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FORMATION OF CaO FROM THERMAL DECOMPOSITION OF CALCIUM CARBONATE IN THE PRESENCE OF CARBOXYLIC ACIDS

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Effect of 5% tartaric, succinic and citric acids on the decomposition of $CaCO_3$ have been studied by TG-DSC and X-ray diffraction techniques. The decomposition temperature of $CaCO_3$ is not decreased and at the same time particle size distribution and morphology of CaO are changed as determined by laser granulometer and SEM studies.

Keywords: *calcium carbonate, calcium oxide, carboxylic acids, decomposition, DSC*

Introduction

Limestone is the main raw material for the manufacture of Portland cement. A good quality limestone contains more than 80% $CaCO_3$. In Portland cement all the mineral constituents are formed by the reaction of CaO obtained by thermal decomposition of limestone. Normally $CaCO_3$ decomposes at about 900°C but this depends on the type and quantity of impurities present in it. Attempts have been made from time to time to lower down the decomposition temperature of $CaCO_3$ in order to get cement mineral phases at lower temperature [1–3] and to save energy in cement industry. Recently Kasselouri *et al.* [4, 5] used number of carboxylic acids of different concentrations (5, 10 and 20 mass%) to lower down the decomposition temperature of $CaCO_3$. The authors claimed that in the presence of acids the decomposition temperature of $CaCO_3$ decreased and the quality of CaO remained unaffected. The reactivity of any solid material such as CaO depends on the temperature of formation, specific surface area, particle size distribution, morphology, type of defects, surface topography etc. In this communication attempts have been made to study the decomposition of pure $CaCO_3$ in the presence of different carboxylic acids with a view to know the decomposition temperature, and particle size distribution, crystallinity and morphology of the decomposition product CaO.

Experimental

Materials

$CaCO_3$, succinic acid, tartaric acid and citric acid, all from E. Merck, Germany were used.

Preparation of samples

10 g $CaCO_3$ was mixed with 5 mL acid solutions of succinic acid, tartaric acid and citric acid (0.5 g acids dissolved in 5 mL water i.e. 5% acid with reference to $CaCO_3$ separately in polyethylene bags and allowed to stand for 24 h. This mixture was then dried at 100°C for 2 h and stored in a desiccator.

The above samples ($CaCO_3$ +5% acids) were heated separately for 2 h at 900°C in a platinum crucible in order to have CaO.

Methods

TG-DSC studies

TG-DSC studies of samples ($CaCO_3$ +5% acids) were recorded with a TG-DSC Netzsch STA 489 instrument at a heating rate of 10°C min^{-1} in nitrogen atmosphere. Al_2O_3 was used as a reference.

Particle size distribution measurements

Particle size distributions of CaO obtained by thermal decomposition of $CaCO_3$ in the presence of 5% acids were recorded with Courter Laser Granulometer.

SEM studies

CaO powders obtained from the thermal decomposition of $CaCO_3$ were coated with carbon and then with gold under the atmosphere of argon. SEM pictures were obtained with Philips XL 30i scanning electron microscope.

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Table 1 Mass losses in $CaCO_3$ carboxylic acid samples (in mass%) at different temperatures

Samples	Temperature/°C											
	100	200	300	400	500	600	650	700	750	800	850	900
$CaCO_3$	0.42	0.23	0.29	0.19	1.33	1.93	2.54	8.0	8.67	23.19	48.84	49.2
$CaCO_3$+tartaric acid	0.63	2.72	3.93	5.73	6.89	7.25	7.51	8.67	11.95	21.74	41.14	47.93
$CaCO_3$+ succinic acid	0.4	2.5	2.5	3.0	4.0	4.8	7.5	8.0	12.0	22.0	41.0	47.5
$CaCO_3$+citric acid	0.73	2.19	2.86	4.17	5.82	6.75	7.04	7.43	9.00	13.26	24.62	46.69

X-ray diffraction studies

X-ray diffraction patterns of samples ($CaCO_3$ +5% acids) and CaO obtained by thermal decomposition were recorded with a Philips PW1710 diffractograph including JCDPS data base using CuK_α radiation.

Results and discussion

TG-DSC curves of $CaCO_3$ +5% acids are shown in Figs 1–4. The mass losses in $CaCO_3$ at different temperatures in the presence and absence of acids are given in Table 1. In the presence of acids, faster mass losses start at much lower temperatures as compared to that of reference i.e. that of $CaCO_3$ alone leading to the formation of larger amount of CaO at lower temperatures. Early mass losses in the presence of acids are due to decomposition of calcium carboxylates formed as a result of interaction between $CaCO_3$ and acids. The formation of carboxylates have been reported earlier [4, 5] and confirmed by X-ray diffraction technique.

Endothermic and exothermic peaks in the DSC curves are given in Table 2. In the case of reference a single endothermic peak appeared at 850°C due to decomposition of $CaCO_3$ whereas in the presence of acids endothermic and exothermic peaks appeared. In the presence of acids, a part of $CaCO_3$ has been converted to carboxylate which contain certain number of water molecules as water of crystallisation and are thermally less stable. The endothermic peaks below 200°C may be due to removal of water molecules and peaks between 200–800°C are due to decomposition of calcium carboxylates. The peak above 800°C is due to decomposition of remaining $CaCO_3$. The over-all results of TG-DSC show that calcium carboxylates decompose at lower temperatures whereas the remaining $CaCO_3$ decompose either at the same temperature (850°C) or slightly at higher temperature. The final mass losses in

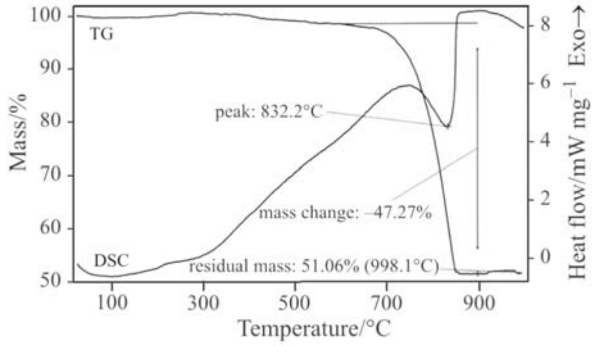

Fig. 1 TG-DSC curves of $CaCO_3$

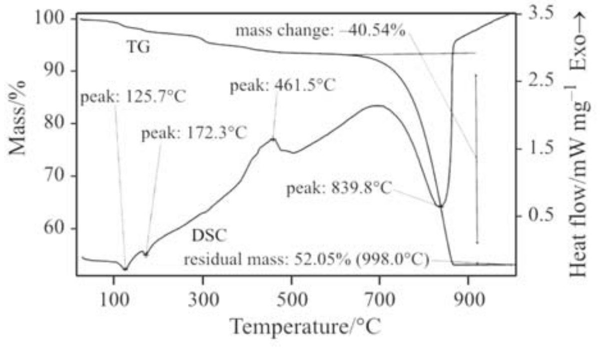

Fig. 2 TG-DSC curves of $CaCO_3$ +5% tartaric acid

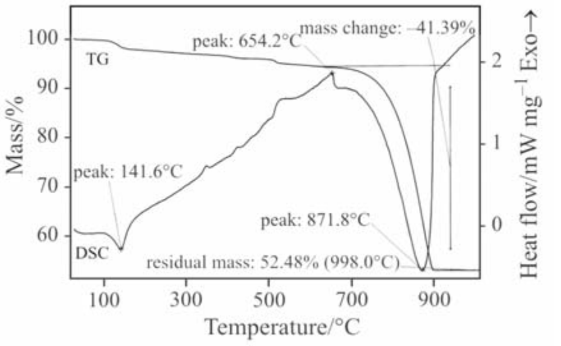

Fig. 3 TG-DSC curves of $CaCO_3$ +5% succinic acid

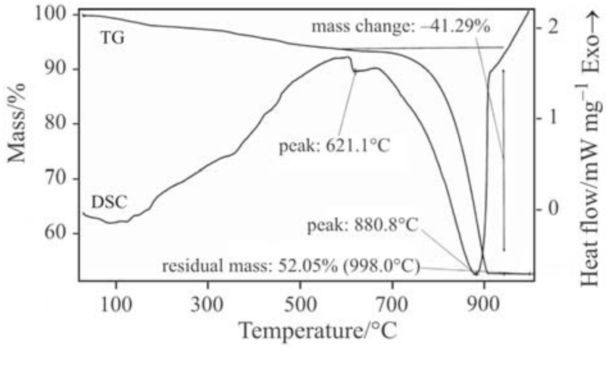

Fig. 4 TG-DSC curves of $CaCO_3$ +5% citric acid

Table 2 Endo and exo peak temperature

Samples	Peaks and peak temperature
$CaCO_3$	endo – 850°C
$CaCO_3$+tartaric acid	endo – 125°C endo – 175°C exo – 475°C endo – 850°C
$CaCO_3$+ succinic acid	endo – 141.6°C endo – 520.9°C endo – 654.2°C endo – 875.0°C
$CaCO_3$+citric acid	endo – 100–200°C (broad) endo – 375°C endo – 625°C endo – 880°C

the presence and absence of acids are higher than the theoretical values. This may be due to varying amounts of moisture in the samples which could not be avoided. As a result of decomposition of carboxylates formed in the presence of acids, the amount of CaO obtained is more at lower temperature. However having larger amount of CaO in the presence of acids will not be economical because it requires acids which are costly. Moreover the process does not decrease the decomposition temperature of $CaCO_3$.

CaO formed in the presence of different acids have almost similar crystalline character as confirmed by X-ray diffraction studies. Freshly prepared calcium oxides have high specific surface area and hence highly reactive. CaO obtained in the presence of acids even for a short exposure to atmosphere, give small amounts of $Ca(OH)_2$ as identified by X-ray diffraction (Fig. 5) and reported by Wolter *et al.* [6].

Particle size distribution (PSD) of CaO obtained from decomposition of $CaCO_3$ in the presence of different acids are given in Figs 6 and 7. PSD is quite narrower/steeper in the case of CaO obtained from the decomposition of $CaCO_3$ alone whereas the PSD in the case of CaO obtained by the decomposition of $CaCO_3$ in the presence of succinic and tartaric acids are almost similar. PSD in the case of CaO obtained from the decomposition of $CaCO_3$ in the presence of citric acid is entirely different and coarser.

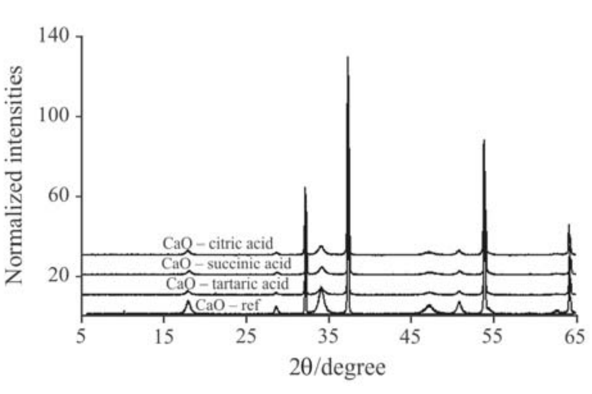

Fig. 5 X-ray diffraction pattern of CaO obtained by decomposition of $CaCO_3$ in presence of acids

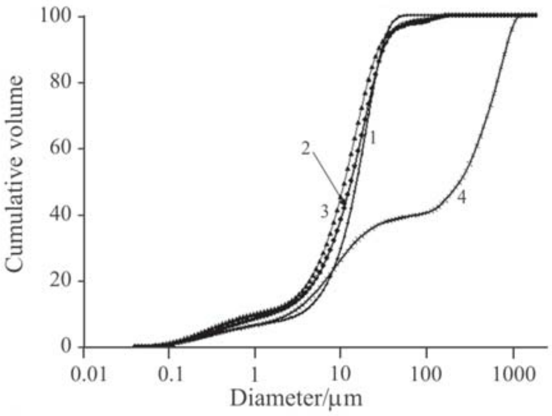

Fig. 6 Particle size distribution of CaO (cumulative volume – diameter) obtained by the decomposition of $CaCO_3$ in the presence of 5% acids: 1 – no acid, 2 – tartaric acid, 3 – succinic acid and 4 – citric acid

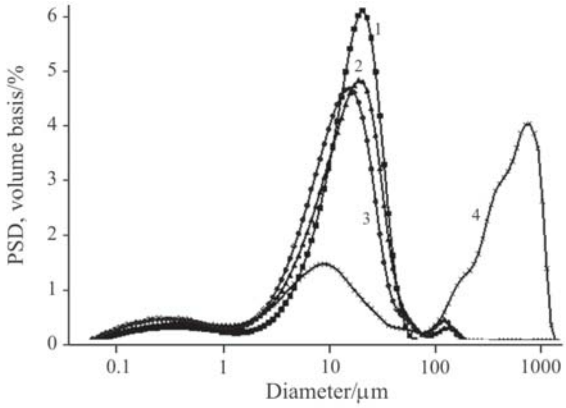

Fig. 7 Particle size distribution of CaO (PSD% volume basis – diameter) obtained by the decomposition of $CaCO_3$ in the presence of 5% acids: 1 – no acid, 2 – tartaric acid, 3 – succinic acid and 4 – citric acid

Scanning electron microscopic pictures of CaO are given in Fig. 8. When $CaCO_3$ was heated alone, CaO particles with higher porosity and higher internal surface area were obtained. The microstructure is similar to that of soft burnt lime as reported by Wolter *et al.* [6]. However in the presence of tartaric and succinic acids, it appears that smaller particles have combined together giving higher surfaces. On the other hand in the presence of citric acid the particles of CaO have sintered to a larger extent. Thus the morphologies of calcium oxides are different and crystallite size of CaO crystals are also different. Therefore the reactivities of CaO obtained in the presence of different acids are expected to be different. Shi *et al.* [7] have also found that the hydration of CaO decreases with the calcination temperature. When calcium oxide is sintered at different temperatures, microstructures are changed

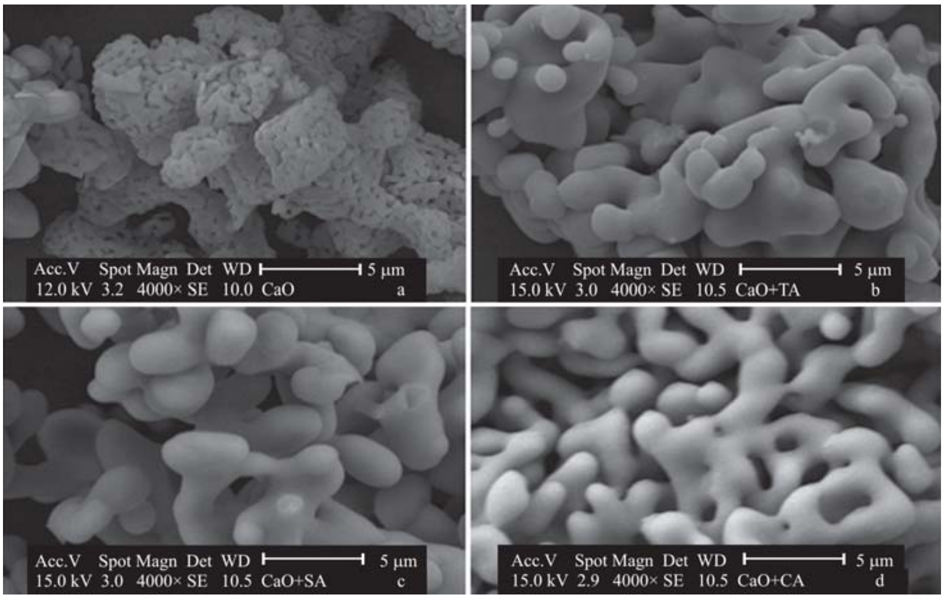

Fig. 8 SEM images of CaO obtained by the decomposition of $CaCO_3$ in the presence of a – no acid, b – 5% tartaric acid, c – 5% succinic acid and d – 5% citric acid

and with the increase of calcination temperature, the crystallite size of CaO crystals increases. The more perfect the lattice of CaO and denser its structure, the lower the free energy of the crystal surfaces and lower the hydration activity of CaO.

Conclusions

Results show that carboxylic acids do not lower the decomposition temperature of $CaCO_3$. Carboxylic acids react with $CaCO_3$ forming hydrated calcium carboxylates which decompose at lower temperatures forming CaO. Particle size distribution and morphology of CaO obtained in the presence of different acids are different.

Acknowledgements

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