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DECOMPOSITION OF $CaCO_3$ IN THE PRESENCE OF ORGANIC ACIDS

V. Kasselouri, G. Dimopoulos, G. Parissakis

Laboratory of Inorganic and Analytical Chemistry
Dept. of Chemical Engineering NTU ATHENS
9 Iroon Polytechniou Str. Athens 157 73, Greece

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ABSTRACT

In the present study the possibility of partial decomposition of $CaCO_3$ up to 80 °C by using organic acids has been investigated. As acids in the acid - $CaCO_3$ reaction, citric and oxalic acid have been used. The formation of the crystalline compounds during the acid reactions as also their decomposition during the burning process have been studied through XRD analysis and loss on ignition measurements. The results led to the conclusion that a variety of organic acids could be successfully used resulting in energy saving by lowering the decomposition temperature.

Introduction

A number of researchers reported the use of various additives with target to effect on the kinetic and thermodynamic parameters during the decomposition of $CaCO_3$ (1-6). Most of the additives proposed regarded the system CaO-SiO_2. So some inorganic additives as $LiCO_3$, $NaCl$, NaF, CaF_2, MgO etc. have been used to achieve lower temperatures in the formation of C_2S followed by a decrease of the $CaCO_3$ decomposition temperature.

A new approach to the problem of the energy consumption during the $CaCO_3$ decomposition process is the use of organic acids as additives.

The organic salts could be decomposed at lower temperature levels than that of $CaCO_3$ and the required amount of $CaCO_3$ which should be calcinated could be smaller.

By this way a reduced energy consumption could be achieved during the burning process of $CaCO_3$.

Experimental

To $CaCO_3$ reagent grade various amounts of oxalic and citric acid were added in a percentage of 5, 10 and 20% w/w in the presence of 20% warm water. The resulting mixtures were dried, grinded and passed through a 100 μ sieve and then were kept for the experiments.

In order to study the effect of the acids upon the decomposition of calcium carbonate, the samples were heated for 1/2 h in an electrical furnace between 250 and 900 °C in order to determine the loss on ignition.

The compounds formed during the acid reaction as well as during the burning process were investigated through XRD analysis.

The relative patterns concerning the mixtures with oxalic acid as well as those with citric acid, are presented in Figures 1,2,3,4 respectively. The various crystalline compounds identified in the XRD patterns at different thermal ranges are given in Table I.

TABLE I.
The formation of crystalline compounds during
the burning of the $CaCO_3$ - acid mixture.

Sample	Crystalline compound	Thermal range °C
$CaCO_3 + H_2C_2O_4$ (oxalic acid)	$(COOH)_2\,2H_2O$	20 - 250
	$(COO)_2Ca\ H_2O$	20 - 250
	a - $(COO)_2\,Ca$	250 - 400
	CaO	> 550
	$CaCO_3$	20 - 900
$CaCO_3 + C_6H_8O_7$ (citric acid)	$C_6H_8O_7$	20 - 250
	$Ca_3(C_6H_5O_7)_2\ 4\ H_2O$	20 - 250
	$Ca_3(C_6H_5O_7)_2$	250 - 400
	CaO	> 550
	$CaCO_3$	20 - 900

In Table II the loss on ignition of the examined mixtures during the burning process is presented. The percentages of $CaCO_3$ and acid have been reacted, as well as the calculated value of $CaCO_3$ decomposed at 550 °C, as they have been determined from the values of Table II, are presented in Table III.

Discussion

From the XRD diagrams (Fig 1) and Table I it is shown that during the reaction of $CaCO_3$ with oxalic acid calcium oxalate hydrate is formed. The amount of the above salt increases by the increase of the acid concentration as indicated in Fig.

TABLE II.
Loss on ignition of mixtures during the burning process

Sample	Temperature °C								
	20	250	350	400	550	600	700	800	900
$CaCO_3$	0.00	0.00	0.00	0.00	0.00	0.45	12.85	24.55	44.01
$CaCO_3$+ 5%$H_2C_2O_4$	0.00	1.21	2.10	3.10	5.13	5.61	19.86	31.58	45.53
$CaCO_3$+10%$H_2C_2O_4$	0.00	2.78	4.00	6.31	10.65	11.41	24.70	32.26	47.25
$CaCO_3$+20%$H_2C_2O_4$	0.00	6.84	9.81	14.06	22.43	21.35	32.88	43.22	51.26
$CaCO_3$+ 5%$C_6H_8O_7$	0.00	1.35	3.29	3.89	5.24	5.66	18.49	30.44	46.07
$CaCO_3$+10%$C_6H_8O_7$	0.00	2.92	6.72	7.99	10.69	12.95	25.55	37.31	48.25
$CaCO_3$+20%$C_6H_8O_7$	0.00	6.84	14.40	16.22	20.57	23.89	39.46	45.18	52.88

TABLE III.
Transformation of $CaCO_3$ during $CaCO_3$ - acid reaction
(calculation based on the Table II)

Sample	%$CaCO_3$ reacted with the acid at 20 °C.	%$CaCO_3$ transformed to CaO at 550 °C
$CaCO_3$	0.0	0.0
$CaCO_3$+ 5%$H_2C_2O_4$	5.7	5.6
$CaCO_3$+10%$H_2C_2O_4$	11.7	11.6
$CaCO_3$+20%$H_2C_2O_4$	25.1	24.7
$CaCO_3$+ 5%$C_6H_8O_7$	3.7	3.6
$CaCO_3$+10%$C_6H_8O_7$	7.7	7.7
$CaCO_3$+20%$C_6H_8O_7$	16.2	15.6

2 from the peaks corresponding to 15.01 2θ°. The water was added in proportions similar to those which are used in the cement production by the semi-dry process.

During heating at 250 °C a transformation of the calcium oxalate hydrate to a - $(COO)_2Ca$ takes place as it is indicated from the peak corresponding to 14.5 2θ°. A premature formation of CaO is observed at the 550 °C due to the complete decomposition of the calcium oxalate, while the decomposition of pure $CaCO_3$ starts at 600 °C. The $CaCO_3$ transformed to CaO at 550 °C via the decomposition of its organic salt, progressively increases from 5.6 to 27.7% following the increase of the acid concentration.

Regarding the behaviour of the $CaCO_3$ - citric acid mixtures, the given results are similar.

From the XRD diagrams (Fig 3,4) it is seen that during the $CaCO_3$ - citric acid reaction calcium citrate tetrahydrate is formed.

The peaks concerning this formation appear at 5.8, 22.5 and 28.9 2θ°.

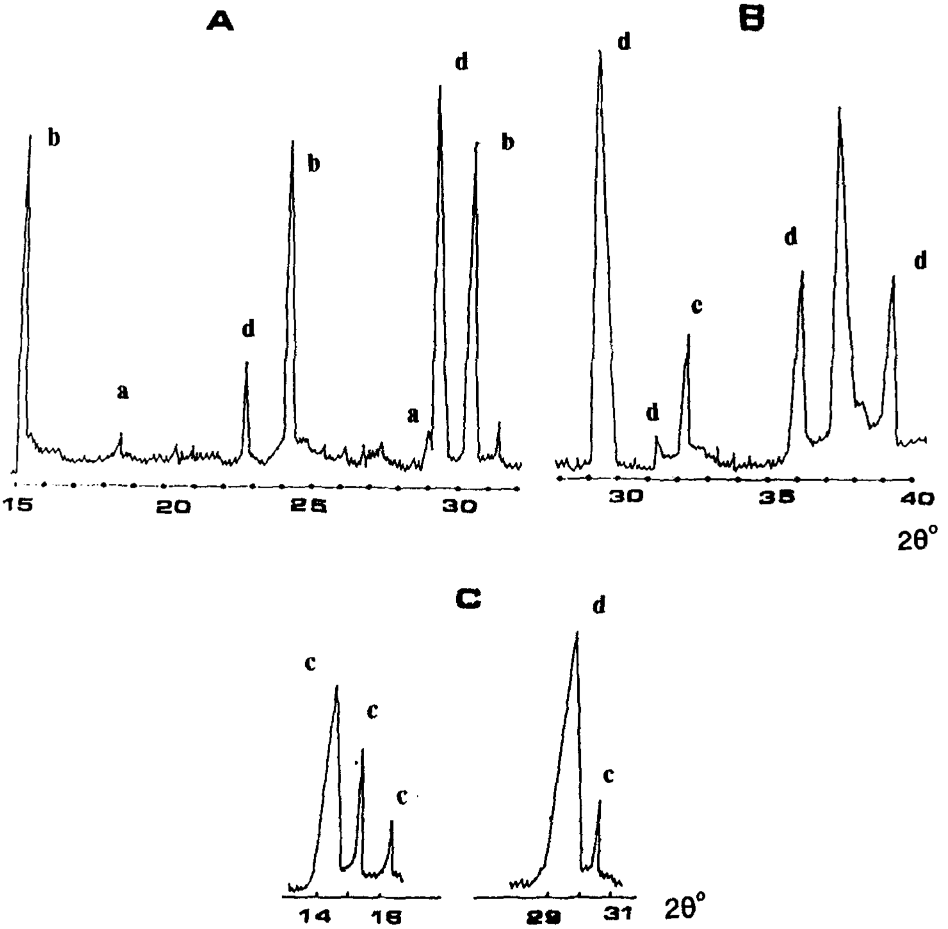

FIG. 1

XRD patterns of $CaCO_3$/20% oxalic acid at various temperatures

A : room temperature, B : 550 °C, C : 250 °C

a : $(COOH)_2 \cdot 2H_2O$, b : $(COO)_2Ca \cdot H_2O$, c : $(COO)_2Ca$, d : $CaCO_3$, e : CaO

When the samples are heated above 250 °C, a transformation of the hydrated citrate salt to anydrous calcium citrate takes place as it is shown from the peaks at 11.5, 22.7 and 30.3 2θ°. As the concentration of citric acid increases from 5 to 20% w/w the amount at $CaCO_3$ tranformed to CaO via the decomposition of its citric salt progressively increases from 3.6 to 15%.

The different reactivity of the oxalic and citric acid can be explained from their different dissociation constants.

Conclusions

The present study leads to the conclusion that the addition of oxalic and citric acid to calcium carbonate, results in the formation of calcium oxalate and calcium

FIG. 2
XRD patterns concerning the compound $(COO)_2Ca \cdot H_2O$ in $CaCO_3$/ oxalic acid mixtures with various amounts of oxalic acid
a:20% oxalic acid
b:10% oxalic acid
c:5% oxalic acid

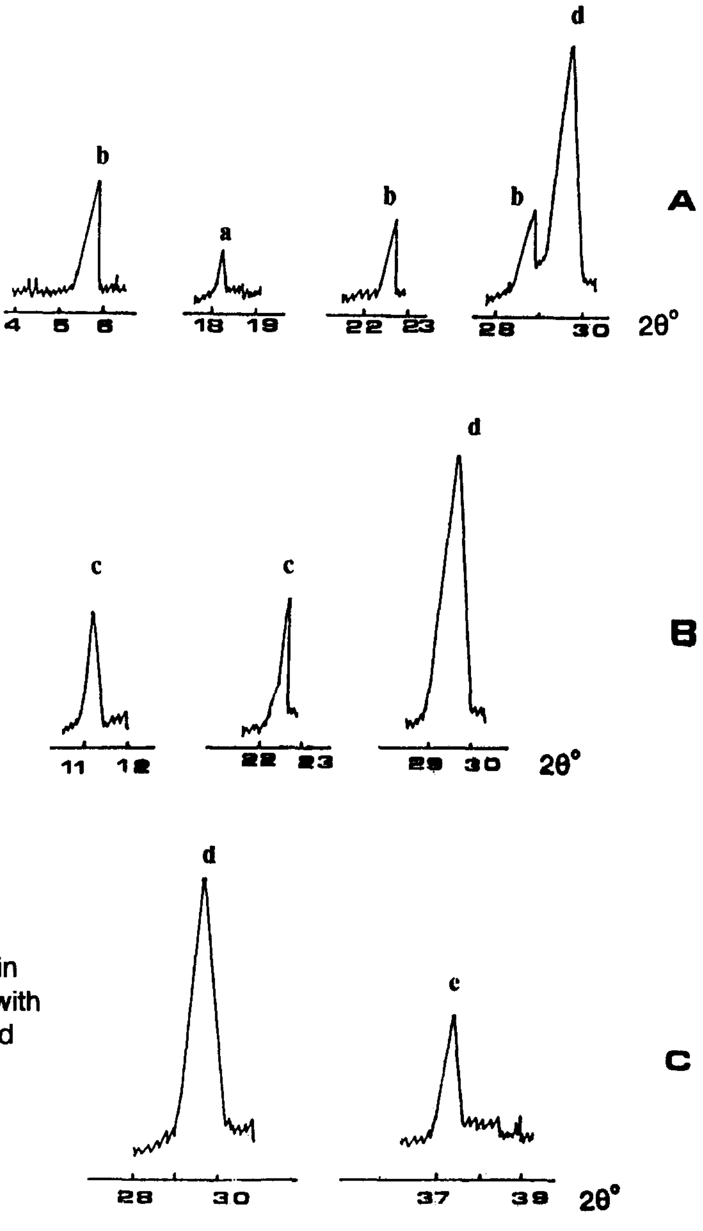

FIG. 3
XRD patterns of $CaCO_3$/20% citric acid at various temperatures
A : room temperature, B : 250 °C, C : 550 °C
a : $C_6H_8O_7$, b : $Ca_3(C_6H_5O_7)_2\ 4\ H_2O$, c : $Ca_3(C_6H_5O_7)_2$, d: $CaCO_3$, e : CaO

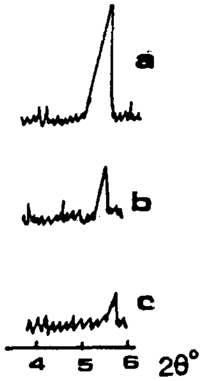

FIG. 4
XRD patterns concerning the compound $Ca_3(C_6H_5O_7)_2\cdot 4\ H_2O$ in $CaCO_3$/ citric acid mixtures with various amounts of citric acids
a:20% citric acid
b:10% citric acid
c:5% citric acid

citrate. The formation of calcium oxide starts earlier than 550 ^{0}C while the pure calcium carbonate starts decomposing at 600 ^{0}C. The amount of CaO at 550 ^{0}C progressively increases by the increase of the concentration of oxalic or citric acid in the starting mixture. This premature calcination takes place due to the complete decomposition of the calcium salts formed during the $CaCO_3$ - acid reaction.

The effect of the organic acids as additives is based upon the decomposition of their calcium salts at temperatures lower than those of pure $CaCO_3$ decomposition. As the decomposition products are only CaO and CO_2 there is no influence upon the quality of the final products.

As in the Mediterranean Countries remarkable amounts of fruits containing organic acids (citrus fruits) are tipping in dumps, a new proposal towards the exploitation of rejected fruits is to use the acids contained in these fruits, as a mean to promote the decomposition of calcium carbonate.

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