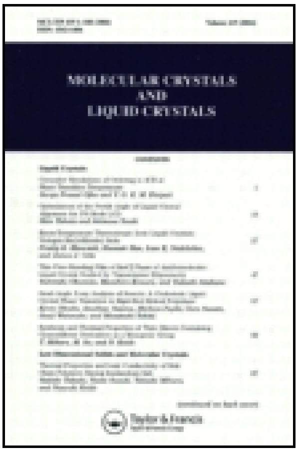

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FUNCTIONALISATION OF THE SURFACE OF CALCIUM HYDROXIDE BY THE GRAFTING OF ORGANIC MOLECULES

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Abstract The surface of a highly crystalline calcium hydroxide sample consisting of thin hexagonal plates was modified so that most of the surface OH groups were replaced by nitrobenzamide silane groups. The reaction only occurs on the free surface of the crystallites leaving their morphology largely intact. This example of functionalised calcium hydroxide has been characterised by Fourier transform ir spectroscopy and thermal methods, and by scanning electron microscopy.

INTRODUCTION

Calcium hydroxide is a chemical which has been in use for a long time (for example, the Greeks and Romans used it as a component of cement), and is currently used in a variety of industrially important processes. Water solutions have been used extensively as a calcium source for preparing coordination compounds of that element, because the pH is advantageous for chelating reactions[1]. Much is known therefore about the solution chemistry of calcium hydroxide, but in spite of the solid material being in substantial use, very little study has been made of its surface or solid state chemistry.

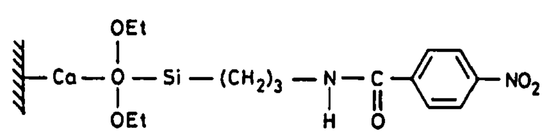
Interest has recently been shown in the functionalisation of the surface of silica gel and of aluminosilicates with organic functions, by reacting with silanes[2]. These solids have been used as cation exchangers and as GC stationary phases for the chiral resolution of racemic mixtures, but suffer from the fact that only a small fraction of the surface OH groups actually react.

In this paper, a first example of the preparation of $Ca(OH)_2$ with a functionalised surface is presented. Our choice of solid has been guided by the fact that it, in common with other molecular composite materials studied previously[3], possesses a layer structure. Continuing work in these laboratories is concentrating on a study of the surface reactivity of $Ca(OH)_2$, on controlling the precipitation process of calcium hydroxide from aqueous and alcoholic solutions, and the systematic modification of the crystalline morphology of the precipitate[4,5,6].

EXPERIMENTAL

An important part of the project was the study of the crystallisation of $Ca(OH)_2$ and the control of its crystal morphology. It was found that by controlling the precipitation conditions by, for example, altering the calcium salt, the base, or the solvent medium, a change in the crystal habit could be achieved in a reproducible way. The morphology was also influenced by the relative concentrations of calcium salt and base, as well as the mixing rates. The reactants were added to the reaction medium using a peristaltic pump, and mixed in an ultrasonic bath, or by using mechanical stirring. In most cases, the crystallite size varied within very narrow limits. Examples of possible morphologies, are shown in the Plate.

The crystals used for the functionalising reaction were thin hexagonal platelets of 20nm thickness, whose shape remained unaffected by reaction with the silane. The reaction used for the grafting of nitrobenzamide silane groups onto the hydroxide surface has been described elsewhere, and is an adaptation of the equivalent reaction for silica gel[7]. The final product has been designated as **1**. Chemical analysis gave the N:C ratio expected for **1**.



$$\mathrm{Ca-\overset{OEt}{\underset{OEt}{O}}-Si-(CH_2)_3-\underset{H}{N}-\underset{O}{\overset{\|}{C}}-C_6H_4-NO_2}$$

1

The characterisation of the final product was carried out by chemical and thermal analysis, spectroscopic techniques (transmittance and diffuse reflectance FTIR and reflectance UV), nitrogen adsorption isotherm determination, and by electron microscopy (SEM and TEM).

DISCUSSION

The morphology of the crystals of $Ca(OH)_2$ varied from octahedra, to hexagonal prisms, to hexagonal platelets to thin sheets, depending on the precipitation conditions. This progression can be understood in terms of the poisoning of certain crystal faces, by the partial incorporation of anions other than OH^- from the calcium salt or solvent molecules. The rate and extent of formation of carbonate, if present, was also a function of the precipitation conditions and also had an effect on the morphology. The crystals which were used in the present study had their surface stabilised by the partial reaction of the OH groups with hexamethyl disilazane. This reaction only affects a few of the OH groups. Increased stability is shown by a rise of the temperature at which $Ca(OH)_2$ was converted to CaO.

Electron diffraction in the TEM has indicated that the large hexagonal faces of the platelets and the sheets are parallel to the (0001) plane. Examination of the crystal structure[8] of $Ca(OH)_2$ indicates that this face is rich in OH groups, as they are all aligned with the c crystallographic axis. Therefore, a crystal which has large (0001) faces, while the other faces are very small, will have a substantial number of its OH groups exposed to the environment. This would clearly facilitate the reaction with the silane to produce **1**, and would account for the high yield of the reaction. The electrom diffraction pattern for **1** shows only distorted hexagonal symmetry, as this has been destroyed by the elimination of OH groups on the surface. Given the thinness (20 nm) and the large aspect ratio of the crystallites, it is logical to expect a surface alteration to have a significant effect.

The fact that the grafting reaction has caused no change in morphology, as established by SEM, suggests that all of the reaction has occurred on the surface. The only difference between reactant and product crystals lies in the aggreggate structure. The change is associated, presumably, with the alteration in the chemical

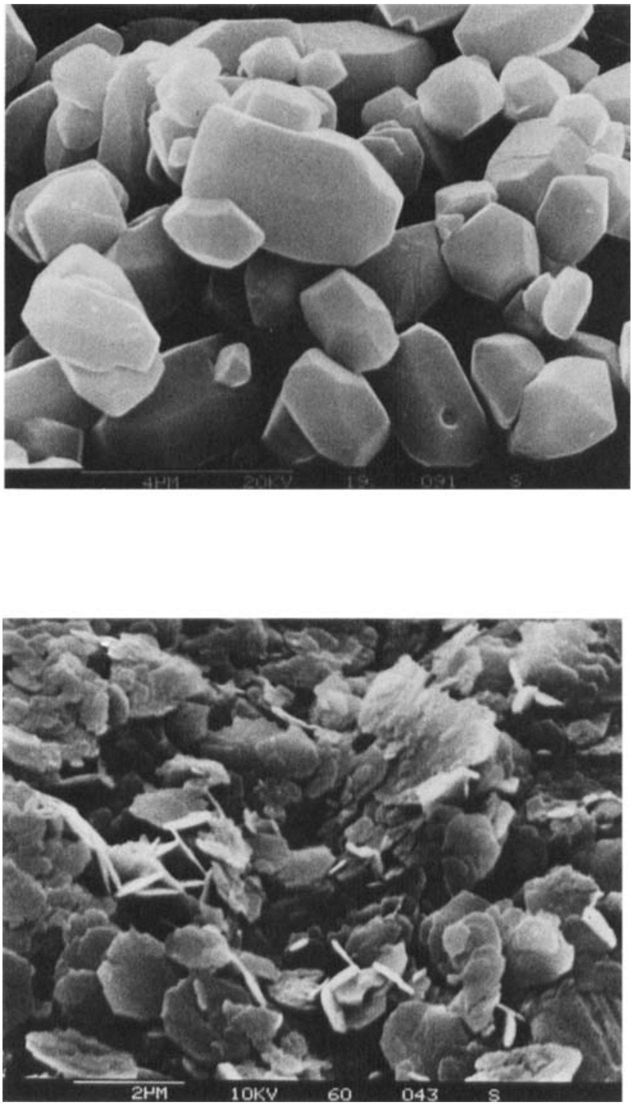


PLATE 1

Top - Prism morphology of $Ca(OH)_2$

Bottom - Platelet morphology of $Ca(OH)_2$

nature of the surface.

Examination of the FTIR spectrum of the product (see Figure 1) shows that the OH band that has been attributed to surface OH groups (3645 cm^{-1}) in pristine $Ca(OH)_2$ has collapsed, indicating that reaction is indeed primarily taking place on the surface. On the other hand the peak which is attributable to bulk OH groups (3531 cm^{-1}) remains intact. The reduction in intensity for the bands associated with the presence of water in 1 as compared with pristine $Ca(OH)_2$, is consistent with a modification of the surface to render it less hydrophilic, by introducing organic groups.

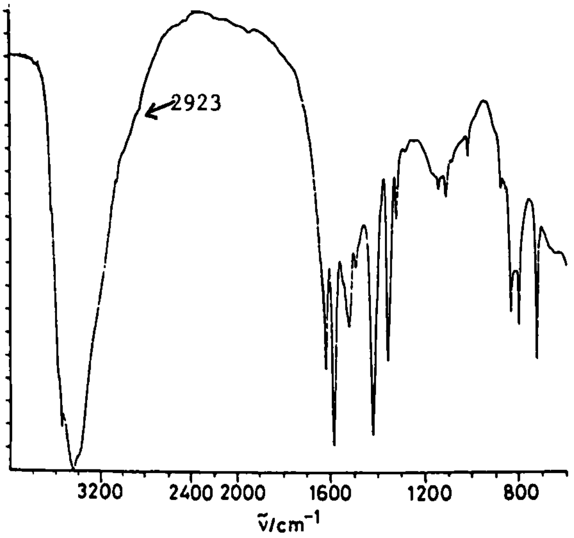


Figure 1: Fourier-transform ir spectrum of 1

The presence of $O\text{-}Si(OEt)_2\text{-}C$ (etc) groups in the sample was confirmed by XPS (X-ray photoelectron spectroscopy). XPS also confirmed the presence of $SiMe_3$ groups from the reaction with silazane. The presence in the FTIR spectrum of 1 of the C-H stretching bands at 2923 cm^{-1} and of the band at 876 cm^{-1} are also characteristic of this group.

The assignments for the O-H stretching frequencies for bulk and surface OH groups, have been confirmed by comparison with the spectrum of $Ca(OH)_2$ exposed to D_2O. Thus, exposure to D_2O causes a shift of the 3645 cm^{-1} band, but not that at 3531 cm^{-1}. Peaks in Fig. 1 which are not present in the spectrum of pristine $Ca(OH)_2$ have all been assigned to various groups and modes in the nitrobenzamide silane moieties. These agree well with published standard spectra.

The fact that the surface of an alkaline earth hydroxide can be functionalised with relative ease, has considerable practical and technological implications. For example, it leads to alteration of the hydrophilic nature of the solid, and renders an inorganic surface into an organic-like one. This can therefore render the inorganic phase compatible with an organic medium. Such functionalisation has hitherto made use of silica gel, which is usually highly porous. Although this is desirable for many applications, it is not so where large organic molecules are involved as guests, in which case non-porous solids such as $Ca(OH)_2$ with reasonably high surface area (here 25 m^2g^{-1}) may offer considerable advantages.

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