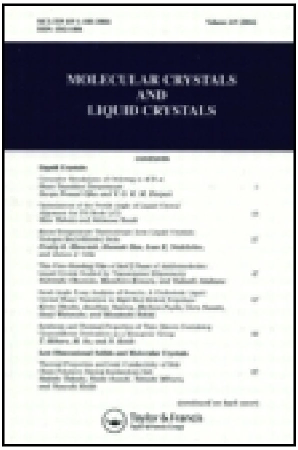

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Control of the Morphology of Crystalline Calcium Hydroxide

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The reaction of solid calcium hydroxide with liquid or gaseous methanol, ethanol and toluene, and the effect this has on the surface properties of the solid was examined, as well as the modification of crystal habit by the presence of these molecules. The effect of the presence of acetate or propionate groups on crystal habit was examined. Reaction with methanol leads to the formation of methoxide groups. Reaction with toluene forms a surface complex, but also there is ingress of the molecules into slit-shaped pores. The presence of these solvents, or the inclusion of anions such as acetate groups during crystallization, can control the crystal habit of calcium hydroxide.

Keywords: crystal morphology; calcium hydroxide; porosity; adsorption

INTRODUCTION

The surface chemistry of oxides and hydroxides, especially those of the alkaline earths, has been of interest to chemists because of the technological importance of such solids. For example, calcium hydroxide is the precursor for the colloidal calcium carbonate additive used in engine lubricating oil [1] as an organic acid scavenger. Calcium hydroxide is also the starting material for the preparation of stearate-coated calcium carbonate which is used inter alia as scouring agent in dentifrice [2]. In these processes calcium hydroxide is used as a solid in contact with an aqueous phase, which may also contain other solvents, such as methanol or toluene. The performance of a specific batch in these applications can be influenced by its surface reactivity and chemistry and texture, as well as crystal size and habit. As part of an on-going investigation into the surface chemistry of this compound we have examined the reaction of solid calcium hydroxide with liquid or gaseous methanol, ethanol and toluene [2-8], and the effect this has on the surface properties of the solid, as well as the modification of crystal habit by the presence of these molecules [4,9]. In addition, the effect of the presence of anions such as acetate and propionate groups on crystal habit was also examined.

EXPERIMENTAL

For the crystal morphology studies, 1M calcium salt (Chloride, acetate or propionate, BDH 99.8% pure) solutions were used, together with sodium hydroxide (BDH, analytical grade) solutions of appropriate strength. Deionised water was used throughout. Solutions were mixed using a Watson-Marlow 101/S/R peristaltic pump at a rate of 0.2 to 53 ml min^{-1}. Efficient mixing of the reactants was assured by the use of high sheer stirring. For some preparations, an ultrasonic bath was used instead. The precipitated material was separated from the reaction medium (water, ethanol or mixtures) by centrifuging at 4000 rpm at room temperature, and subsequently dried at 358K for 15 min.

Commercial samples of $Ca(OH)_2$ (BDH 99.8% pure) were used for the adsorption and spectroscopic studies without any further purification. N_2

adsorption isotherms were measured at 77 K by the volumetric method using an automated Micromeritics instrument (ASAP 2000) after *in situ* outgassing of the samples overnight at different temperatures (300, 373 and 573 K) as described in reference [9].

Sorption of toluene or ethanol was performed by exposing $Ca(OH)_2$ to a 100 percent toluene atmosphere at a reduced pressure, at room temperature in an evacuable glass chamber overnight. Prior to toluene exposure, calcium hydroxide samples were outgassed at 300, 373 and 573 K, and were exposed to toluene vapour without coming to contact with the atmosphere. IR spectra (KBr transmittance and DRIFTS) were carried out on a Shimadzu FTIR spectrometer (FTIR-8501) at room temperature and in the open atmosphere, and TGA analysis by a Shimadzu thermo-gravimetric analyser (TGA-50) under flowing nitrogen, in the region 300 to 1273K at temperature increase rate of 10° min^{-1}.

Morphological studies were carried out using a Cambridge Stereoscan 250 electron microscope, using a 10 keV or 20 keV electron beam.

DISCUSSION

Table 1 summarizes the nitrogen adsorption results for pristine $Ca(OH)_2$ after outgassing at different temperatures, and Table 2 the corresponding data for samples which were exposed to toluene vapour, after outgassing at 300K. The corresponding isotherms were of type II in the IUPAC classification, typical of non-porous materials. The isotherms obtained from this work were similar to those observed previously [6].

As it can be seen from the Tables, the differences in the surface parameters of samples outgassed at 300 and 373 K were only slight, and can be assigned to the removal of physisorbed molecular water to different extents. Outgassing at 573 K led to more significant changes with respect to the pristine sample, presumably due to the partial decomposition of the material to calcium oxide, and water. It has been shown previously [6] that heat treatment under similar conditions led to only partial decomposition and a large surface area solid with a very open structure.

TABLE 1

Nitrogen Adsorption Data for $Ca(OH)_2$ Samples

Outgassing Temperature/K	BET Surface Area /m^2g^{-1}	Average Pore Diameter/nm
300	14.6	16.7
373	14.5	18.4
573	18.7	15.5

The elimination of water molecules from the solid would leave voids behind, thus resulting in the formation of a highly porous solid. This was reflected in the isotherm analysis data and resulted in the sorption of higher amounts of toluene by the partially decomposed sample, ie where toluene sorption took place at high temperatures (Table 2). The presence of toluene in the sample, was confirmed by FTIR and DRIFTS spectra.

Comparison of analysis data prior and after toluene sorption in Table 1 and Table 2 shows that changes in the apparent surface area caused by toluene adsorption were negligible despite the relatively high amount of toluene adsorbed (estimated from the sample weight change to be in excess of 6%). The apparent lack of change in surface texture became more surprising because of the thermogravimetric observation that the desorption of toluene took place at temperatures over 800K, suggesting an irreversible adsorption process. It is suggested that a molecule such as toluene, can ingress to the inner surface known to develop upon water removal in calcium hydroxide [6,8] through the narrow openings known to connect the slit-shaped pores with the exterior. From FTIR spectra, it appears that toluene forms a π-π with the surface. Exposure to toluene (and outgassing) at 573K appears to lead to a slight increase in BET surface area after toluene adsorption. That is presumably connected to an openning of the structure, due to the partial decomposition of calcium hydroxide.

TABLE 2

Nitrogen Adsorption Data After Toluene pre-Sorption

Temperature of exposure to toluene/K	Toluene sorbed/w%	BET Surface Area /m^2 g^{-1}	Average Pore Diameter /nm
300	3	13.6	19.1
373	3.5	13.7	18.3
573	6.5	20.6	15.2

The reaction with methanol has the effect of forming surface methoxide groups detectable by FTIR [10]. If the reaction is allowed to proceed beyond a certain point, then it ceases to be a surface only reaction, and proceeds to the bulk, with the result of forming a separate phase [7, 10]. In the case of the reaction with either methanol or toluene, this appears to be irreversible, and influences the surface reactivity of the solid, for example *vis a vis* reaction with carbon dioxide to form calcium carbonate. The calcium hydroxide surface, also reacts with ethanol vapour [8].

A study was carried out of the factors that influence the crystal habit of precipitated calcium hydroxide. The effect of the nature of the calcium precursor, concentration of reactants (calcium ions and sodium hydroxide solutions), speed of mixing and precipitation medium (water, ethanol, methanol, or mixtures thereof) was studied. It was found that slow addition at 10 ml min^{-1} of one reactant to the other led to well formed uniformed sized crystals. An excess of sodium hydroxide resulted in octahedral crystals about 10 µm in height (see Plate 1). Equi-molar amounts of base and calcium ions resulted in hexagonal prisms of about 10 µm length (Plate 2). A stoichiometric mixture of hydroxide and calcium ions led to the formation of small (*ca* 2 µm height) hexagonal prisms. These results are summarised in Table 3.

TABLE 3
Precipitation Data for Calcium Hydroxide

Sample	Reagents and Ratios				Crystal Habit
	NaOH	$CaCl_2$	$Ca(OAc)_2$	EtOH	
1	1	0.005	0	No	Octahedra
2	1	1	0	No	Large Hexagonal Prisms
3	2	1	0	No	Small Hexagonal Prisms
4	5	1	4	No	Layered Prisms (Hexagonal)
5	2	1	1	Yes	Platelets
6	1	0	1	No	Platelets
7*	2	1	1	Yes	Sheets

* fast mixing of precipitants (3750 ml min^{-1}, using calcium propionate instead of acetate

Reaction of equi-molar amounts of sodium hydroxide and calcium acetate (sample 6 in Table 3) resulted in thin hexagonal platelets, shown in Plate 3. A mixture of calcium chloride and acetate such as that used for sample 4 in Table 3, led to layered hexagonal prisms, of about 4 μm length. For the preparation of Sample 5, a mixture of ethanol and water was used, leading to the formation of thin platelets of calcium hydroxide. The higher the ethanol content the thinner were the plates. Sample 7 resulted from the reaction of hydroxide with calcium propionate in a pure ethanolic medium, with a fast mixing rate. Plate 4 indicates that the sample consists of sheets 200 μm across and 20 nm thick.

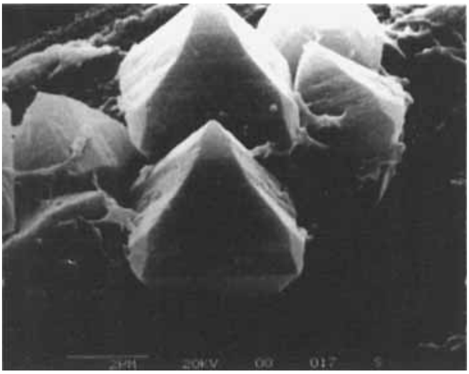

PLATE 1 SEM micrograph of Sample **1**

It is suggested that these observations can be rationalised as follows. Calcium hydroxide has a brucite-like hexagonal structure, with the OH groups aligned along the [0001] axis, which is parallel to the long axis of the hexagonal prismatic crystals observed. By using ideas similar to those developed by Lahav, Leiserowitz and others [11] for the case of organic crystals, it can be seen that poisoning of the (0001) faces by introducing large anions such as acetate which may be incorporated in the growing crystal, prisms can be converted to platelets, and these latter ones ultimately to sheets. A TEM study of sample 7, confirmed that the [0001] is indeed perpendicular to the sheets.

A similar case can be made for the effect of the addition of ethanol (or methanol) to the reaction medium. These molecules will form hydrogen bonds with the hydroxide ions on the surface of the growing crystal, thus inhibiting further growth of the crystal face, ie the (0001). Further, considerable evidence has been presented in this paper regarding the adsorptive properties of calcium hydroxide towards organic molecules.

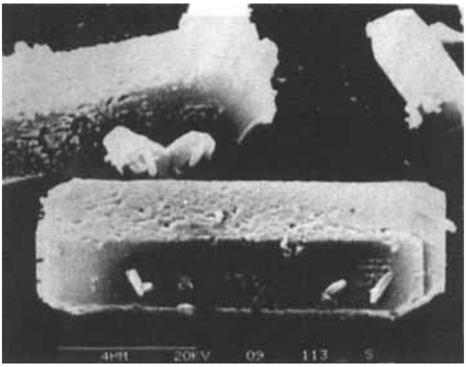

PLATE 2 SEM micrograph of Sample **2**

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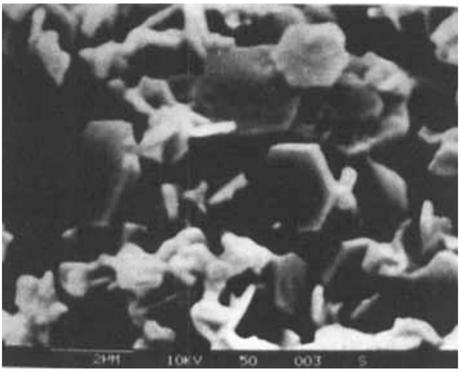

PLATE 3 SEM micrograph of Sample **6**

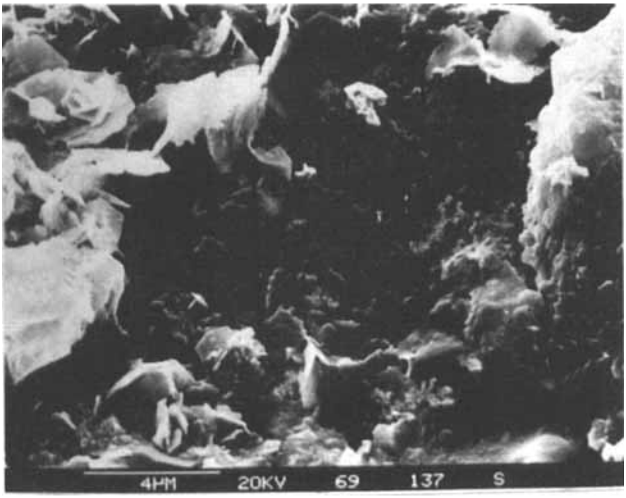

PLATE 4 SEM micrograph of Sample 7

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