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Topotactic crystallisation of calcite under hydrothermal conditions

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It is shown that control of the phase of calcium carbonate produced during hydrothermal crystallisation can be achieved by the use of titania as a catalyst. In this work it was demonstrated that if either amorphous or the rutile phase of titania is added the aragonite polymorph of calcium carbonate is produced to the exclusion of all other phases. When anatase is the major titania form present then the calcite phase of calcium carbonate is favoured though some aragonite is still produced. The selectivity towards calcite is enhanced by increasing the hydrothermal processing temperature from 120°C to 135°C. It is suggested that the titania phase present catalyses the crystallisation by providing nucleation sites for the calcium carbonate to grow from. © *2003 Kluwer Academic Publishers*

1. Introduction

Calcium carbonate exists in a number of crystallographic modifications. In order of increasing solubility, they are calcite, aragonite, vaterite, calcium carbonate monohydrate, and calcium carbonate hexahydrate [1]. Calcite is the thermodynamically stable phase, and has found various applications in the communications industry as a waveguide material [2]. The other polymorphs are metastable, and can be converted to calcite by firing at high temperature (<375°C) [3]. The Clapeyron diagram (Pressure against Temperature) is known, and the solid state equilibrium between calcite and aragonite reversible transformation is in the region 240–410 MPa at room temperature [4]. Titania also exists in three stable polymorphic forms, anatase, brookite, and rutile, the latter of which is the thermodynamic product. Again, the metastable polymorphs can be converted to rutile by firing above 900°C [5].

In a recent study of the hydrothermal processing of praseodymium doped calcium titanate (a potential low voltage phosphor for field emission devises phosphor), it was noted that under hydrothermal conditions, there is a reaction between urea and calcium nitrate in the presence of amorphous titania powder to form calcium carbonate [6]. This reaction is not observed under conventional co-precipitation conditions (below 100°C, and 0.1 MPa), where calcium titanate is formed.

Selective crystallisation of specific polymorphs of calcium carbonate has been the topic of numerous studies, and the precipitation and stabilisation of the polymorphs has been shown to be strongly dependent on the precipitation conditions such as the pH, ionic medium, and the concentration and types of impurities [7, 8]. For example, it has been reported that the presence of magnesium ions can inhibit the precipitation of calcite from supersaturated solutions, but leave the growth rate of aragonite unchanged [9]. Ferrous, ferric, copper, and zinc ions have all been reported to inhibit calcium carbonate precipitation [10]. Long chain organic molecule additives have also been reported to have a strong influence. Polyphosphates, glycerophosphate and benzene polycarboxylic acids and phosphonates have been reported to inhibit calcium carbonate precipitation through a surface adsorption mechanism [11].

Under the hydrothermal conditions, the presence of the titania is not necessary to cause precipitation of calcium carbonate, however, early experiments demonstrated that the titania powder did play a role in the crystallisation process [12]. Previous studies have

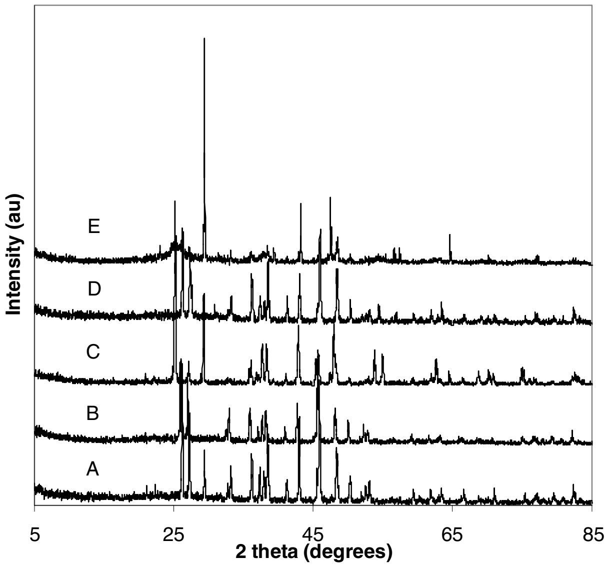

Figure 1 X-ray powder diffraction data for materials referred to in text.

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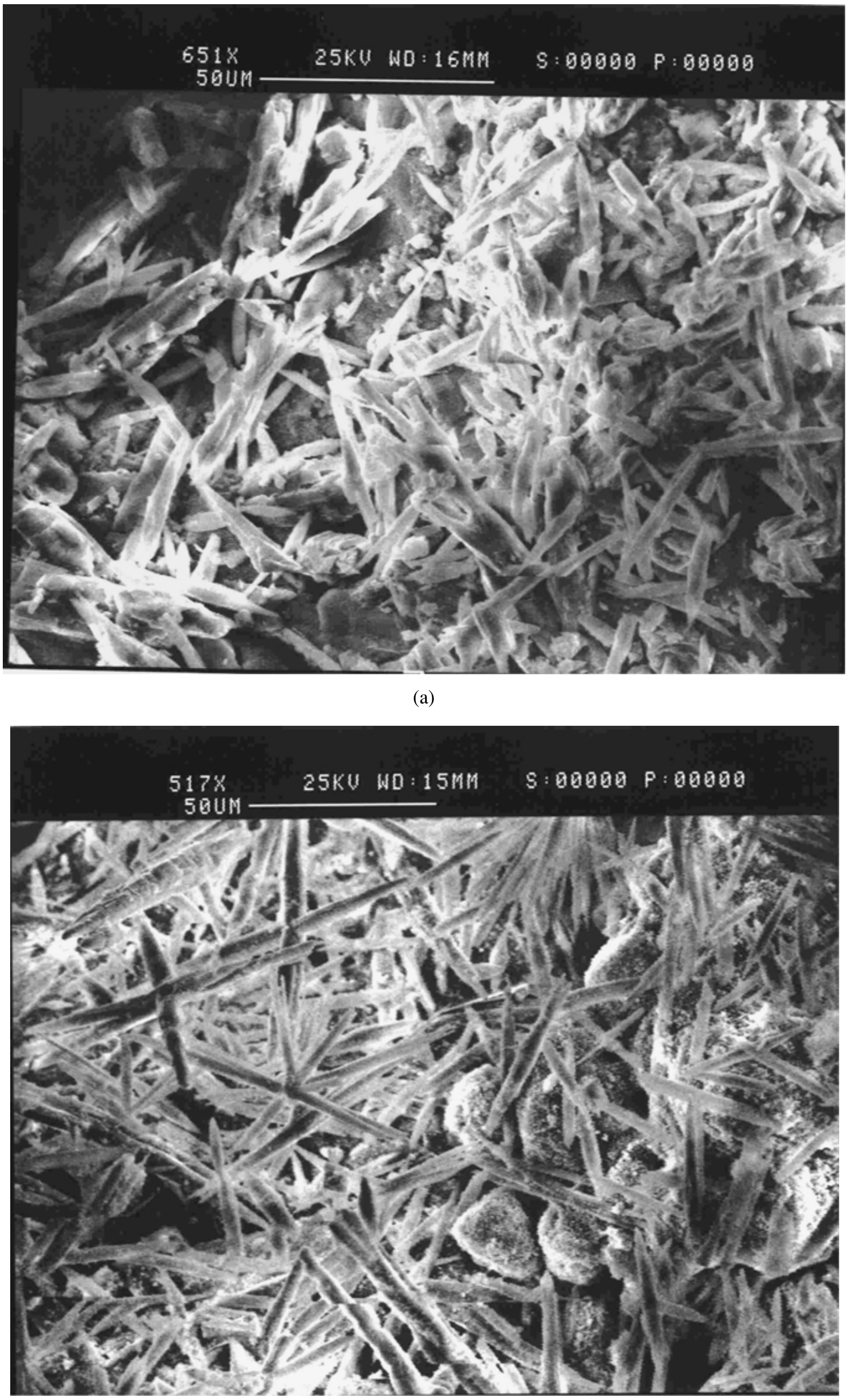

(a)

(b)

Figure 2 SEM images of materials referred to in text.

shown that the preparation method of amorphous titania can have a strong influence on its crystallisation properties under hydrothermal conditions [13]. Here we report on the influence of titania on the crystallisation of calcium carbonate.

2. Experimental

Amorphous titania was prepared as follows:

- $Ti(OPr)_4$ (10 ml) was diluted in a beaker with 100 ml of water, and then 2 ml of ammonia solution (conc.) was added with stirring. The white precipitate formed was vacuum filtered and dried in an oven at 80°C for two hours. The white powder produced was amorphous titania (AP1).
- The hydrothermal treatments 0.5 g of amorphous titania, anatase supplied by Aldrich, or rutile (prepared by firing the amorphous titania at 1100°C for 1 hr) was added to 3.48 g $Ca(NO_3)_3$ and 40 ml 1.67 M urea solution. Hydrothermal processing was carried out using teflon lined polycarbonate autoclaves. The vessels were heated using

microwaves (CEM MDS-2100 microwave autoclave system) to a range of temperatures from 120°C to 175°C. Higher temperatures could not be attained due to the development of excessive pressure from the decomposition of urea within the vessels. All reactions were carried out for 1 hr. The precipitates were all vacuum filtered, and dried in an oven at 80°C for 24 hrs.

- X-ray powder diffraction (XRD) was carried out using a Philips pw1710 diffractometer. A step size of 0.02° 2-theta was used with a scan speed of 0.5° per minute. XRD spectroscopy showed that the initial titania powders were indeed amorphous, and free from any crystalline phases, as no peaks were observed. Scanning electron microscopy (SEM) studies were carried out using a Cambridge Instruments Stereoscan 90 scanning electron microscope, equipped with a LINK systems electron dispersive X-ray analysis (EDX).

3. Results and discussion

Fig. 1 shows the XRD spectra for the as-produced powders for the hydrothermal reactions at 120°C for 1 hr. From the XRD traces we can see that in all cases calcium titanate has not in fact been formed by the hydrothermal processing, but instead, calcium carbonate has formed. This is the result of the urea decomposition, which produces CO_2 and NH_3. The CO_2 can then react with the calcium nitrate to form $CaCO_3$, which is insoluble under hydrothermal conditions. It can also be seen from Fig. 1 that the polymorphic modification of the titania in the vessel also has a strong influence on the phase of the calcium carbonate product. When no titania is present, a phase mixture of aragonite and calcite is formed (Fig. 1A). When amorphous titania is used, only aragonite is produced, although there is also a small amount of anatase produced, as would be expected under hydrothermal conditions (Fig. 1B). When anatase is used, however, the major calcium carbonate product is calcite rather than aragonite (Fig. 1C). When the rutile modification of titania is used, the product returns to aragonite with no calcite present (Fig. 1D). Using $TiCl_4$ instead of titania powder, again resulted in the formation of calcite as the major product (Fig. 1E). There was also some production of microcrystalline anatase.

Fig. 2 shows SEM micrographs of the powder products from the reaction at 120°C. The aragonite (shown in Fig. 2a) consists of short irregularly shaped needles, whose orientation appears to be random. The small particles visible, which are not needles are amorphous titania particles (confirmed by EDX). These are randomly mixed with the aragonite, and in no way attached to the aragonite needles. The calcite shown in Fig. 2b consists of finer needles, which tend to grow out along the vertices of an octahedron. The needles are much more pointed than those of the aragonite. Also visible, are more the globular anatase powder agglomerates, which were used to selectively catalyse the growth of the calcite (again confirmed by EDX). Quite clearly, the titania is not incorporated into the structure of the calcite, but merely gives the crystals a nucleation site from which to grow along a specific crystallographic axis.

In order to further prove that the titania was not incorporated into the calcite, and thus a useful catalyst for the crystallisation, anatase was pressed into a disc, and added as before into the reaction vessel. Fig. 3 shows the surface of the pellet, with crystallites of calcite growing on the surface. In this case, it seems that the favoured nucleation and growth sites are in the pores of the pellet, and this was observed in several other micrographs of the pellet. On reaching a certain size,

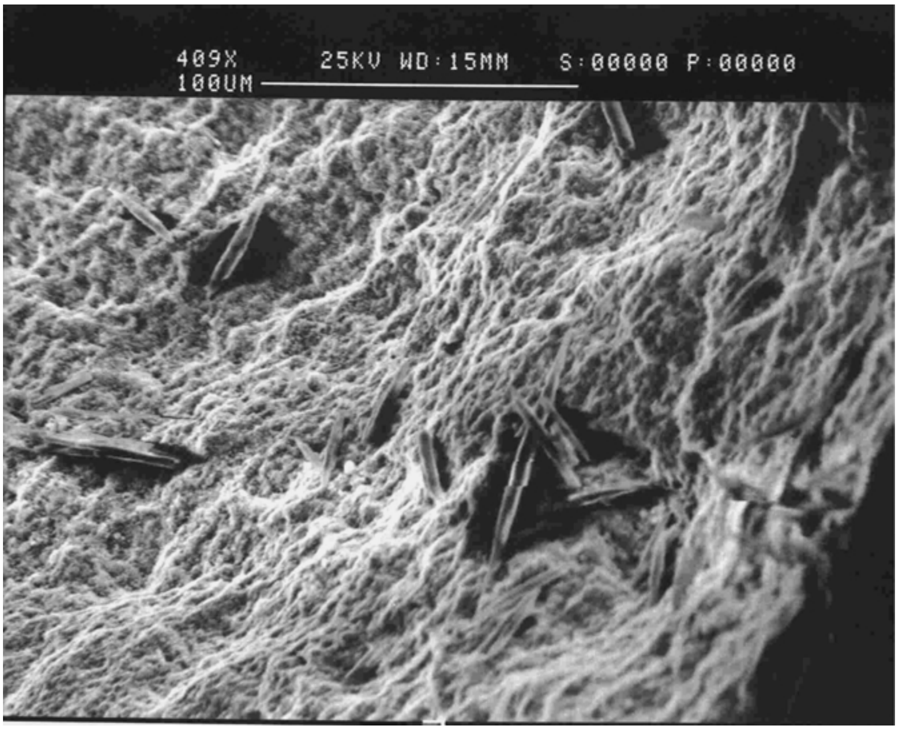

Figure 3 SEM image of anatase pellet after hydrothermal treatment.

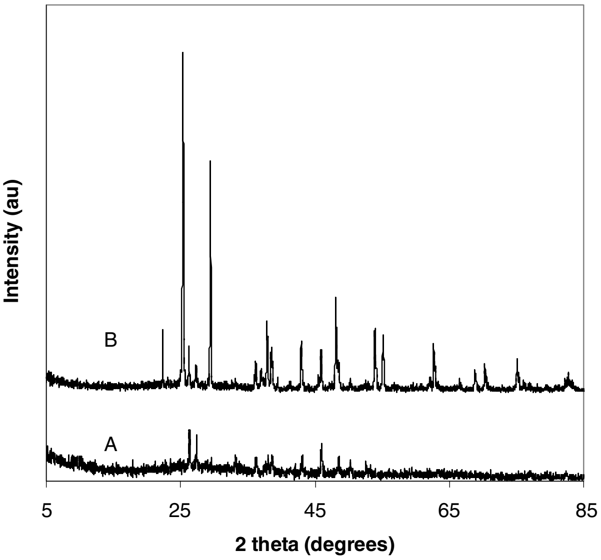

Figure 4 X-ray powder diffraction data for materials referred to in text.

however, the crystallites fall off the surface, making way for further nucleation. This suggests that a sintered porous body of anatase would make a useful reusable catalyst for calcite crystallisation at low temperature, without leading to contamination of the calcite with titania.

Increasing the hydrothermal processing temperature to 135°C (the maximum possible due to pressure constraints on the autoclaves) had little effect on the products of the reactions containing no titania, anatase, or rutile. There was, however, an increase in the crystallinity of the titania as microcrystalline anatase begins to form. The aragonite appeared to be less crystalline (smaller XRD peaks). This can be attributed to the accelerated formation of anatase under these conditions. When anatase was used, however, raising the temperature resulted in improved selectivity for calcite over aragonite (Fig. 4B). This may be due to accelerated kinetics of the calcite formation compared to the aragonite formation, or elimination of amorphous material from the anatase surface. No change was observed when rutile was used at the higher temperature.

4. Conclusions

Addition of titania to the hydrothermal crystallisation of calcium carbonate can be used to improve the phase selectivity of the crystallisation process. In the absence of titania, a phase mixture of aragonite and calcite is produced. On addition of either amorphous titania, or rutile, the aragonite polymorph is produced to the exclusion of all others. Addition of anatase improves the selectivity towards the calcite polymorph. This selectivity for calcite can be improved by increasing the processing temperature from 120°C to 135°C. This is in agreement with the Clappeyron diagram which indicates that higher temperatures and pressures favour calcite production. The titania catalyses the reactions by providing a nucleation site for the calcium carbonate to grow from, however, the titania is not incorporated into the calcium carbonate. When grown on an anatase pellet surface, the calcite tends to grow across the pores before falling off.

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