	244
C7	121.8	227
C8	118.9	212
C10	118.6	185
C12	121.2	170
C13	118.7	166

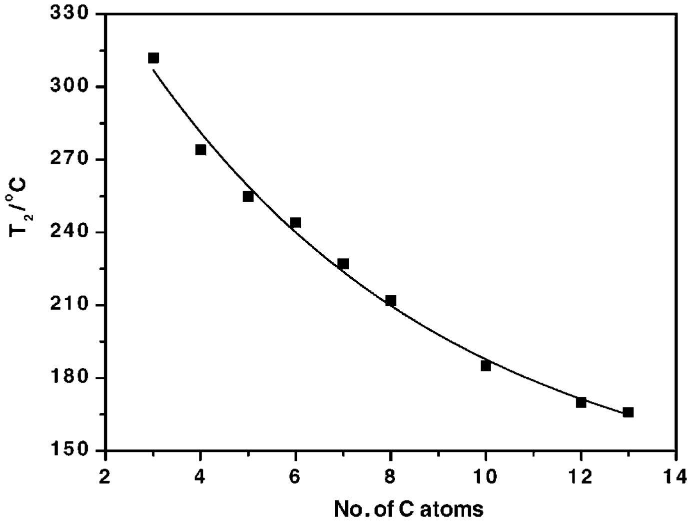

Fig. 3. The temperature T_2 of the start of the decomposition processes is plotted against the number of carbon atoms in the chain.

reflecting a decrease in the thermal stability of the salts as the chain length increases.

From the XRD, it could be established that dehydration is accompanied by a phase transformation and with a certain loss of crystallinity. Also it could be seen that after T_2 samples decompose giving calcium carbonates as solid products. Fig. 4a shows the changes in the diffraction patterns for sample C6, measured as synthesized and after heat treatments at 150 and 300 °C for 1 h. The sample treated at

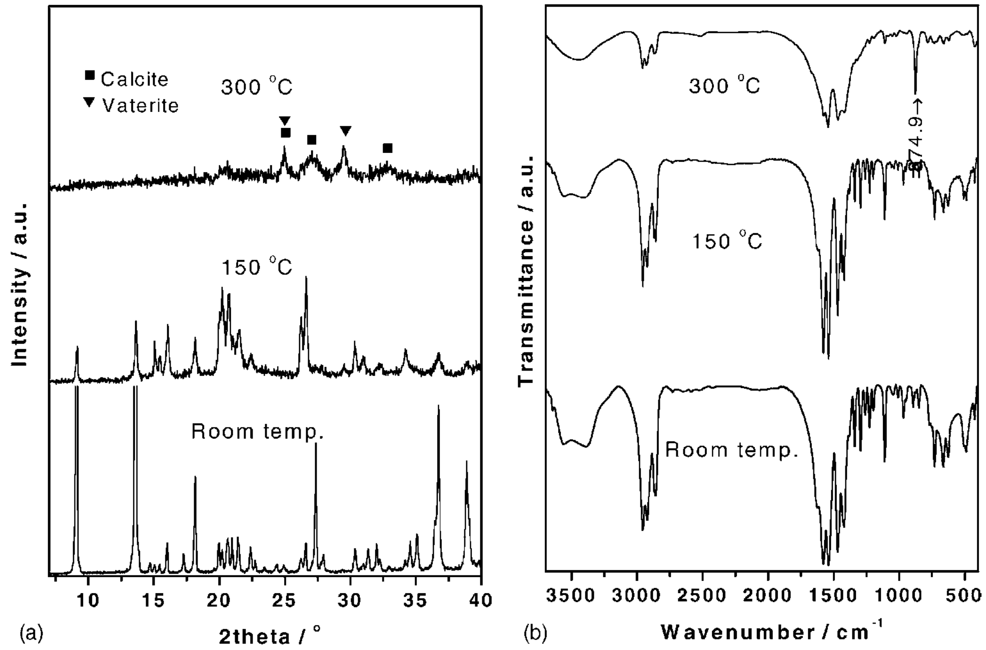

Fig. 4. (a) XRD powder patterns of C6 measured for the synthesized sample and for the same sample after heat treatment at 150 and 300 °C for 1 h. (b) IR spectra for the same sample before and after the heat treatments.

150 °C shows a loss of crystallinity, but the observed peaks are those expected for anhydrous calcium caproate. The similarity of the XRD patterns suggests that the anhydrous phase might have a crystalline cell that is a sublattice of the monohydrated phase cell. The pattern of the sample treated at 300 °C contains no peaks from the calcium carboxylate and peaks corresponding to the calcium carbonates are present. These results agree with those reported in [4] for calcium propionate. All the other salts show similar XRD powder patterns, with the appearance of the anhydrous phase after T_1 and the presence of carbonates after T_2.

The dehydration and decomposition of the salts was also monitored by IR spectroscopy. Fig. 4b shows the IR spectra of the sample C6 and of the same sample subjected to thermal treatment. The most important differences in these spectra are apparent in the strong decrease of the water bands between 3100 and 3700 cm^{-1} (O–H stretching modes) and at about 1600 cm^{-1} (δ (H–O–H) bending) with the increase of temperature of the heat treatment. The uncoordinated water present in the spectra of the dehydrated samples is attributed to the KBr matrix. At 300 °C, the absoption for skeletal vibrations in the region 1260–450 cm^{-1} attributed to the aliphatic chain, (C–C stretching and deformation and the CH_3 rocking vibrations) have almost disappeared. However, the bands corresponding to the symmetric (1470–1420 cm^{-1}) and asymmetric (1576–1538 cm^{-1}) vibrations of the carboxylate group are still present, indicating that the decomposition mainly involves the aliphatic chain. Meanwhile, a new band at 875 cm^{-1} corresponding to carbonate can be seen in this spectrum.

It is expected that the crystalline cells of the studied salts have a similar structure to that of the calcium stearate. There, the polar groups are situated in planes $x = 1/4$ and $x = 3/4$, while the methylene groups CH_2 are arranged in layers defined by subcells stacked parallel to crystalline axes a, and with parameters (a_0, b_0, c_0) that agree with long range crystalline

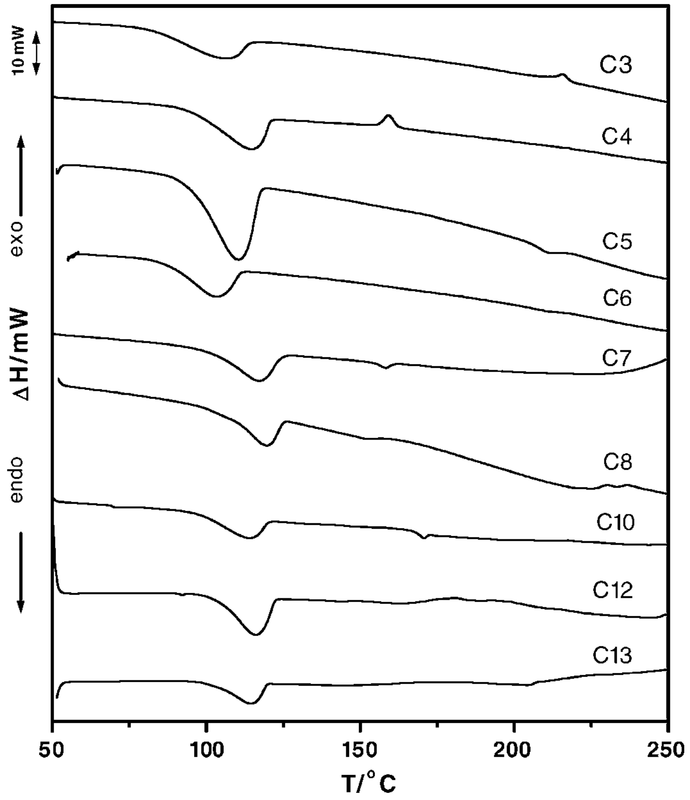

Fig. 5. DSC curves of the selected samples heated 10° min^{-1} in dry air.

parameters *a*, *b*, *c* [4]. With the growth of the aliphatic chain length the number of such subcells increases. Because the binding forces of such arrangements are weaker than the ionic bond in the polar group, it should be expected the decomposition to begin precisely from the chain. For the same reason, when the relative volume fraction of these subcells increases (with the growth of the number of carbon atoms in the chain), the thermal stability of the salts should decrease, in accordance with the observed behavior in Fig. 3.

To study thermal processes responsible for the changes in the crystalline state of the samples between T_1 and T_2, DSC measurements were carried out. Fig. 5 shows the DSC curves. Thermograms for all the samples contain an endothermic peak at about 100 °C, corresponding to dehydration. For C3 and C4, an exothermic peak can be clearly seen between T_1 and T_2, indicating to the occurrence of a recrystallization process. For C5, C6, C7 and C10, there is a reversible endothermic peak in this same interval that corresponds to melting of the samples. One sample from each of these two groups was subjected to heat treatment at temperatures that correspond to points before and after the transition. Sample C4 was kept for 1 h at 125 and 170 °C, and then examined by XRD. In Fig. 6a, the resulting patterns are presented. After being treated at 125 °C the pattern for the anhydrous phase contains peaks that correspond to a new structure (compared to the monohydrate) but the loss of crystallinity can be established from the observed peak broadening. From the comparison of this pattern to the XRD pattern of the sample treated at 170 °C, it can be concluded that in this interval of temperature a recrystallization process takes place. This is reflected in the increase of the intensity of the diffraction peaks for the sample heated at 170 °C and in the decrease of the full with at the half maximum (FWHM) of the peaks.

Sample C7 was treated at 148 and 170 °C for 1 h. The diffraction patterns of these samples (Fig. 6b) show also the anhydrous phase at 148 °C and evidence that after being melted at about 170 °C and cooled back to room temperature, the anhydrous and a new phase recrystallizes. In the Fig. 6b, peaks corresponding to this new phase are marked with arrows.

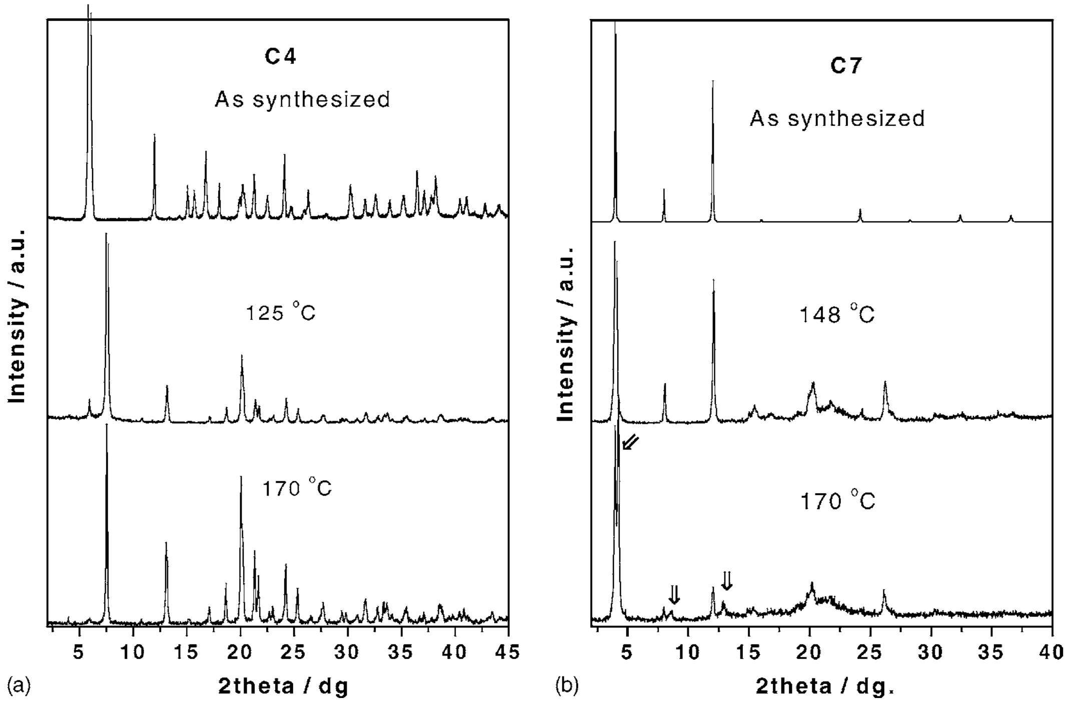

Fig. 6. (a) XRD patterns of sample C4, and the same sample treated for 1 h at 125 and at 170 °C. (b) XRD patterns of sample C7, before and after the heat treatments at 148 and 170 °C for 1 h.

4. Conclusions

Calcium salts of carboxylic acids prepared from calcium hydroxide and the corresponding acids exist as monohydrates. At temperatures about 110 °C, dehydration takes place. Dehydration leads to a phase transformation and certain lost of the crystallinity of the samples.

At certain temperature T_2, decomposition of the salts begins. This temperature varies from salt to salt and decreases exponentially with the increase in the number of carbon atoms in the aliphatic chain. The decomposition to calcium carbonate takes place in a broad range of temperatures, extending beyond 350 °C.

Between the dehydration and decomposition, samples may be subjected to recrystallization or melting.

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