

Metastable Calcium Carbonate Polymorphs Analyzed by Solid-State ^{43}Ca NMR

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Introduction and Objectives

Polymorph selection has been a pivotal engineering objective in material science and industrial crystallization, due to the strong structure-function relationships between different crystalline polymorphs and their macroscopic properties, including mechanical, electrical, optical, and solubility. We have demonstrated that it is possible to rationally design and operate crystallization processes to select a desired polymorph, regardless of its thermodynamic stability. In particular, the precipitation of CaCO_3 by reacting gas-phase carbon dioxide with Na_2CO_3 and CaCl_2 in aqueous alkaline solutions is of high general importance for CO_2 capture technologies. However, multiple CaCO_3 polymorphs are typically formed during continuous precipitation processes, which have been exceedingly difficult to control. While thermodynamically stable calcite is generally considered to be valueless, metastable vaterite has potential applications as a “green” structural material.

Experimental

We have developed a new macroscopic model and design for continuous crystallization processes that enables the selective production of even a metastable polymorph, by judicious choice of process conditions.¹ As an example, we have applied these insights to choose process conditions that selectively yielded pure metastable vaterite, during continuous CaCO_3 precipitation. The polymorphs and phase purities of the precipitated CaCO_3 were determined by powder X-ray diffraction, scanning electron microscopy, and solid state ^{43}Ca NMR spectra. Single-pulse ^{43}Ca MAS NMR spectra were acquired on the 19.6 T Bruker DRX NMR spectrometer at the NHMFL at 5 kHz MAS, 25° C, using a 4 μs 90° pulse, a 0.5 s recycle delay, and 48 h measuring time. The use of high magnetic fields (19.6 T) conditions were crucial to obtain sufficient signal sensitivity and resolution from ^{43}Ca , which is low- γ , low isotopic abundance (0.14%), and quadrupolar nucleus ($I=7/2$).

Results and Discussion

Based on solid-state ^{43}Ca MAS NMR, powder X-ray diffraction, and scanning electron microscopy analyses in Figure 1, nearly pure, thermodynamically metastable vaterite was produced during continuous precipitation of CaCO_3 under carefully selected conditions. All major reflections in the XRD pattern in Figure 1a are indexable to vaterite, along with a minor reflection from a small amount of calcite (<1%). The ^{43}Ca MAS NMR spectrum (Fig. 1b) exhibits a single broad peak centered at 3 ppm that is characteristic of vaterite. The spheroidal crystallites in the scanning electron micrographs (Fig. 1c, d) are consistent with vaterite.

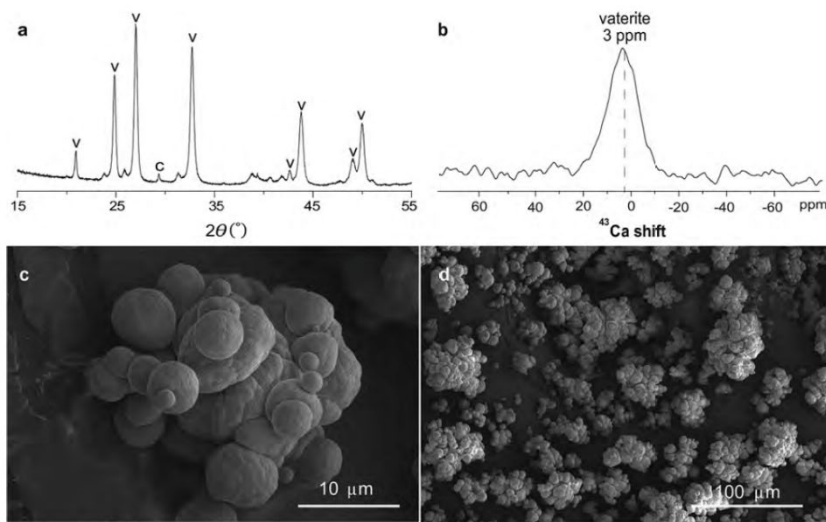


Fig. 1. (a) Powder X-ray diffraction pattern, (b) solid-state, single-pulse ^{43}Ca MAS NMR spectrum, and (c, d) SEM images of the product collected from a continuous precipitation process operating under steady-state conditions, with a residence time of 6 min at 25 °C and 0.15 M inlet concentration.

References

[1] Farmer, T., *et al.*, *Cryst. Growth Des.*, **18**, 4306–4319 (2018).

Conclusions

The experimental measurements confirmed model predictions and showed that even metastable polymorphs can be selectively obtained through judicious selection of process conditions that manipulate the dynamic stability of competing steady states in a continuous crystallizer. Under such circumstances, the resulting process is inherently simple to control, and process disturbances tend to decay with time. Furthermore, the thermodynamically metastable vaterite crystals generated in this way do not transform to the more stable calcite polymorph over the time scales we have thus far measured and observed (>12 months).

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