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Thermal decomposition of hydrotalcite with hexacyanoferrite(II) and hexacyanoferrate(III) anions in the interlayer

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Abstract

The mechanism for the decomposition of hydrotalcite remains unsolved. Controlled rate thermal analysis enables this decomposition pathway to be explored. The thermal decomposition of hydrotalcites with hexacyanoferrite(II) and hexacyanoferrate(III) in the interlayer has been studied using controlled rate thermal analysis technology. X-ray diffraction shows the hydrotalcites studied have a d(003) spacing of 11.1 and 10.9 Å which compares with a d-spacing of 7.9 and 7.98 Å for the hydrotalcite with carbonate or sulphate in the interlayer.

Calculations based upon CRTA measurements show that 7 moles of water is lost, proving the formula of hexacyanoferrite(II) intercalated hydrotalcite is $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.5}$ .7 H_2O and for the hexacyanoferrate(III) intercalated hydrotalcite is $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.66}$ * 9 H_2O**.** Dehydroxylation combined with CN unit loss occurs in three steps between a) 310 and 367°C b) 367 and 390°C and c) between 390 and 428°C for both the hexacyanoferrite(II) and hexacyanoferrate(III) intercalated hydrotalcite.

Keywords: hexacyanoferrite(II), hexacyanoferrate(III), hydrotalcite, takovite, pyroaurite, controlled rate thermal analysis, CRTA

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Introduction

Hydrotalcites, or layered double hydroxides (LDH's) are fundamentally anionic clays, and are less well-known than cationic clays like smectites [1, 2]. The structure of hydrotalcite can be derived from a brucite structure ($Mg(OH)_2$) in which e.g. Al^{3+} or Fe^{3+} (pyroaurite-sjögrenite) substitutes for some of the Mg^{2+} cations [3-14]. This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes [15, 16]. Further mixtures of these mineral phases with multiple anions in the interlayer are observed. When LDHs are synthesised any appropriate anion can be placed in the interlayer. These anions may be any anion with a suitable negative charge including the hexacyanoferrate(II) and hexacyanoferrate(III) ions [17-19]. The incorporation of these ions has implications in electrochemistry [19-23].The hydrotalcite may be considered as a gigantic cation which is counterbalanced by anions in the interlayer. In hydrotalcites a broad range of compositions are possible of the type $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}.yH_2O$, where M^{2+} and M^{3+} are the di- and trivalent cations in the octahedral positions within the hydroxide layers with x normally between 0.17 and 0.33. A^{n-} is an exchangeable interlayer anion [24]. In the hydrotalcites reevesite and pyroaurite, the divalent cations are Ni^{2+} and Mg^{2+} respectively with the trivalent cation being Fe^{3+}. In these cases, the carbonate anion is the major interlayer counter anion. Of course when synthesising hydrotalcites any anion may be used [7, 14, 25-27]. Reevesite and pyroaurite are based upon the incorporation of carbonate into the interlayer with d(003) spacings of around 8 Å [28, 29]. Normally the hydrotalcite structure based upon takovite (Ni,Al) and hydrotalcite (Mg,Al) has basal spacings of ~8.0 Å where the interlayer anion is carbonate.

Thermal analysis using thermogravimetric techniques enables the mass loss steps, the temperature of the mass loss steps and the mechanism for the mass loss to be determined [6, 11, 30-34]. Thermoanalytical methods can provide a measure of the thermal stability of the hydrotalcite. Controlled rate thermal analysis (CRTA) has proven extremely worthwhile in the study of the stability and thermal decomposition pathways of minerals and modified minerals such as mechanochemically activated kaolinite and intercalated kaolinites [34-41]. The application of CRTA technology to the study of the thermal stability of hydrotalcites has to the best of our knowledge never been reported.

In this work we report the thermal analysis using CRTA technology of hydrotalcite with hexacyanoferrite(II) and hexacyanoferrate(III) anions in the interlayer

Experimental

Synthesis of hydrotalcite samples

Hydrotalcites are able to be synthesised in the laboratory using analytical grade chemicals. The reason for using synthetic compounds as opposed to the natural minerals is that difficulties associated with multiple anions in the interlayer can be minimised, and allow for trends and characteristics to be more readily determined. The hydrotalcites reported below were synthesised by the co-precipitation method.

A mixed solution of aluminium and magnesium nitrates ($[Al^{3+}]$ = 0.25M and $[Mg^{2+}]$ = 0.75M; 1M = 1mol/dm^3) and a mixed solution of sodium hydroxide ($[OH^-]$ = 2M) and the desired anion, at the appropriate concentration, were placed in two separate vessels and purged with nitrogen for 20 minutes (all compounds were dissolved in freshly decarbonated water). The cationic solution was added to the anions via a peristaltic pump at 40mL/min and the pH maintained above 9. The mixture was then aged at 75°C for 18 hours under a N_2 atmosphere. The resulting precipitate was then filtered thoroughly, with room temperature decarbonated water to remove nitrates and left to dry in a vacuum desiccator for several days. In this way hydrotalcites with different anions in the interlayer were synthesised. The phase composition was checked by X-ray diffraction and the chemical composition by EDAX analyses.

Thermal Analysis

Dynamic experiment

Thermal decomposition of the hydrotalcite was carried out in a Derivatograph PC type thermoanalytical equipment (Hungarian Optical Works, Budapest, Hungary) capable of recording the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves simultaneously. The sample was heated in a ceramic crucible in static air atmosphere at a rate of 5 °C/min.

Controlled Rate Thermal analysis experiment

Thermal decomposition of the intercalated hydrotalcite was carried out in the Derivatograph under static air in an open ceramic crucible at a pre-set, constant decomposition rate of 0.15 mg/min. (Below this threshold value the samples were heated under dynamic conditions at a uniform rate of 1.0 °C/min). With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage.

X-ray diffraction

The X-ray diffraction patterns for the hexacyanoferrite(II) and hexacyanoferrate(III) interlayered hydrotalcites are shown in Figure 1. For comparison the XRD patterns of the sulphate and carbonate intercalated hydrotalcite are shown. The XRD patterns clearly show the formation of the hydrotalcites with the different anions in the interlayer. The XRD patterns also show no impurities in the synthesised hydrotalcites. Hydrotalcite normally has a d(003) spacing of 7.9 Å. The sulphate intercalated hydrotalcite has a spacing of 7.99 Å. The hexacyanoferrite(II) complex has a spacing of 10.9 Å and the hexacyanoferrate(III) hydrotalcite 11.1 Å. The increased interlayer spacing is due to the bigger size of the anion between the brucite-like layers.

Thermal Analysis

Dynamic Thermal Analysis of hexacyanoferrite(II) intercalated *hydrotalcite*

The dynamic thermal analysis of 157.95 mg of the *hexacyanoferrite(II)* intercalated *hydrotalcite* is shown in Figure 2. Comparing the curves the following conclusions can be drawn. In the temperature range from ambient to about 500°C two significant decomposition stages can be observed in the DTG curve: from 50 to 260°C with ~20% mass loss, and between 260 and 500°C with ~26% mass loss. According to mass spectrometric data (not shown here) the first mass loss step is associated with dehydration. The second one actually consists of 5 processes: (i) 260-310°C, partial loss of CN units; (ii-iv) with peak temperatures of 361°C, 374°C and 387°C, dehydroxylation and HCN liberation; and (v) with peak temperature of 445°C, CO_2 liberation from carbonate impurity. The final products of thermal decomposition are oxides of Mg, Al and Fe.

The proposed reaction pathways are as follows:

Dehydration (under 260°C)

$Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.5}$ x $H_2O \rightarrow Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.5}$ + x H_2O

Dehydroxylation and decomposition of the interlayer anion (above 260°C)

$Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.5} \rightarrow 6MgO + Al_2O_3 + 0.5\ FeO + 3HCN + 6.5\ H_2O$

The FeO formed is oxidized to Fe_2O_3:

$0.5\ FeO + 0.125\ O_2 \rightarrow 0.25\ Fe_2O_3$

Dynamic Thermal Analysis of hexacyanoferrate(III) intercalated hydrotalcite

The dynamic thermal analysis of the *hexacyanoferrate(III) intercalated hydrotalcite* is shown in Figure 3. Similarly to the iron(II) sample the thermal decomposition of the *hexacyanoferrate(III) intercalated hydrotalcite* takes place in two major stages. From ambient to about 260°C dehydration takes place with a mass loss of about 22%. In the second stage between 260 and 500°C a mass loss of ~24% is observed. According to mass spectrometric data (not shown here) in the second stage dehydroxylation and the liberation of the CN unit take place in 4 steps: (i-iii) with peak temperature of 361°C, 374°C and 387°C, dehydroxylation and HCN liberation; and (iv) at 445°C; CO_2 liberation from carbonate impurity. The final products of thermal decomposition are oxides of Mg, Al and Fe.

The proposed reaction pathways are as follows:

Dehydration (under 260°C)

$Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.66}$ x $H_2O \rightarrow Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.66}$ + x H_2O

Dehydroxylation and decomposition of the interlayer anion (above 260°C)

$Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.66} \rightarrow 6MgO + Al_2O_3 + 0.33\ Fe_2O_3 + 4\ HCN + 6\ H_2O$

In order to better resolve the decomposition processes, controlled rate thermal analysis (CRTA) experiments were carried out as well in the same equipment using the CRTA control facility. In this case the decomposition of the mineral was carried out at a preset, constant, slow rate to provide enough time for the slow heat and mass transfer processes to occur. The essence of the technique lies in that each sample particle shall be heated under identical conditions. With the slow and constant decomposition rate of 0.10 mg/min the decomposition is carried out under quasi-equilibrium conditions. This is achieved by the control of the furnace temperature regulated by the DTG signal through the computer.

Controlled Rate Thermal Analysis of hexacyanoferrite(II) intercalated hydrotalcite

The CRTA curves of 156.22 mg sample are shown in Fig. 4. The mass loss data are summarized in Table 1. In the ambient to 267°C range a non-isothermal process can be observed that belongs to the loss of hydration water (18.9%). The calculations given in the appendix show the loss of 7 moles of crystallization giving the formula of *hexacyanoferrite(II) interlayered hydrotalcite* as $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.5}.7\ H_2O$**.** Normally a dehydration process follows an isothermal course on under CRTA conditions. The non-isothermal nature of dehydration in this case can be explained with the simultaneous reduction in d-spacing. Due to the partial collapse the liberation of hydration water is hindered. Therefore higher energy (i.e. higher temperature) is needed to maintain the preset, constant rate of decomposition.

In the temperature range between 267 and 310°C a non-isothermal stage can be observed due to cyanide loss (0.8%). After 310°C three isothermal stages can be seen at 362, 377 and 390°C. These temperatures are in good correlation with the temperature values of the dynamic measurement and can be assigned to the loss of OH and CN units.

Controlled Rate Thermal Analysis of hexacyanoferrate(III) interlayered hydrotalcite

The CRTA curves of 143.76 mg sample are shown in Fig. 5. The mass loss data are summarized in Table 1. In the ambient to 270°C range a non-isothermal process can be observed due to the loss of crystallization water (21.4%). According to the calculations given in the appendix formula of the *hexacyanoferrate(III) interlayered hydrotalcite* is $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.66}.9\ H_2O$**.**

In the temperature range between 270 and 700°C two isothermal (at 361 and 374°C) and one non-isothermal (at a peak temperature of 440°C) stage can be observed. The isothermal stages belong to the loss of OH and CN units. It means that the degradation of the mineral occurs under quasi-equilibrium conditions. The temperature of isothermal processes is reproducible and independent of such parameters than the rate of heat and mass transport. Thus, a comparison of the decomposition patterns of hydrotalcites having different anions in the interlayer space is feasible. The mass loss stage at 440°C (5.1%)is due to the decomposition of carbonate impurity and the further degradation of the mineral matrix).

Conclusions

The thermal decomposition of hydrotalcites based upon a Mg/Al ratio of 6/2 with hexacyanoferrite(II) and hexacyanoferrate(III) in the interlayer has been studied using dynamic and controlled rate thermal analysis techniques complimented with X-ray diffraction.

The non-isothermal nature of dehydration in the CRTA experiment indicates a partial collapse of the layers (reduction in d-spacing). Dehydroxylation and cyanide decomposition occur isothermal steps between 310 and ~430°C. Both mineral contain a small amount of carbonate impurity as evidence mass spectrometric investigations.

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Appendix

Calculation of the water content for hydrotalcite with hexacyanoferrite(II):

Composition: $\mathbf{Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.5} * x\ H_2O}$

Loss of water up to 267°C is 29.50 mg (1.637 mmol)

Mass of the dehydrated mineral is 137.32 mg (0.238 mmol)

Thus, the amount of crystallization water is 6.88 mol giving the formula of

$$\mathbf{Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.5} * 7\ H_2O}$$

Calculation of the water content for hydrotalcite with hexacyanoferrate(III):

Composition: $\mathbf{Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.66} * x\ H_2O}$

Loss of water up to 270°C is 30.70 mg (1.704 mmol)

Mass of the dehydrated mineral is 116.06 mg (0.190 mmol)

Thus, the amount of crystallization water is 8.97 mol giving the formula of

$$\mathbf{Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.66} * 9\ H_2O}$$

Decomposition process	**hydrotalcite with hexacyanoferrate(II) (sample mass: 156.22 mg)**			**hydrotalcite with hexacyanoferrate(III) (sample mass: 143.76 mg)**		
	Temp. range (°C)	**Mass loss**		**Temp. range (°C)**	**Mass loss**	
		mg	**%**		**mg**	**%**
Dehydration	31-267	29.5	18.9	22-270	30-7	21.4
Dehydroxylation/CN Loss	267-310	1.3	0.8	270-366	6.6	4.6
	310-367	6.1	3.9			
	367-383	15.2	9.7	366-427	26.7	18.6
	383-428	13.0	8.3			
CO_2 loss	428-693	10.1	6.5	427-694	7.4	5.1

Table 1 Mass loss data under CRTA conditions

List of Figures

Figure 1 X-ray diffraction patterns of hydrotalcite with carbonate, sulphate, hexacyanoferrite(II) and hexacyanoferrate(III) anions in the interlayer.

Figure 2 Dynamic thermal analysis of hexacyanoferrite(II)-interlayered hydrotalcite.

Figure 3 Dynamic thermal analysis of hexacyanoferrate(III)-interlayered hydrotalcite.

Figure 4 Controlled rate thermal analysis of hexacyanoferrite(II)-interlayered hydrotalcite.

Figure 5 Controlled rate thermal analysis of hexacyanoferrate(III)-interlayered hydrotalcite.

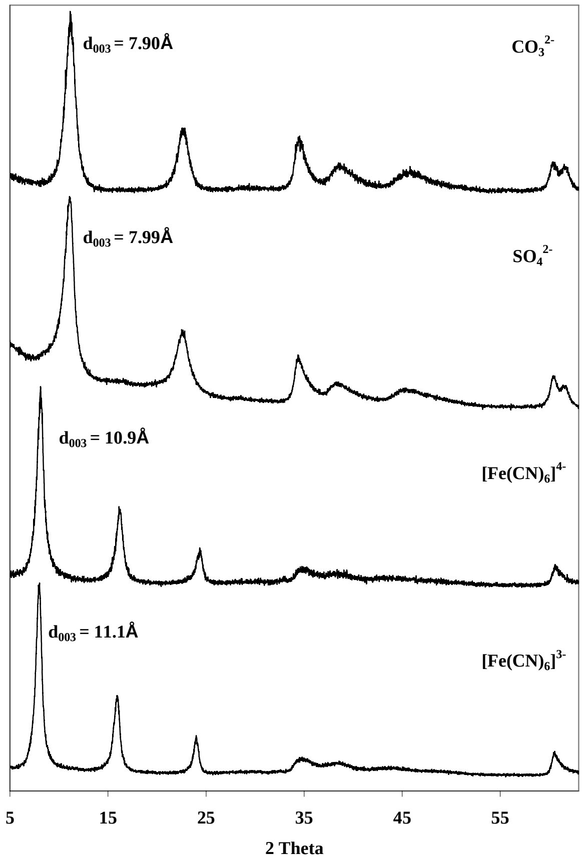
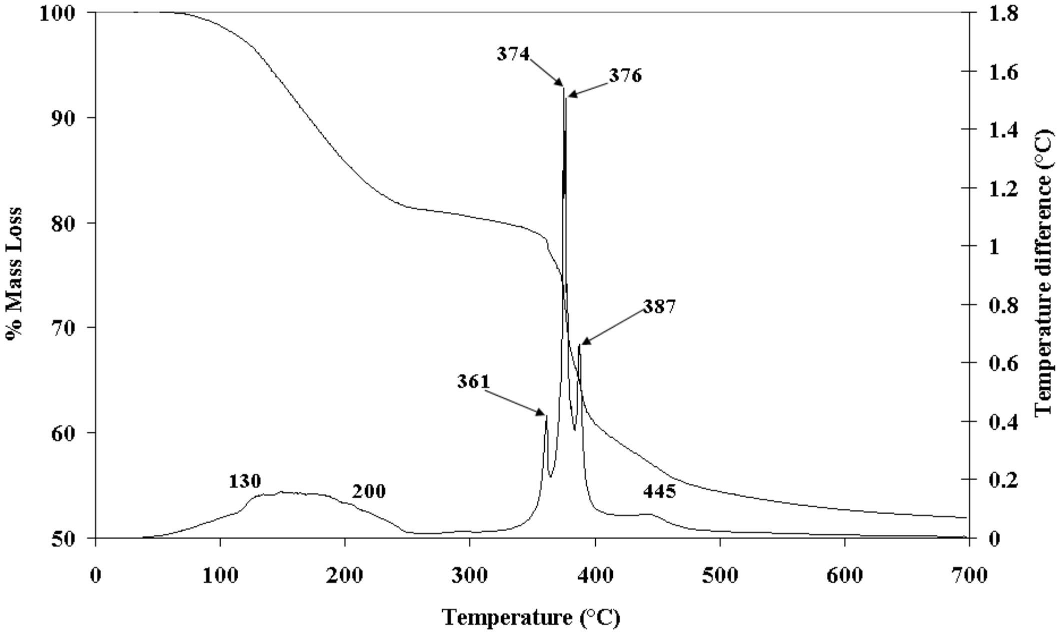

d_{003} = 7.90Å
CO_3^{2-}
d_{003} = 7.99Å
SO_4^{2-}
d_{003} = 10.9Å
$[Fe(CN)_6]^{4-}$
d_{003} = 11.1Å
$[Fe(CN)_6]^{3-}$
5
15
25
35
45
55
2 Theta

Figure 1


100
90
80
70
60
50
% Mass Loss
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Temperature difference (°C)
0
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200
300
400
500
600
700
Temperature (°C)
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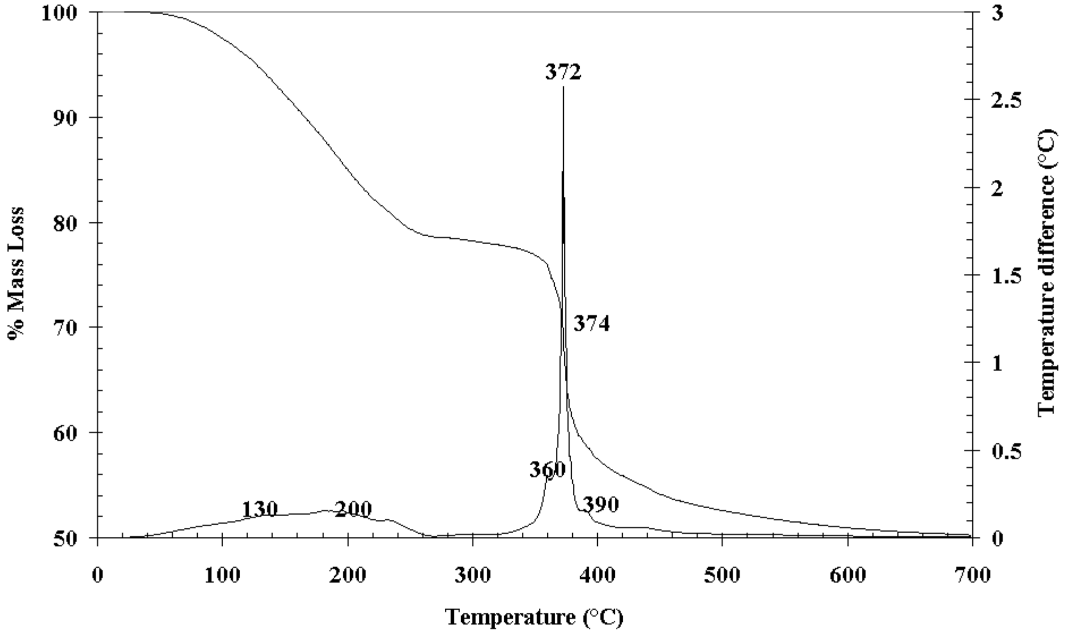
376
387
361
130
200
445

Figure 2


100
90
80
70
60
50
% Mass Loss
3
2.5
2
1.5
1
0.5
0
Temperature difference (°C)
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360
130
200
390
0
100
200
300
400
500
600
700
Temperature (°C)

Figure 3

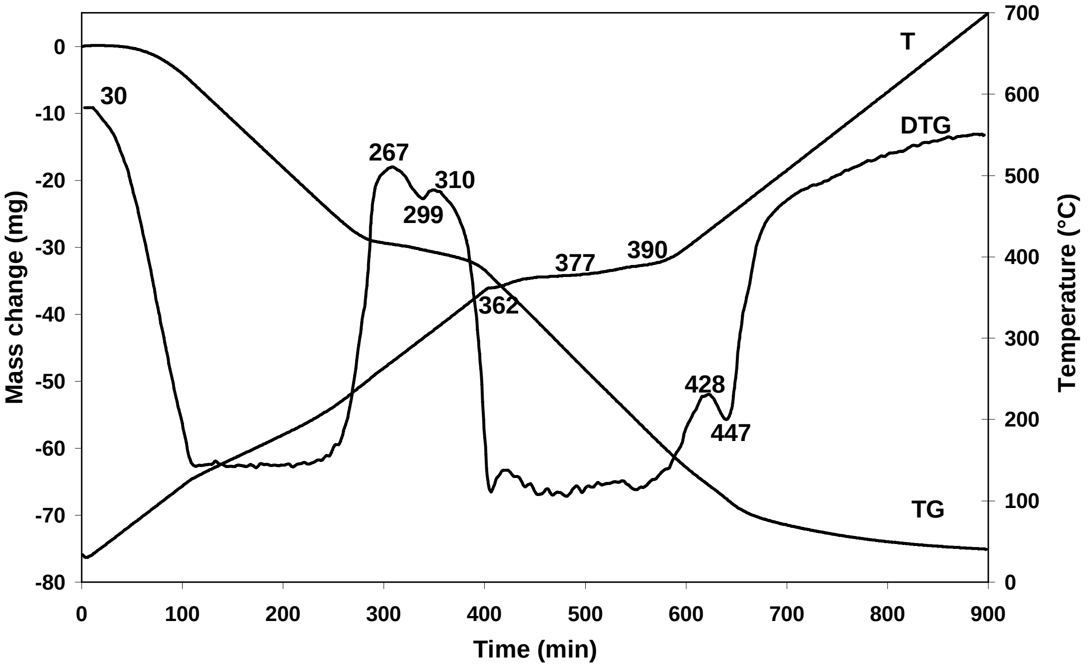
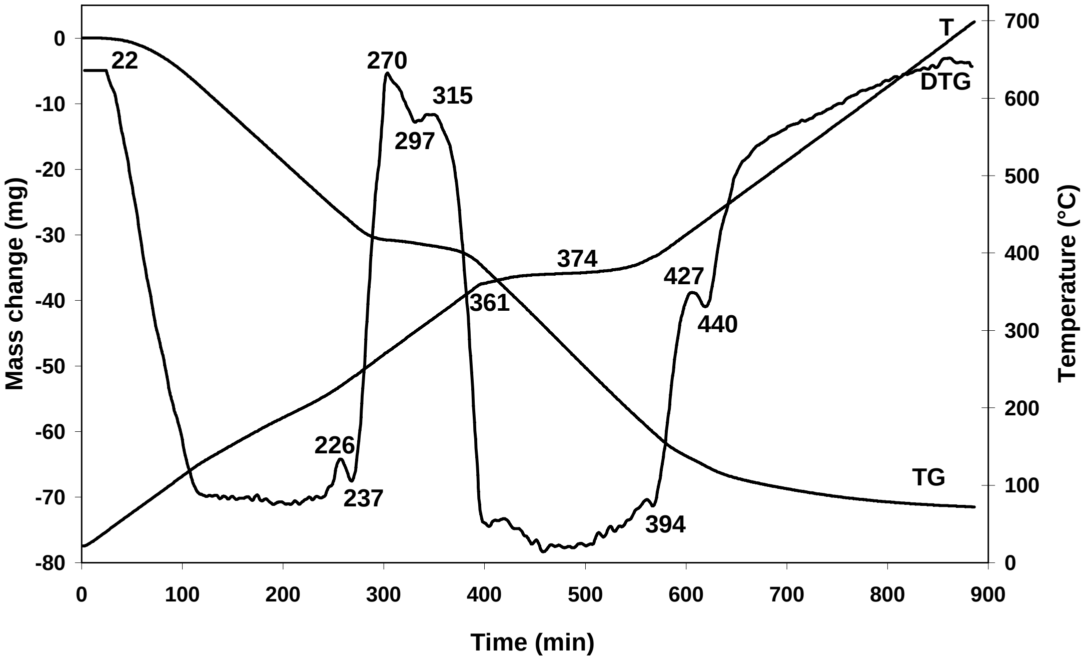

T
DTG
TG
30
267
310
299
362
377
390
428
447
Mass change (mg)
0
-10
-20
-30
-40
-50
-60
-70
-80
Temperature (°C)
700
600
500
400
300
200
100
0
Time (min)
0
100
200
300
400
500
600
700
800
900

Figure 4


Mass change (mg)
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-20
-30
-40
-50
-60
-70
-80
Temperature (°C)
700
600
500
400
300
200
100
0
Time (min)
0
100
200
300
400
500
600
700
800
900
T
DTG
TG
22
270
315
297
374
427
361
440
226
237
394

Figure 5