Investigating the optimum conditions for the formation of calcium oxide, used for CO2 sequestration, by thermal decomposition of calcium acetate

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Investigating the optimum conditions for the formation of calcium oxide, used for CO_2 sequestration, by thermal decomposition of calcium acetate

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Abstract. Calcium oxide, CaO, has long been recognized as an effective, regenerative sorbent for the sequestration of CO_2. Calcium acetate hydrate, CaAc, $(Ca(CH_3COO)_2 \cdot xH_2O)$ has been highlighted as one of the most efficient precursors for CaO production with regards to CO_2 sequestration. In this study, thermal decomposition of CaAc to CaO, via an intermediate phase of calcium carbonate $(CaCO_3)$, has been examined at different heating rates using thermal and powder diffraction analysis. The decomposition from CaAc to CaO has yet to be analysed in detail at the particulate level, however, knowledge of how the transformation proceeds at this level should lead to control over the size and morphology of the final CaO product. Bulk characterisation using X-ray diffraction (XRD) and thermogravimetric analysis (TGA) has been used to benchmark the transformation at different heating rates and final calcination temperatures. TEM imaging is used to show how the chemical changes proceed particularly at the particle level.

1. Introduction

The drive for low carbon technologies, particularly carbon capture and storage (CCS), is an area of significant interest due to the rise in emissions of carbon dioxide and the widely recognised effects of global warming. Such effects have led to a proposed minimum worldwide target of a 50% reduction in CO_2 emissions (relative to 1990 levels) by the year 2050 for which CCS will play a pivotal role in helping to reach [4, 5]. One method for sequestration of CO_2 gas, prior to its exposure to the atmosphere, is to capture it using a calcium-based sorbent such as calcium oxide, CaO (e.g. calcined limestone). CaO is known to absorb CO_2 in a flue gas to produce calcium carbonate $CaCO_3$ (carbonation, equation 1), a process which is reversible. Once the metal oxide has reached its ultimate conversion, thermal regeneration can be utilised whereby $CaCO_3$ is heated beyond its calcination temperature (~750 °C) to reform CaO and near pure CO_2 gas which can be collected and stored (calcination, equation 2) [3, 11].

$$CaO + CO_2 \rightarrow CaCO_3 \qquad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (2)$$
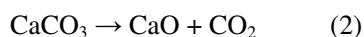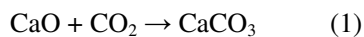
Calcium acetate hydrate, CaAc, $(Ca(CH_3COO)_2 \cdot xH_2O)$ has been recognised as an effective precursor for the production of CaO [6, 9]. The cyclic capture of CO_2 using CaO is an area of great interest [1, 7, 2], however sintering during calcination leads to a decline in the adsorption capacity of CaO [10]. By carefully monitoring the decomposition process of CaAc to CaO, it is hoped that sintering of the first CaO product can be minimised, subsequently allowing for a larger surface area to be available for CO_2 pick-up.

2. Experiment

The decomposition of commercial CaAc (Acros Organics, 99%, extra pure) was firstly monitored using thermogravimetric analysis (Shimadzu TGA-50). A sample was heated to 1000 °C at a rate of 20 °C min^{-1}, in air. For X-ray diffraction (XRD), a CaAc sample was analysed with a temperature controlled heating stage (up to 800 °C) using a Philips PanAnalytical X'pert Diffractometer with Cu Kα radiation source. Each temperature interval was reached at a rate of 20 °C min^{-1}, and then held for

~ 1 hour. Samples for TEM imaging were produced by firstly directly heating CaAc samples in air, by direct insertion into preheated furnaces for 10 minutes at 500 °C and 800 °C respectively. Three further samples were prepared by a slow decomposition from room temperature to 200, 500 and 800 °C (at 20 °C min⁻¹); each held at the respective temperatures for 1 hour. Both sets of samples were immediately removed from the furnace after calcination, and air cooled. TEM analysis was performed using an FEI Tecnai F20 FEG-TEM operated at 200 kV and fitted with a Gatan Orius SC600A CCD camera.

3. Results & Discussion
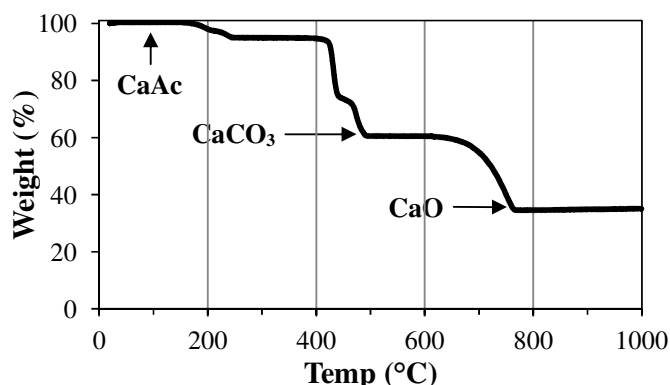
Temp (°C)	Mass Loss (%)
~150-240	5.0
~400-520	37.2
~650-765	26.6
Total Loss =	**65.8**

Table 1: Percentage mass loss for thermal decomposition of CaAc.

Figure 1: TGA curve showing that the thermal decomposition of calcium acetate to CaO is completed by 800 °C.

TGA data displays CaAc decomposed at a constant rate of 20 °C min⁻¹ to 1000 °C. The thermal decomposition of CaAc measured here (Fig. 1) is in good agreement with previously reported data [8, 9]. Table 1 highlights the percentage mass loss at three given temperature ranges. There is an initial two-stage mass loss of water molecules, the first at ~150-200 °C, and the second at ~200-240 °C , with a total percentage mass loss of 5% (calculated xH_2O molar loss = 2.3) [8]. Between ~400-520 °C, literature indicates that the dehydrated CaAc breaks down to form acetone and $CaCO_3$, seen here as a combined percentage mass loss of 37.2% [8]. The loss observed at ~440 °C is likely to be attributable to the eventual loss of acetone [8]. The calcium carbonate then decomposes to form calcium oxide from ~650 °C to completion at ~765 °C [8].

XRD data (Fig. 2) shows how CaAc decomposes when heated (at 20 °C min⁻¹) and held at 100 °C intervals for 1 hour. The breakdown of hydrated CaAc to dehydrated CaAc is seen to occur via an apparent amorphous compound at 200 °C; this leads to dehydrated CaAc at 300 °C. This subsequently breaks down further to form $CaCO_3$ at 400 °C. At 600 °C traces of CaO are evident, indicating the start of the breakdown of $CaCO_3$. Decomposition to CaO is complete at 700 °C.
Due to the slower decomposition rate of CaAc, using hot-stage XRD, decomposed phases ($CaCO_3$ and CaO) are allowed a greater time for formation, and subsequently are formed at slightly lower temperatures than those produced with a quick heating rate, using TGA.

TEM images (Figs. 3 & 4) highlight the transformation from CaAc to CaO at a particle level. As received CaAc particles (Fig. 3a) display long lath-like structures, (typical length = 1-10 μm). Figures 3b-c display CaAc directly placed, in a pre-heated furnace, at 500 and 800 °C respectively for 10 minutes, to simulate a rapid decomposition, relatable to TGA data. CaAc heated by direct insertion into a preheated furnace at 500 °C provides $CaCO_3$ (Fig. 3b) with particles which vary from rounded and faceted shapes, which are slightly sintered, typically 100-200 nm in length. CaO (Fig. 3c), produced from direct insertion into at 800 °C preheated furnace, displays highly sintered agglomerates of fine platelet-like particles (<100 nm).

Figures 4a-c display a slower rate of decomposition, with powders decomposed from room temperature to 200, 500 and 800 °C respectively (at 20 °C min⁻¹) and held at that temperature for 1h, simulating the XRD analysis. At 200 °C, observed particles are likely to be broken laths (typical length = 1-5 μm) of CaAc; future experiments will examine this apparent amorphous phase further. The $CaCO_3$ formed at 500 °C after 1h (Fig. 4b) appears as much finer, sintered agglomerates in

comparison to the rounded particles formed upon direct heating, this may suggest progression to the eventual decomposition of $CaCO_3$. The CaO formed at 800 °C after 1h (Fig. 4c) displays larger and heavily sintered agglomerates in relation to CaO formed by direct heating. There is also a significant amount of porosity evident, which is not observed in the CaO formed by direct heating. This may be due to a fast rate of sintering entrapping CO_2 or air between the particles; future experiments will investigate this further.
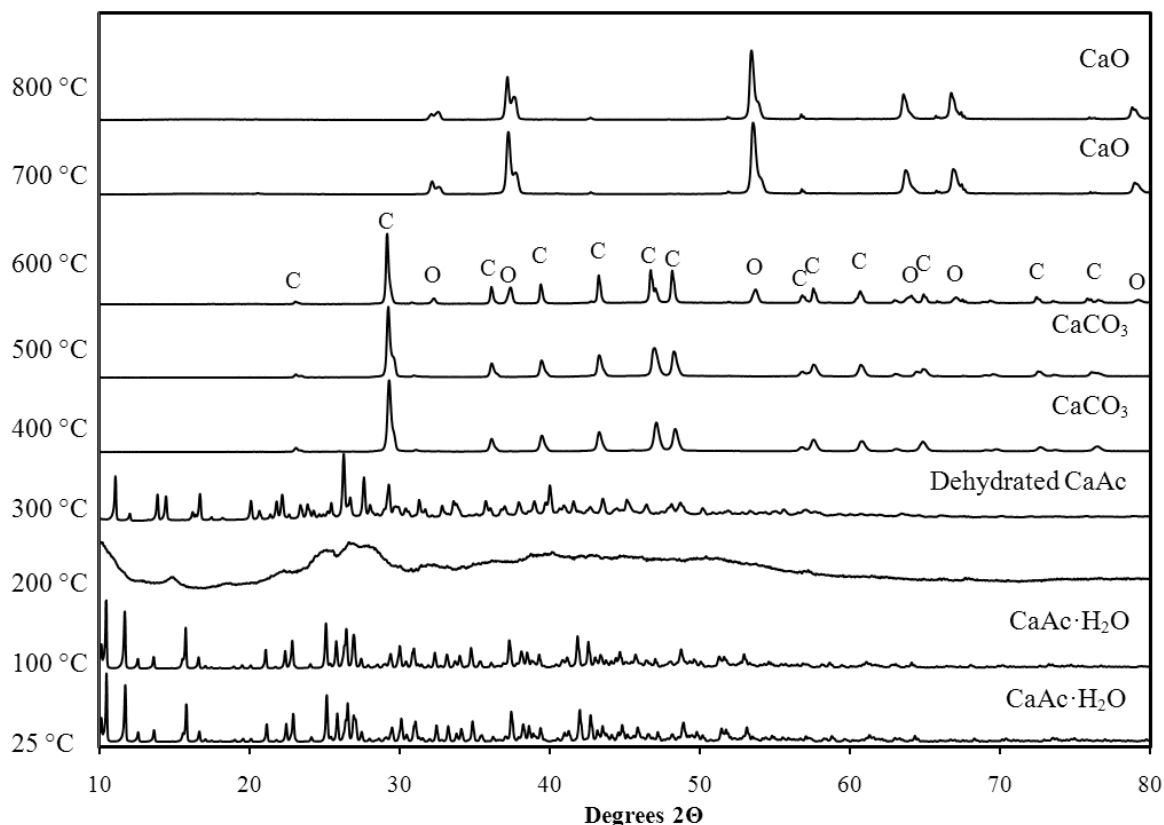

Figure 2: XRD data for the decomposition of CaAc from room temp (25 °C) up to 800 °C at intervals of 100 °C, held for 1h. CaAc patterns at 25 and 100 °C are in close agreement with JCPDS file number 019-0199. The pattern at 300 °C is in reasonable agreement with dehydrated CaAc: JCPDS file number 00-019-0198. Peaks labelled 'C' corresponds to $CaCO_3$: JCPDS file number 00-05-0586, and peaks labelled 'O' denote CaO: JCPDS file number 04-006-5940
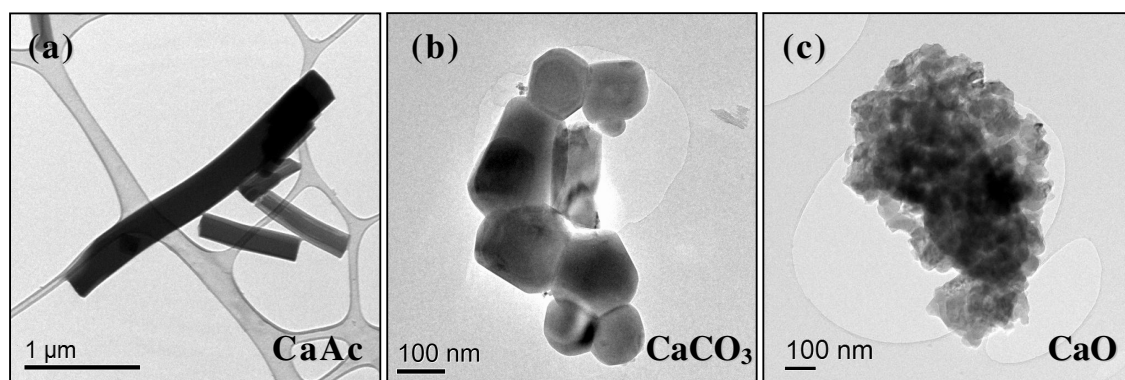

Figure 3: TEM images of (a) as received CaAc, with (b) $CaCO_3$ and (c) CaO formed from CaAc direct insertion into preheated furnaces at 500 and 800 °C respectively.
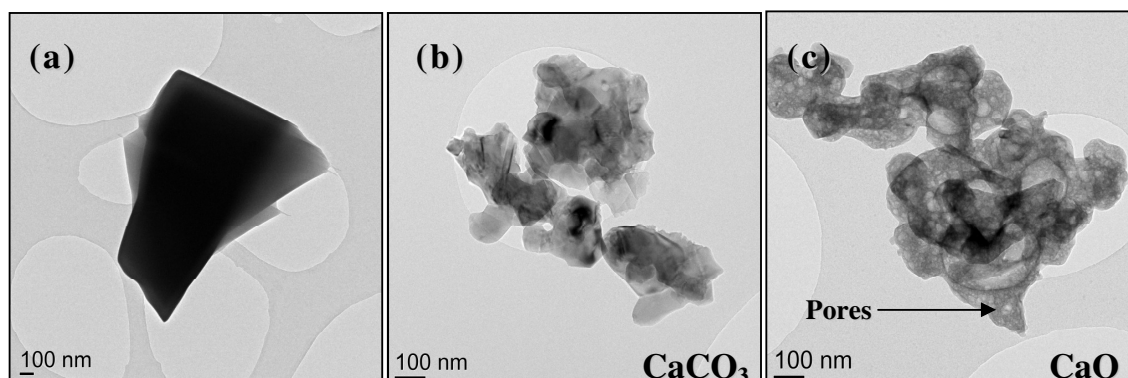
Figure 4: TEM images of (a) CaAc heated to 200 °C and held for 1h (b) CaAc heated to 500 °C (CaCO$_3$) and held for 1h, and (b) CaAc heated to 800 °C (CaO) and held for 1h.

4. Conclusion

CaAc has been decomposed at different heating rates using TGA and hot-stage XRD, to investigate its transformation to CaO. TGA and XRD data suggest the heating rate significantly affects the temperature of formation of CaO, with a slower heating rate, with 100 °C intervals of 1h temperature holds (using hot-stage XRD), showing a full conversion to CaO at 700 °C; and at a faster rate (20° C min^{-1} without hold, using TGA) at just below 800 °C. TEM images confirm this and display a high level of sintering of the final CaO products, a problem likely to affect sequestration of CO$_2$ to be carried out in future work; however porosity in the CaO product held for 1h at 800 °C may prove beneficial towards CO$_2$ uptake. Further experiments investigating careful control of final calcination temperature, heating rate and addition of particulate spacers will hopefully allow for a reduction in CaO sintering. Future work will also aim to confirm the cause of the porosity observed in CaO, produced by 1h decomposition of CaAc at 800 °C.

5. References
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