Colloidal Particles of Ca(OH)2: Properties and Applications to Restoration of Frescoes

5 **AUTHORS**, INCLUDING:

Moira Ambrosi
University of Florence
24 PUBLICATIONS   604 CITATIONS

SEE PROFILE

Luigi Dei
University of Florence
80 PUBLICATIONS   1,554 CITATIONS

SEE PROFILE

Rodorico Giorgi
University of Florence
73 PUBLICATIONS   981 CITATIONS

SEE PROFILE

Piero Baglioni
University of Florence
448 PUBLICATIONS   8,083 CITATIONS

SEE PROFILE

Colloidal Particles of Ca(OH)₂: Properties and Applications to Restoration of Frescoes

Moira Ambrosi,[†] Luigi Dei,* Rodorico Giorgi, Chiara Neto, and Piero Baglioni*

Department of Chemistry and CSGI, University of Florence, via Gino Capponi, 9 I-50121 Florence, Italy

We studied the synthesis and characterization of Ca(OH)₂ colloidal particles and their application to the restoration of wall paintings. Submicrometer Ca(OH)₂ crystalline particles have been obtained by mixing equal volumes of NaOH and CaCl₂ aqueous solutions with different degrees of supersaturation (from 2 to 10) and in the temperature range 60−90 °C. The Ca(OH)₂ particles are crystalline and have the appearance of hexagonal platelets with thicknesses of a few nanometers, as determined by scanning electron microscopy, transmission electron microscopy, X-ray diffractometry, and atomic force microscopy techniques. The kinetic stability of dispersions of Ca(OH)₂ particles in water and propan-1-ol has also been studied in view of their possible application in wall painting conservation. A successful example of this application to the restoration of Santi di Tito's wall paintings (16th century) in the Santa Maria del Fiore Cathedral in Florence is also reported.

Introduction

Several studies[1−5] have been published on the synthesis and characterization of metal oxide, hydrous oxide, and hydroxide nanoparticles obtained by precipitation from salt solutions. In particular, most of these studies concern metal oxides and hydroxides with very low water solubility and the effect of temperature, pH, ionic concentration, organic additives, and the presence of co-ions on the characteristics of the obtained particles.[1,3,5,6] High temperature has been shown to be necessary in order to obtain very fine particles, while the properties of the inorganic materials synthesized strongly depend on the conditions of the environment in which they are generated.[1,7] To achieve a temperature higher than 100 °C, a new method has been recently developed to produce nanosized In(OH)₃ particles based on diols as a medium of reaction.[7] This method involves several peptizations of the particles synthesized because the diols tend to be adsorbed on the particle surface keeping them aggregated in micron-sized agglomerates.[7] All the nanocompounds studied have very low solubility and can be easily prepared in high supersaturation conditions. The synthesis of colloidal particles can be complicated for compounds with relatively high solubility into the continuous phase because it becomes difficult to achieve a high supersaturation degree and the effect of co-ions at these concentrations can be critical. Therefore, the literature on the preparation of inorganic submicrometer materials with high solubility products is quite scarce. An example of the synthesis of calcium sulfate ($K_{sp} \approx 2.3 \times 10^{-4}$) nanoparticles in microemulsion has

been published only recently.[8] Recently, Ca(OH)₂ nanoparticles have been obtained by synthesis in diols at 160 °C.[9] The present work concerns the synthesis and characterization of colloidal particles of Ca(OH)₂, a moderately soluble hydroxide ($K_{sp} \approx 4.8 \times 10^{-5}$), in an aqueous medium to avoid effects of particle agglomeration.[7,9] Aqueous solutions of Ca(OH)₂ have a very high pH (pH ≈ 12.7) that complicates the synthetic pathway of the particles[8] and raises interesting issues in fundamental research. The characterization of Ca(OH)₂ particles has been performed by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) measurements in air. The AFM technique has also been used to obtain information in situ on the particles dispersed in the liquid phase. This was particularly interesting in view of the preparation of Ca(OH)₂/alcohol stable dispersions (vide infra). A previous study[10] has shown that dispersions of commercial slaked lime (micron-sized Ca(OH)₂ particles) in short-chain aliphatic alcohols present an interesting enhanced stability with respect to water and can be used to re-adhere lifted and detached paint layers in wall painting conservation. We expected submicrometer particles of Ca(OH)₂ to be more effective in wall painting restoration. Moreover, the smaller size of the particles ensures a greater stability of their dispersions, a higher penetration efficacy in the painted surface layers, and very weak white glazing of the fresco surface after Ca(OH)₂ application.

Materials and Methods

(1) Materials. Sodium hydroxide, NaOH, potassium hydroxide, KOH, calcium chloride dihydrate, CaCl₂·2H₂O, and propan-1-ol (purity > 99.5%) were supplied by Merck, Darmstadt, Germany, and were used without further purification. Ca(OH)₂ as slaked lime paste (a mixture of calcium hydroxide powder (c) and water (w) in a weight ratio c/w = 0.8) was purchased from Ceprovip, Medolago (BG), Italy. The particle size of Ca(OH)₂ powder is in the micrometer range. Water was purified with a Millipore Milli-RO 6 and a Milli-Q (Organex system) water system

* Corresponding authors. Fax: + 39-055240865. E-mail: dei@csgi.unifi.it; baglioni@csgi.unifi.it.

† Present address: University of Durham, Department of Chemistry, South Road, Durham DH1 3LE United Kingdom.

(1) Hamada, S.; Kudo, Y.; Minigawa, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 102.

(2) Matijevic, E.; Scheiner, P. *J. Colloid Interface Sci.* **1978**, *63*, 509.

(3) Hamada, S.; Matijevic, E. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2147.

(4) Matijevic, E. *Acc. Chem. Res.* **1981**, *14*, 22.

(5) Matijevic, E.; Cimas, S. *Colloid Polym. Sci.* **1987**, *265*, 155.

(6) Arai, Y. *Chemistry of Powder Production*; Powder Technology Series; Scarlett, B., Ed.; Chapman & Hall: London, 1996; Chapter 4.

(7) Pérez-Maqueda, L.; Wang, L.; Matijevic, E. *Langmuir* **1998**, *14*, 4397.

(8) Rees, G. D.; Evans-Gowing, R.; Hammond, S. J.; Robinson, B. H. *Langmuir* **1999**, *15*, 1993.

(9) Salvadori, B.; Dei, L. *Langmuir* **2001**, *17*, 2371.

(10) Giorgi, R.; Dei, L.; Baglioni, P. *Stud. Conserv.* **2000**, *45*, 154.

(water resistance $\geq$ 18 MΩ cm). Polyvinyl Formvar was obtained from Taab Chemicals & Equipment for Microscopy Ltd., England.

(2) Synthesis of Ca(OH)$_2$ Particles from Homogeneous Phase. NaOH solution (100 mL) (0.2, 0.4, 0.8 M) and 100 mL of CaCl$_2$ solution (0.1, 0.2, 0.4 M) were separately heated to the selected temperature in the range 60–90 °C. When the selected temperature was reached, the two solutions were rapidly mixed under stirring keeping the temperature of the mixture constant within ±1 °C. The supersaturation degree, defined as the ratio $[Ca^{2+}]/[Ca^{2+}]_{sat}$ where $[Ca^{2+}]_{sat}$ is the concentration of Ca^{2+} cations in the Ca(OH)$_2$ saturated solution, was kept in the range 2–10. The Ca(OH)$_2$ suspension was allowed to gradually reach room temperature under a nitrogen atmosphere to avoid Ca(OH)$_2$ carbonation. The supernatant solution was discarded, and the remaining suspension was washed five times with water to reduce NaCl concentration below 10^{-6} M. Each time, the dilution ratio between the concentrated suspension and washing solution was about 1:10. The complete removal of NaCl from the suspension was controlled by AgNO$_3$ tests. The suspension was then concentrated in a vacuum at 40 °C up to a weight ratio Ca-(OH)$_2$/water of 0.8, that is, the same as the standard slaked lime paste taken as the reference. All the following measurements were carried out on this paste according to different procedures that will be illustrated in the next sections.

(3) Characterization of the Particles. The size and shape of the particles were determined by SEM, TEM, and AFM, while the crystal structure of the obtained solid was checked by X-ray diffractometry (XRD). SEM and TEM apparatuses were Philips XL20 and Philips EM201C, respectively. The samples for these measurements were prepared according to common procedures. XRD spectra were obtained on dried particles using a Philips PW1050/70 apparatus with a Co Kα X-ray (λ = 1.78 Å) source. AFM measurements were made in contact mode using an Explorer TMX 2000 (Topometrix) apparatus both in air and in liquid. The sample preparation was made according to the procedure reported in the literature.[11]

(4) Kinetic Stability of the Ca(OH)$_2$ Dispersions. The dispersions were prepared by vigorous stirring at room temperature of 0.25 g of Ca(OH)$_2$ (colloidal or microparticles) in 40 mL of water or propan-1-ol dispersion medium. The relative kinetic stability of the dispersion has been calculated from the ratio of the optical densities of the supernatant liquid and of the original dispersion determined at 600 nm (UV–vis Lambda 5 Perkin-Elmer spectrophotometer).[12–14]

Results and Discussion

(1) Particle Characterization. The particles prepared at 60 °C show the hexagonal (prismal) habitus typical of Ca(OH)$_2$[6,15] with a high degree of particle agglomeration. The size of the hexagonal side ranges between 0.3 and 0.6 μm,[6,16] and many different crystal morphologies are evidenced (data not reported). Increasing the temperature of the synthesis up to 90 °C causes a decrease of the mean particle dimensions as shown in Figure 1. The hexagonal habitus is better evidenced than at 60 °C, and the average size of the hexagonal side is 100–250 nm. Similar information on the morphology of the Ca(OH)$_2$ particles prepared at 90 °C has been obtained from TEM measurements. Figure 1 (bottom) shows a single hexagonal particle of Ca(OH)$_2$ with a side of about 100 nm. We conclude that smaller particles, less agglomeration, and higher symmetry of the Ca(OH)$_2$ crystals are produced by increasing the temperature from 60 to 90 °C. Platelet thickness was not determined from SEM or TEM because it was very difficult to orient the hexagonal platelets perpendicularly
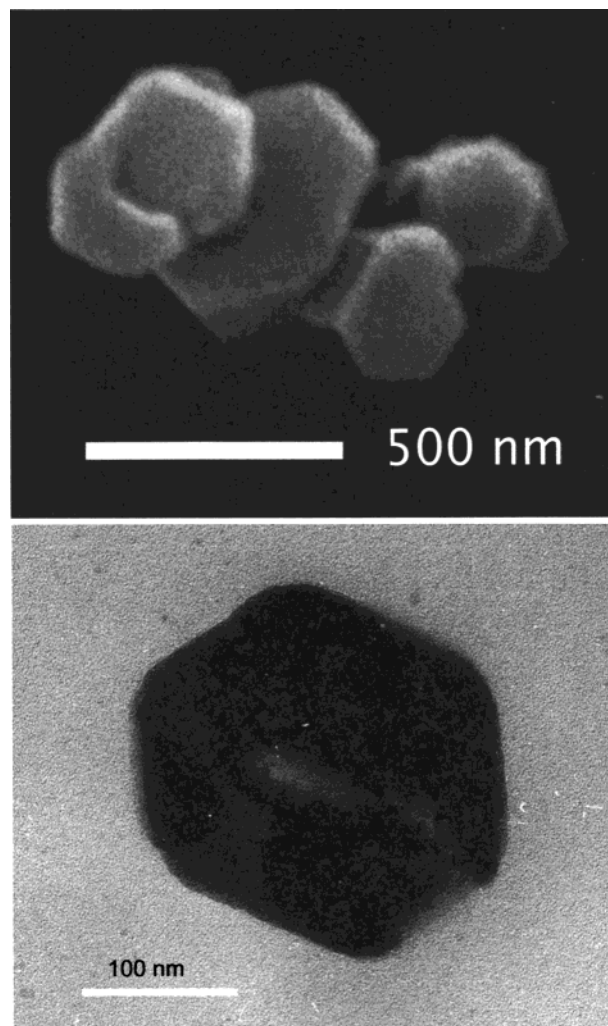
(11) Neto, C.; Aloisi, G.; Baglioni, P.; Larsson, K. *J. Phys. Chem. B* **1999**, *103*, 3896.
(12) Esumi, K.; Takamine, K.; Ono, M.; Osada, T.; Ichikawa, S. *J. Colloid Interface Sci.* **1993**, *161*, 321.
(13) Ma, C.; Xia, Y. *Colloids Surf.* **1992**, *66*, 215.
(14) Gabrielli, G.; Cantale, F.; Guarini, G. G. T. *Colloids Surf., A* **1996**, *119*, 163.
(15) Arai, Y. *Gypsum Lime* **1985**, *198*, 54.
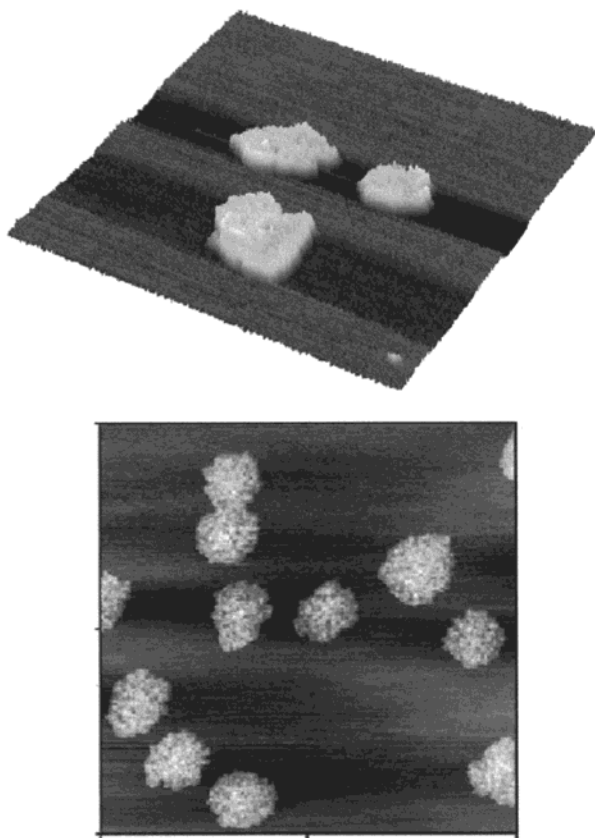(16) Yasue, T.; Tsuchida, Y.; Arai, Y. *Gypsum Lime* **1984**, *189*, 17.

Figure 1. Top: SEM micrograph of Ca(OH)$_2$ particles obtained from homogeneous phase at 90 °C; bottom: TEM micrograph of a single Ca(OH)$_2$ particle prepared from homogeneous phase at 90 °C showing the hexagonal habitus.

to the aluminum stub surface (SEM) or to the copper grid (TEM). We determined platelet thickness using AFM. Moreover, AFM experiments were also carried out in propan-1-ol dispersion, that is, imaging the Ca(OH)$_2$ particles directly in situ. Figure 2 shows an AFM image of Ca(OH)$_2$ particles adsorbed on mica in air. The particles appear clearly faceted. The number of sides of the structures is not always equal to six, but often we recognize the nearly 120° inner angle. Similar findings have been recently found[11] with lipid hexosomes, and this discrepancy has been attributed either to the orientation of the particles with respect to the mica surface or to the friction exerted by the scanning of the tip. These two aspects can also be considered to explain our data. Furthermore, it is to be underlined that a weak adsorption of the Ca(OH)$_2$ particles on the mica surface can originate a dragging effect resulting in a deformation of the hexagonal image. All the particles examined have sides between 180 and 300 nm in good agreement with the SEM and TEM data. The apparent height of the particles on the mica surface is between 2 and 40 nm (Figure 2 shows the thinnest particles observed with thickness of ca. 2–5 nm). Figure 2 (bottom) shows the particles in propan-1-ol. The particles appear quite well monodispersed, and in some cases the hexagonal symmetry is detectable. The average size of the particle side in Figure 2 (bottom) is ca. 130 nm. In other experiments, we obtained values ranging between 130

Figure 2. Top: AFM image taken in air of the Ca(OH)$_2$ particles synthesized at 90 °C; image dimension 1630 × 1630 nm^2. The height scale extends to 5.25 nm. The particles have mean dimensions of the sides around 250 nm and apparent height on the mica surface of 3–5 nm. Bottom: AFM image taken under propan-1-ol of the same particles; image dimensions 1.5 × 1.5 μm^2. The particles appear to have mean dimensions of the sides around 130 nm.

and 250 nm. These in situ measurements establish that both the morphology and the size of the synthesized particles are not altered by the drying and the vacuum procedure for SEM and TEM experiments or for AFM measurements in air. Furthermore, the surface of the particles appears rough in both the liquid and air images (Figure 2, top and bottom), confirming that the roughness is not due to the drying process.

To investigate the crystallinity of the Ca(OH)$_2$ nanomaterial, XRD measurements on the particles synthesized at 90 °C and on the microparticles of the commercial slaked lime were carried out. Figure 3 shows these two XRD spectra. These are practically identical and correspond to the structure of crystalline Ca(OH)$_2$ (portlandite).[17] IThe peak at ca. 3 Å relative to the {100} plane of CaCO$_3$[17] is missing, indicating that Ca(OH)$_2$ crystals were not carbonated by atmospheric CO$_2$.

(2) Particle Dispersions. The kinetic stability of the dispersions of synthesized colloidal particles and of microparticles used as a standard reference (slaked lime paste) was determined according to the procedure illustrated in Materials and Methods. Figure 4 shows the behavior of the stability parameter ξ[12–14] for the dispersions of Ca(OH)$_2$ colloidal particles [curves a and c] and microparticles [curves b and d]. The ξ parameter, expressed in %, was monitored as a function of time. Its
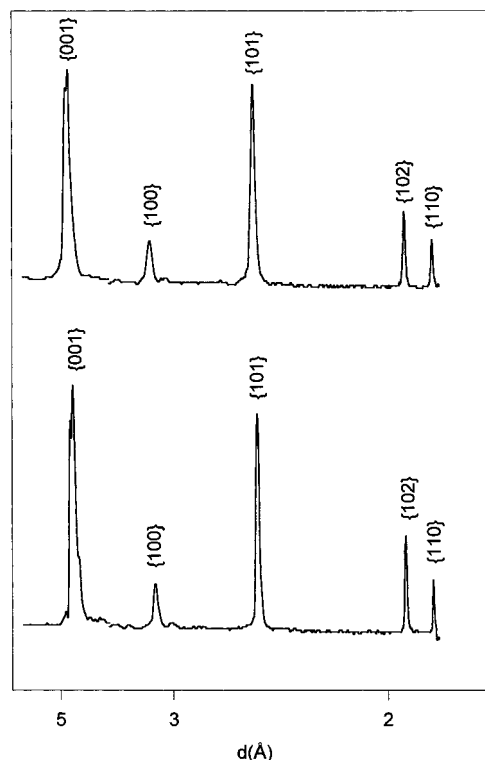
(17) Bayliss, P.; Erol, D. C.; Mrose, M. E.; Sabina, A. P.; Smith, D. K. *Mineral Powder Diffraction File. Data Book*; International Centre for Diffraction Data: Swarthmore, PA, 1986; Tables 4-733, 938 and Tables 5-586, 172.

Figure 3. X-rays diffractograms of Ca(OH)$_2$ crystals prepared from homogeneous phase at 90 °C (top) and comparison with commercial Ca(OH)$_2$ microparticles (bottom).
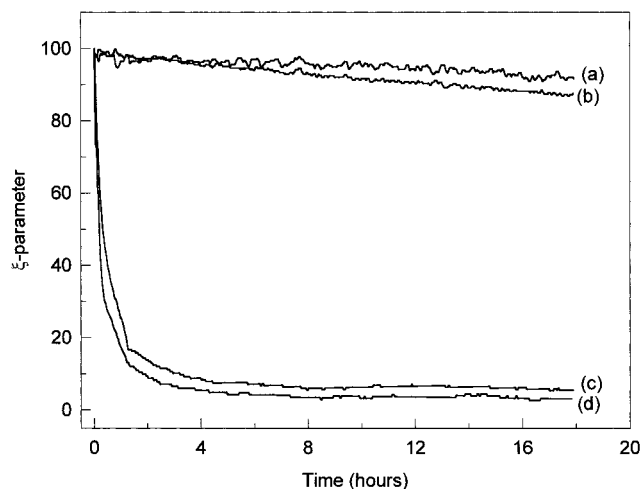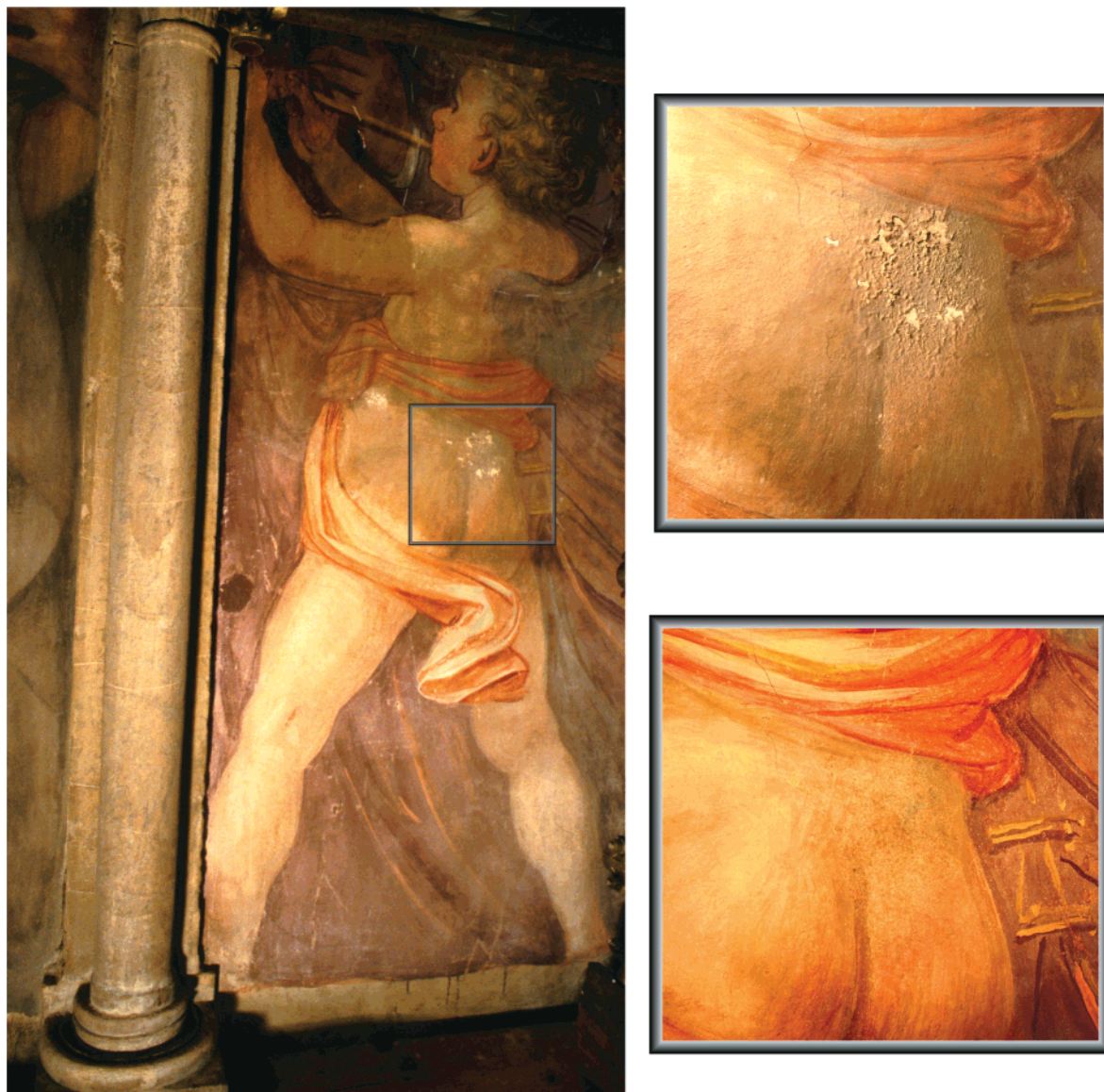

Figure 4. Behavior of the stability parameter ξ for dispersions of Ca(OH)$_2$ colloidal particles and microparticles in water and propan-1-ol: (a) colloidal particle/propan-1-ol, (b) microparticle/propan-1-ol, (c) colloidal particle/water, and (d) microparticle/water.

values range from 0 (complete sedimentation, unstable dispersion) to 100 (no settling of the particles, perfect kinetic stability of the dispersion).[14] In particular, Figure 4a,b refers to dispersions in propan-1-ol, while Figure 4c,d refers to dispersions in water. Submicrometer dispersions are more stable than microparticle ones ($\xi_{(a)} > \xi_{(b)} \gg \xi_{(c)} > \xi_{(d)}$) both in propan-1-ol and water. Water dispersions are consistently less stable than propan-1-ol ones, as indicated by the high slope of the initial portion of curves c and d. The ξ parameter for propan-1-ol dispersions decreases from 100 (value at the beginning of the settling process) to 92 ± 1 (colloidal particles) or to 87 ± 1 (microparticles) in 18 h, showing a good kinetic stability. Indeed, the difference between samples a and b (or samples

Figure 5. Example of application of $Ca(OH)_2$ platelike submicrometer crystals dispersed in propan-1-ol during the preconsolidation in the restoration of the wall paintings by Santi di Tito (16th century) *Gli Angeli Musicanti* on the Counterfaçade of the Santa Maria del Fiore Cathedral in Florence. The region labeled with the box is that treated with the particles: (top) before the restoration and (bottom) after the restoration.

Table 1. ξ' Values for the Four Dispersions Examined[a]

dispersion	ξ' value/hr^{-1}	time range/hr[b]
a	-0.30 ± 0.05	$0-18$
b	-0.60 ± 0.08	$0-18$
c	-105 ± 12	$0-0.5$
d	-138 ± 15	$0-0.5$

[a] The meaning of the labels is the same as in Figure 4. The error is the standard deviation over five measurements. [b] Range of time used to evaluate the slope ξ'.

c and d) is significant only for $t > 12$ h (a/b) or $t > 1.5$ h (c/d). For lower times, curves a and b (or curves c and d) of Figure 4 are practically identical in the limit of the experimental error. The slope ξ' of the curves reported in Figure 4 can be considered an indirect estimate of the particle settling rate. Table 1 shows the ξ' values for the four dispersions examined. Changing the continuous phase from water to propan-1-ol strongly decreased the rate of particle settling. An opposite behavior has been found for $Al(OH)_3$.[18] Further studies are in progress to determine

the mechanism of such an enhanced stability of $Ca(OH)_2$/propan-1-ol dispersions that seems common to other short-chain aliphatic alcohols.[19] Another feature deduced from Table 1 and Figure 4 is the dependence of the relative kinetic stability on the particle size. Reducing the particle size by a factor of ca. 10 produces a small increase of the dispersion stability. This means that the Stokes law for the sedimentation rate, that states a dependence of the settling rate on the square of the particle radius,[20] cannot be applied in our case. This can be mainly attributed to (i) a nonspherical shape of the particles,[20,21] (ii) the roughness and porosity of the particle surface,[22,23] and (iii) the high concentration of the dispersions.[24]

Finally, the dispersions in propan-1-ol have been used to restore a degraded region of some 16th century wall

(18) Romo, L. A. *Discuss. Faraday Soc.* **1966**, *42*, 232.

(19) Giorgi, R. Unpublished results, Chemistry Degree Thesis, University of Florence, Florence, Italy, 1996.

(20) Kissa, E. *Dispersions. Characterization, Testing, and Measurement*; Surfactant Science Series, Vol. 84; Marcel Dekker Inc.: New York, 1999; Chapter 9.

(21) Hostomsky, J.; Halász, Z.; Liszi, I.; Nyvlt, J. *Powder Technol.* **1986**, *49*, 45.

paintings in the Cathedral of Florence. In particular, they were applied according to a conservation methodology[10,25] recently developed in our laboratories on the painted surface of the wall, to re-adhere detached paint layers on the wall substrate. The particles synthesized at 90 °C gave the most stable dispersions (Figure 4a), and they were therefore chosen as the fixative material for the wall paintings decorating the Counterfaçade of Florence Cathedral. The colloidal particles granted higher penetration into the painted surface layers than the usual microparticles. Moreover, the high kinetic stability of the dispersions in propan-1-ol enabled avoiding sedimentation of the particles onto the painted surfaces. This is very important in wall painting restoration, because a fast sedimentation of the lime dispersion can produce an irreversible white glazing on the painted surfaces. Finally, our colloidal particles are submicrometer platelike crystals, that are known to determine some important properties of lime-putty-based mortars.[26] In particular, these small platelike particles present a superior behavior for fresco conservation concerning, for example, a great capacity to adsorb water, that is fundamental to ensure a good carbonatation process.[26] Figure 5 shows the wall painting selected for the experiment and the region where the colloidal particles were tested as a new consolidant material. The particles are very efficient in re-adhering the lifted paint layers, and the final result was highly satisfactory.

Conclusions

The present study showed that Ca(OH)₂ colloidal particles can be easily synthesized in aqueous media working at 90 °C and at high degrees of supersaturation. The particles obtained by this method are crystalline, hexagonally (prismal) shaped, with hexagon sides in the range 100−300 nm and thickness of 2−40 nm. AFM measurements in air and in the liquid phase (propan-1-ol) showed that the particle surface is quite rough and that both the morphology and the dimensions of the particles are not affected by the particle/environment interface (solid/gas or solid/liquid).

The obtained Ca(OH)₂ submicrometer crystals were used to prepare dispersions in water and propan-1-ol to be applied in wall painting restoration. It was found that water dispersions are highly unstable, while dispersions in propan-1-ol show a consistent stability enhancement. Furthermore, the Ca(OH)₂ particles synthesized in the present work are more stable than the dispersions of commercial Ca(OH)₂ microparticles.

The Ca(OH)₂ platelike crystals dispersed in propan-1-ol were applied, instead of organic glues, as fixatives to re-adhere lifted paint layers during the restoration of the wall paintings by Santi di Tito in the Cathedral of Florence. The results achieved were highly positive. Paper deacidification using these dispersions is under investigation. Preliminary investigations on 15th century manuscripts show an excellent performance.

LA010269B

(22) Dynys, F. W.; Halloran, J. W. *J. Am. Ceram. Soc.* **1983**, *66*, 655.

(23) Hietala, S. L.; Smith, D. M. *Powder Technol.* **1989**, *59*, 141.

(24) Kaye, B. H. *Direct Characterization of Fine Particles*; Chemical Analysis Series, Vol. 61; John Wiley: New York, 1981.

(25) Baglioni, P.; Dei, L.; Ferroni, E.; Giorgi, R. Italian Patent No. FI/96/A/000255, October 31, 1996.

(26) Rodriguez-Navarro, C.; Hansen, E.; Ginell, W. S. *J. Am. Ceram. Soc.* **1998**, *81* (11), 3032 and references therein.