A Novel Calcium Hydroxide Molecular Composite: Preparation and Characterisation

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The surface of a highly crystalline calcium hydroxide sample consisting of thin hexagonal plates was modified by a two-step reaction, so that the majority of surface OH groups were replaced by nitrobenzamide silane groups. This reaction formerly carried out on silica gel surfaces, occurs here to a larger extent because of the lack of porosity, and because of the basic nature of the $Ca(OH)_2$ hydroxide groups. The reaction only occurs on the free surface of the crystallites leaving their morphology largely intact. This example of a functionalised calcium hydroxide composite has been characterised by spectroscopic and thermal methods, and by scanning electron microscopy.

Considerable interest has been shown recently in a new class of materials which consist of layers of inorganic moieties separated by layers of organic molecules. The organic and inorganic moieties are usually chemically bonded together, hence the naming of this new class of material as molecular composites.

The importance of these solids arises from the so-called pillared clays. Clays are layer aluminosilicates, many of which can be made to swell. An important feature of the structure of clays is that isomorphous substitution of Al or Si by other atoms leads to a negatively charged layer. This charge is counterbalanced by cations, which are located in between the layers. The swelling in water results from the extra hydration of the interlamellar cations. This is the best known example of intercalation. The usefulness of clays as catalysts is limited by the collapse of the layer structure which often occurs at elevated temperatures. One way of preventing this collapse is by inserting pillars, usually of an inorganic character but more rarely organic, which serve to keep the individual layers apart. More recently, other layer inorganic structures, such as acid zirconium and vanadyl(IV) phosphates haves been used as hosts for a variety of intercalated organic species; α-$Zr(HPO_4)_2 \cdot H_2O$ is particularly useful in this context, because of its swellability. Refs. 1 and 2 are recent reviews of this subject.

Much interest has been shown in the functionalisation of the surface of silica gel and of layer aluminosilicates with organic functions.[3–5] These solids have been used as specific cation exchangers for a variety of transition-metal ions,[3] as stationary phases in high-performance liquid chromatography for the chiral resolution of racemic mixtures,[6] and as catalysts.[7,8] All of these applications rely on the reaction of surface OH groups with the requisite silane or chlorosilane in solution. The main disadvantage of this route lies in its low yield, which results in the majority of the surface remaining uncovered.

In this paper, we present what we believe to be a first example of a molecular composite based on calcium hydroxide. Water solutions have been used extensively as a calcium source for preparing co-ordination compounds of that element,[9] in spite of its low solubility, because the pH of these solutions is advantageous for chelating reactions. However, no evidence has been found in the literature for the use of solid calcium hydroxide in reactions with organic molecules. Our choice of solid has been guided by a variety of factors, including the fact that it, in common with other compounds used previously, possesses a layer structure. Work in these laboratories has hitherto concentrated on the control of the precipitation of calcium hydroxide from aqueous and alcoholic solutions, and the systematic modification of the crystalline morphology of the precipitate, an area which has hitherto received only scant attention.[10] Details of the precipitation conditions, and the various crystal shapes thus obtained, will be given elsewhere.[11]

For the present study, thin hexagonal prismatic crystals of calcium hydroxide were chosen. All crystallites were of approximately equal size and shape, which can be reproduced routinely. The crystals have been stabilised against aggregation by treating some of the OH groups with hexamethyldisilazane. This reaction, which left the morphology of the crystals unchanged, results in the introduction of bonded O–$SiMe_3$ groups on the surface of the $Ca(OH)_2$ layers. This reaction has been used in the case of crystalline aluminosilicates in order to block acidic OH surface groups,[12] thus modifying the surface acidity of the solid. The extent to which the reaction takes place on calcium hydroxide is minimal, but enough to make the methyl groups detectable by Fourier-transform i.r. spectroscopy, and therefore most OH groups remained available for further reaction. This solid has been designated as (**1**).

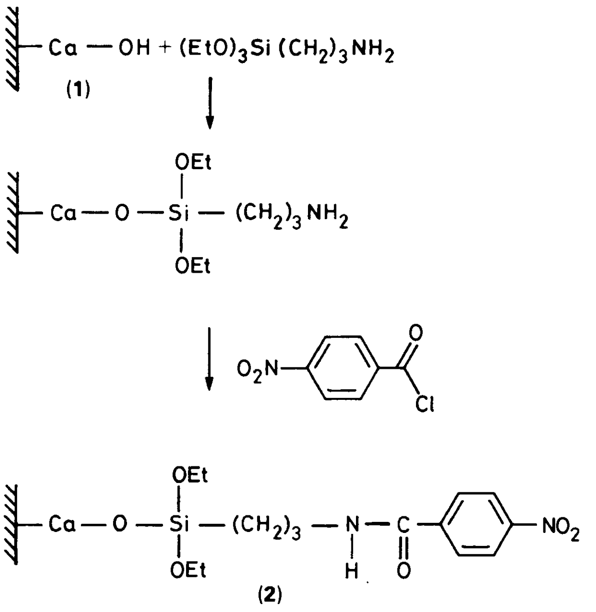
Experimental

A 20% solution (50 cm^3) of 3-aminopropyltriethoxysilane in sodium-dried toluene was added to 1 g of the calcium hydroxide material (**1**) (1 g) and the suspension was refluxed for 4 h. This reaction resulted in aminopropylsilane groups on the surface. The product was vacuum filtered and washed with dry toluene, and dried for 1 h at 343 K. This material was then contacted with a solution of *p*-nitrobenzoyl chloride (2.5 g) and triethylamine (2.5 g) in chloroform (50 cm^3). The suspension was then maintained at 323 K for 48 h, after which the solid was filtered off and dried under vacuum. The final product, had nitrobenzamide silane groups on the surface, and is designated as (**2**) (see Scheme).

The characterisation of the final product was carried out by chemical and thermal analysis, spectroscopic techniques, nitrogen adsorption isotherm determination, and by electron microscopy. The spectroscopic techniques used included Fourier-transform i.r. spectroscopy in both reflectance and transmission modes using a Perkin-Elmer 1710 spectrometer, and reflectance u.v.–visible spectroscopy using a Perkin-Elmer Lambda 9 spectrometer. Scanning electron microscopy (s.e.m.) was carried out on a Cambridge stereoscan 250 instrument, and transmission electron microscopy (t.e.m.) on a JEOL CX-100.

Results

Figure 1(*a*) shows the Fourier-transform i.r. spectra for (**1**), and Figure 1(*b*) the spectrum after heating to 773 K. Figure 2 shows the corresponding spectrum of (**2**). The surface area of the starting material (**1**) was found to be 25 m^2 g^{-1} by nitrogen



Scheme.

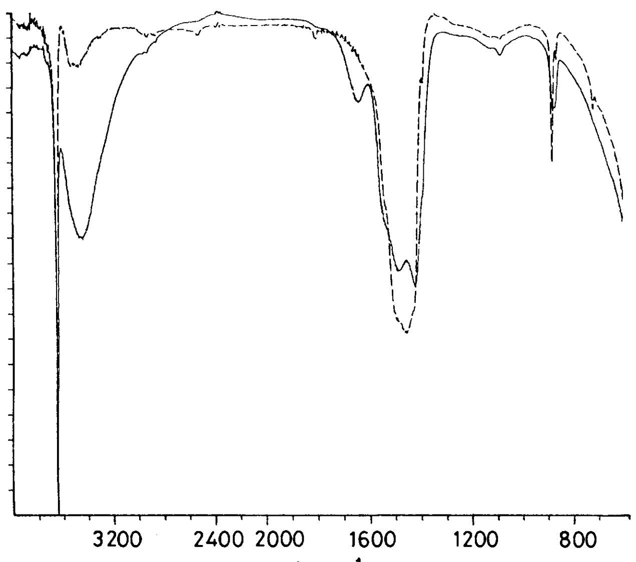


Figure 1. Fourier-transform i.r. spectrum of $Ca(OH)_2$ containing some O–$SiMe_3$ groups (——), and (**1**) after heating at 773 K (- - - -)

adsorption (77 K). The thickness of the platelets of (**1**) as measured by t.e.m. was found to be 20 nm. Reflectance u.v.–visible spectroscopy showed (**1**) to be largely transparent in the wavelength region 250—700 nm, but (**2**) showed a strong absorption at 320 nm.

Thermal analysis (d.t.a.–t.g.a) for various $Ca(OH)_2$ samples gave the temperatures at which these decomposed to CaO. Thus, non-silanated $Ca(OH)_2$ [*i.e.* the precursor for (**1**)] decomposed in air in the range 685—692 K, and (**1**) decomposed at 907—918 K. Material (**2**) decomposed at 1 038 K, but this was preceded by the exothermic decomposition of the organic component at 618 K. In a nitrogen atmosphere, decomposition took place at slightly higher temperatures. It is of note that decomposition of the organic component of (**2**) took place even in this inert atmosphere, albeit with a lower evolution of heat. Chemical analysis for (**2**) gave 10.65 C, 2.40 H, and 1.51% N. The H:C ratio was thus higher than that required by the formula for (**2**). This is probably due to the presence of $SiMe_3$ groups from reaction with hexamethyldisilazane, or to the presence of small amounts of water adsorbed on the surface. The temperature at which the compound was heated for analysis was not high enough to decompose $Ca(OH)_2$, which therefore caused no interference. The N:C ratio, however, was that expected for (**2**).

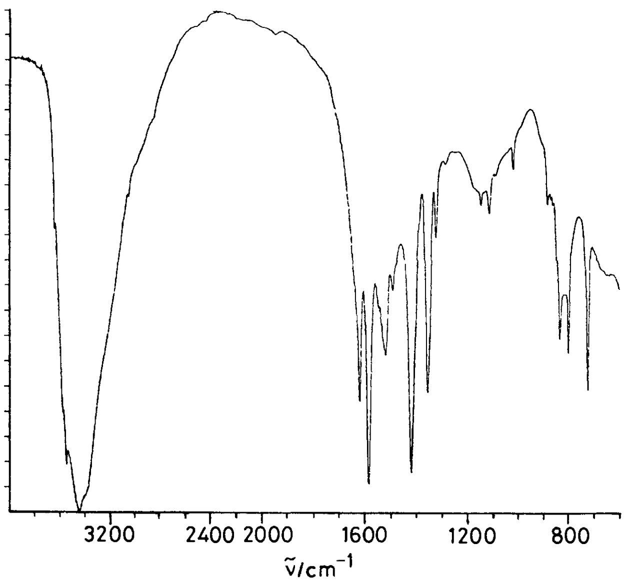


Figure 2. Fourier-transform i.r. spectrum of composite (**2**)

Discussion

The method used for immobilising the organic molecules on the hydroxide surface was adapted from that described by Hill,[4] Suguwara, and co-workers[5] and Karim[13] for the immobilisation of chelating agents on silicate or silica surfaces. That the reaction should be successful for surfaces so different as those of silica gel and calcium hydroxide is at first glance remarkable. Comparison of Fourier-transform i.r. spectra of (**2**) with its silica gel analogue indicates that reaction on the hydroxide surface has occurred to a larger extent than on silica gel. This can be rationalised in terms of the surface acidity of these two solids: the OH groups on silica gel are mildly acidic or neutral, but those on calcium hydroxide are basic. Given that the Si–OH group on the silane in solution is mildly acidic, it would be logical to expect the acidic group to react more with the basic OH groups, rather than the neutral ones. It is also likely that in porous silica gel many of the potentially reactive OH groups would be inaccessible by being inside pores too narrow for easy access by the organic reactants. An estimation of the number of surface OH groups that have reacted is difficult; the upper limit should be set by the number of benzene rings that can be packed on the surface. Comparison between the area of the ring and the area of the $Ca(OH)_2$ unit cell leads to the conclusion that this upper limit is 33% of the surface OH groups.

T.e.m. in the electron-diffraction mode has indicated that the large hexagonal faces (see Figure 3) of the prismatic crystals are the (0001). Examination of the crystal structure[14] 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 product (**2**).

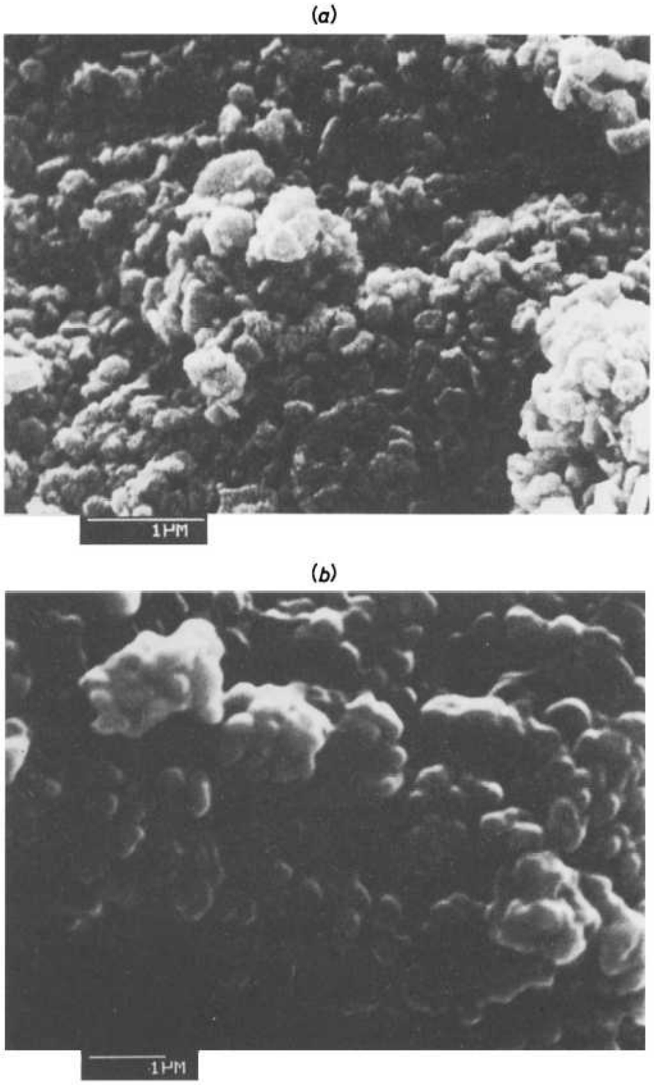


Figure 3. S.e.m. micrographs of (*a*) (**1**) and (*b*) (**2**)

Comparison of s.e.m. micrographs for compounds (**1**) and (**2**) (Figure 3) shows that reaction of (**1**) with the liquid silane has not resulted in any change in crystal shape. This suggests that most, if not all, of the reaction has occurred on the surface. As explained in the previous paragraph, it is expected that an appreciable fraction of the OH groups in a crystallite would be present in the hexagonal faces, which would make a heterogeneous reaction more likely. The only differences between Figure 3(*a*) and 3(*b*) are in the aggregate structure, which is probably changed, because of the alteration in the chemical nature of the surface. The increase in the temperature at which decomposition to CaO takes place for (**2**) as compared with (**1**) is another pointer towards the reaction having taken place predominantly on the surface.

The reflectance u.v.–visible spectrum for material (**2**) shows a strong band at 320 nm, expected for a nitrobenzamide moiety, such as that present in (**2**). Examination of the Fourier-transform i.r. spectrum of (**2**) (Figure 2) in both reflectance and transmission modes indicates a series of bands not present in the spectrum for (**1**) [Figure 1(*a*)] which can all be assigned to nitrobenzamide and correspond well with published positions and reference spectra. Since it is suggested that reaction between the silane and the $Ca(OH)_2$ surface involved surface OH groups, it is appropriate to look at these more carefully. From Figure 1(*a*) it can be seen that water (presumably present on the surface) gives rise to two broad peaks centred at 3 500 (strictly speaking hydrogen bonded O–H stretch) and 1 638 cm^{-1} (H–O–H bend). Non-hydrogen-bonded OH groups, presumably the structural groups of the hydroxide, give rise to two sharp bands, at 3 645 and 3 531 cm^{-1}. This latter is normally masked by the water peak, but can be observed after removing most of the water by heating to 473 K. This temperature is not high enough to decompose the solid hydroxide. The broad OH band that remains has been shifted to 3 468 cm^{-1}, due to one of two reasons: either the water molecules that remain after heating are held on the surface in a different way to those that have been removed, or surface OH groups are hydrogen-bonded to water molecules sorbed on the surface. It should be noted that the band at 1 638 cm^{-1}, which is generally considered a good indication of the presence of water, has disappeared upon heating [Figure 1(*b*)].

It is suggested that the band at 3 645 cm^{-1} is due to OH groups at or near the surface of the crystallites, and that at 3 531 cm^{-1} to the bulk groups. Upon reaction with the silane the OH band at 3 645 cm^{-1} collapses (compare Figures 1 and 2), indicating that reaction is indeed taking place primarily with the surface OH groups. The band at 3 545 cm^{-1} in Figure 2 corresponds with the bulk OH groups, whilst the broad band at 3 436 cm^{-1} can be assigned to the amide group. The assignments have been confirmed by comparison with the spectrum of $Ca(OH)_2$ exposed to D_2O. The reduction in intensity of the bands associated with the presence of water is consistent with a modification of the surface so as to render it less hydrophilic, by introducing organic groups. The presence of $O{-}Si(OEt)_2{-}C$ (*etc.*) groups in the sample is confirmed by *X*-ray photoelectron spectroscopy, which also confirms the presence of $SiMe_3$ groups from the reaction with silazane.

Acknowledgements

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