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Synthesis and X-Ray Diffraction Analyses of Calcium Hydroxide Nanoparticles in Aqueous Suspension

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ABSTRACT

Calcium hydroxide nanoparticles in aqueous suspensions (also called *nanolime*) were successfully employed in Cultural Heritage conservation thanks to the ability of favoring re-adhesion of the pictorial layer on original carbonatic substrates or allowing to a better superficial cohesion and protection of treated stones. In this work, we have synthesized nanolime particles in aqueous suspension by two different methods. The produced particles were characterized in the laboratory, in terms of structural and morphological features, by means of X-Ray diffraction powder (XRD) and by transmission electron microscopy (TEM), respectively. Nanoparticles were crystalline, regularly shaped, hexagonally plated and with side dimensions generally ranging from 300 nm to 30 nm or less. Crystal structure of nanolime particles directly in the aqueous suspension, has been also analyzed by synchrotron diffraction from X-ray synchrotron radiation (SR-XRD); data have been analyzed by means of the Rietveld method and we have investigated the structure of $Ca(OH)_2$ particles in suspension in terms of cell parameters, atomic coordinates, bond lengths and angles.

Keywords: Nanoparticles; Calcium Hydroxide; Crystal Structure; X-Ray Diffraction; Crystal Morphology

1. Introduction

Calcium hydroxide ($Ca(OH)_2$), has been largely employed thanks to the well-known carbonation reaction and to the characteristics of the calcium carbonate ($CaCO_3$) obtained. The low solubility and the compatibility between the latter compound and material substrates offer a favorable use in many lime-based superficial conservative treatments [1]. In all its applications, a high reactivity is of paramount importance, so that $Ca(OH)_2$ particles with sub micrometric dimensions (*nanolime*) have been recently successfully employed on Cultural Heritage conservation, offering the possibility to penetrate deep into damaged zones (less limitations due to the particle size), high reactivity and fast reactions (such as carbonatation), high purity and defined composition [2-4 and refs. therein]. Nanolime is typically synthesized by a chemical precipitation process in supersaturated aqueous solutions of reactants; in particular, the method starts from aqueous sodium hydroxide solution (NaOH) added drop by drop in an aqueous calcium chloride ($CaCl_2$) solution, maintained at high temperature [5 and refs. therein].

The synthesis allows to obtain $Ca(OH)_2$ nanoparticles directly in suspension, as they are used in the applications. It is fundamental to verify that the obtained nanoparticles, very reactive thanks to their dimensions, don't show the carbonatation process inside the suspension, but only during the applicative use, when the solvent is completely evaporated.

The aim of this work has been to synthesize $Ca(OH)_2$ nanoparticles by different methods and to compare the obtained results, in terms of structural features of the particles both in the aqueous suspension and after the solvent was completely evaporated. In particular, two nanolime synthesis methods, reported in our previous works [2,6], have been followed. According to method (A), synthesis has been carried out by adding (*drop by drop*) an aqueous NaOH solution into a $CaCl_2$ one, maintained at 90˚C. According to method (B), a surfactant agent (Triton X-100) was previously added to the two initial aqueous solutions that were later mixed *simultaneously*, at the fixed temperature of 90˚C. The method (B) allows to obtain $Ca(OH)_2$ nanoparticles easily and drastically reducing the time of synthesis. In fact, especially if tenths of grams were prepared, we passed

from several hours for the *drop by drop* method to few minutes; this difference in time scales with the quantity of the preparation, allowing us to scale-up the nanolime production only when the method (B) is followed.

The morphology and particles size have been investigated by transmission electron microscopy (TEM).

We have investigated the phases formed after the synthesis procedure, by means of X-ray diffraction powder technique (XRD). The XRD diffraction is a powerful, non-destructive and useful technique that allow to quickly analyze unknown materials, in terms of crystallinity and phases identification, and to perform materials characterization in many scientific fields such as engineering, metallurgy, mineralogy, sciences, archeology, etc. The great advantages of this technique are: the simplicity in sample preparation, the rapidity of measurement, the ability to analyze mixed phases, the structure determination directly in laboratory. In particular, XRD technique can easily allow to investigate the reactivity, in terms of carbonatation process efficiency, of the produced calcium hydroxide nanoparticles. For this reason, we have considered different agglomeration conditions of the nanoparticles (that could strongly influence the carbonatation process) partially substituting water with 2-propanol, as disagglomerating agent [2]. In particular, for each method, four nanolime suspensions were prepared, characterized by different residual water contents in the precipitated phase.

We have also investigated the $Ca(OH)_2$ nanoparticles crystalline structure directly in aqueous suspension by using synchrotron radiation at the European Synchrotron Radiation Facility (ESRF)-Grenoble, France. In fact, the high energy and high flux of this source allowed diffraction measurements in transmission of the particles inside the aqueous medium. X-ray synchrotron diffraction data have been analyzed by means of the Rietveld method and we have investigated the structure of $Ca(OH)_2$ particles in suspension in terms of cell parameters, atomic coordinates, bond lengths and angles.

2. Experimental Details

2.1. Synthesis of $Ca(OH)_2$ Nanoparticles

Calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$), sodium hydroxide (NaOH) and 2-propanol pro analysi products, supplied by Merck, have been used without further purification. In case of method B) polyoxyethylene (10) tertoctylphenyl ether, Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_{10}$), a high-purity, water-soluble, liquid, non-ionic surfactant, purchased from Fluka has been used too. Water has been purified by a Millipore Organex system ($R \geq 18$ MΩ cm).

Method (A). We have prepared two different aqueous solutions of 100 ml, containing 0.3 mol/l of $CaCl_2{\cdot}2H_2O$ and 0.6 mol/l of NaOH respectively. The NaOH alkaline solution (used as precipitator) has been added *drop by drop* into the $CaCl_2$ solution (speed ≈ 4 ml/min, temperature of 90˚C). After about 24 hours two distinct phases have been observed, a limpid supernatant solution and a white precipitated phase; to remove the NaCl produced, several deionised water washings have been performed. Aqueous nanolime suspension (with a $Ca(OH)_2$ concentration of 10 mg/ml) has been defined as sample **A**.

Method (B). (4.00 ± 0.02) g of Triton X-100 has been previously added to the initial aqueous solutions containing 0.3 mol/l of $CaCl_2{\cdot}2H_2O$ and 0.6 mol/l of NaOH respectively (each solution was 100ml in volume). These initial solutions have been then mixed together *simultaneously*, at the temperature of 90˚C. A suspension of 200ml of final volume has been obtained, characterized by a $Ca(OH)_2$ concentration of 10 mg/ml (sample **B**). As in method (A), we have performed several deionised water washings to remove the NaCl produced and the surfactant too.

For both the methods, different residual water contents were considered preparing four samples, named A_{100}, A_{75}, A_{50}, A_{25}, B_{100}, B_{75}, B_{50}, B_{25}, respectively: the subscript represents the percentage of water content in each sample.

2.2. Characterization of $Ca(OH)_2$ Nanoparticles

By TEM technique (*Philips CM* 100), the dried particles morphology of the samples under study have been analyzed; measurements have been performed on the samples dried under vacuum, following the common procedure.

As concerns XRD measurements (*Philips X'Pert PW* 1830), performed in our laboratory to determine the crystalline degree and the phases of the formed particles, the sample was prepared maintaining each aqueous suspension for 20' in ultrasonic bath (US) and then depositing 0.2 ml of the suspension itself on a silica sample holder; measures were performed on dry sample, in laboratory conditions (T = 20˚C, relative humidity RH = 40%). Each experimental diffraction spectrum has been elaborated by a Profile Fit Software (*Philips PROFIT v*.1.0) and each crystalline phase has been attributed by JCPDS patterns; the ratio between the calcium carbonate peaks area and the spectrum total area has been assumed as the carbonatation process efficiency (*yield*).

Crystal structure of the nanolime particles directly in aqueous suspension has been investigated by SR-X ray measurements on GILDA (BM08) beamline at ESRF; the patterns were collected in Debye-Scherrer geometry on a 2D image plate detector. The experiment was performed at an incident beam wavelength of $\lambda = 0.7277$ Å and the sample-to-detector distance adjusted to obtain data within the 6˚ - 53˚ 2θ-angle range. Data were collected from 0.2

ml of aqueous suspension sealed within a cell with Kapton windows, mounted on a rotating sample holder in order to avoid deposition of the nanoparticles during the measurement, to make a good average of the structural characteristics of the particles in suspension and to improve statistics. Patterns of water alone and Triton X-100 have been also collected to consider their contribution to the background in aqueous $Ca(OH)_2$ suspensions spectra. Data have been collected on a 2D image plate and integrated, after standard calibration and corrections, to obtain I(2θ) data, then analyzed by Rietveld method (FullProf package [7]). $Ca(OH)_2$ structural refinements have been performed considering the P-3 m1 space group, taking ICSD data as initial values [8]. We have refined zero point, scale factor, cell parameters, bond lengths and angles, Debye Waller factors and preferred orientation parameters. By Rietveld analysis we have also determined the coherent domain size for each considered sample. In particular, the average apparent size has been calculated using the different reciprocal lattice vectors as reported in Fullprof manual [7].

3. Results and Discussion

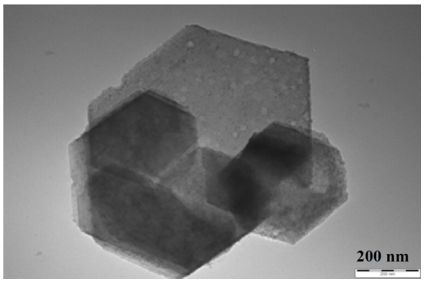
From TEM measurements, here we have reported some images taken as representative micrographs for each sample analyzed.

In particular, in **Figure 1(a)** TEM images on sample **A**, showed as the particles appear hexagonally plated and regularly shaped with side dimension up to 400 nm, as reported in our previous work [4]. As concerns sample **B** (**Figure 1(b)**), characterized by the presence of a surfactant content that could be not completely removed by washings, we have observed that some particles have the side dimension of about 100 - 150 nm; moreover, many particles with diameter less than 20 nm have been observed too.

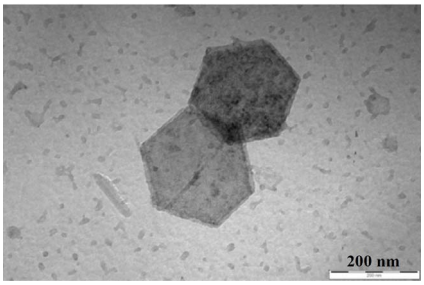
The results obtained by TEM images, could be explained considering that the surfactant can affect the nanolime formation. It could be supposed that, during the growth of the nanolime crystals, the molecular units of the surfactant stick on the surface of the crystals by weak forces; they gradually could form a film that prevents the growth of the formed crystals.

XRD spectra, in relation to the different water content in the nanolime suspension, have been reported in **Figure 2** while in **Table 1** we have reported the results of the estimated yield values (T = 20˚C, RH = 40%).

From **Table 1**, we have observed that water play an important role in the carbonatation process; in fact, samples characterized by water percentage ≤ 50% show the lowest *yield* values. Moreover, as concerns the sample without the surfactant (sample **A**), 2-propanol seems to improve disagglomeration of the particles, and so a higher specific surface, so favoring the carbonatation up to

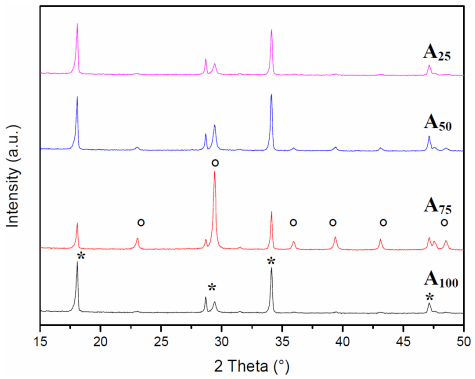


(a)

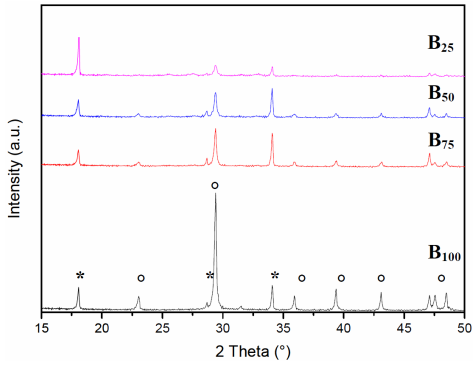


(b)

Figure 1. TEM micrographs on: (a) sample A—$Ca(OH)_2$ particles, hexagonally plated and regularly shaped, with side dimension up to 400 nm [4]; (b) sample B—many particles with dimension < 20 nm were observed together with few particles of side dimension up to150 nm.



(a)



(b)

Figure 2. XRD patterns of the aqueous nanolime suspensions after 30 minutes of air exposition time: (a) sample A; (b) sample B. Legend: $^{*}Ca(OH)_2$; $^{\circ}CaCO_3$

Table 1. Yield values estimated by XRD measurements in relation to different residual water content of nanolime suspensions synthesized without or with the surfactant agent (samples A and B, respectively).

Nanolime suspension	Sample	Residual water content (%)	2-propanol (%)	Yield (%)
A	A_{100}	100	-	50
	A_{75}	75	25	80
	A_{50}	50	50	33
	A_{25}	25	75	15
B	B_{100}	100	-	80
	B_{75}	75	25	60
	B_{50}	50	50	50
	B_{25}	25	75	30

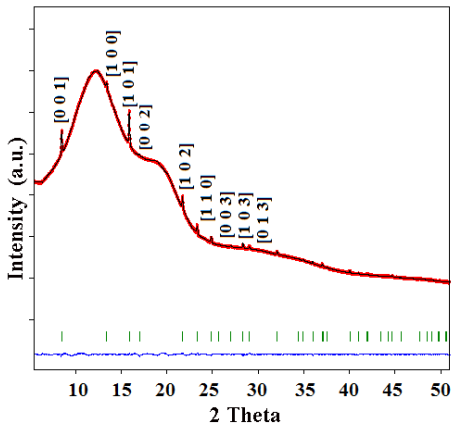
80% (sample $\mathbf{A_{75}}$).

On the contrary, in sample **B** (where the surfactant is present), all the carbonatation *yield* values were probably higher due to the particles decreasing, as confirmed by TEM investigation (**Figure 1**). Nevertheless, this tendency was not observed in sample $\mathbf{B_{75}}$, as if the alcohol ability to disagglomerate the nanoparticles was reduced by the presence of the surfactant.

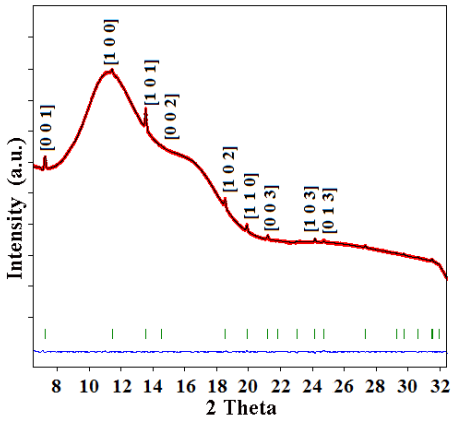
Analysis of the SR-XRD data allows us to determine that the $Ca(OH)_2$ nanoparticles don't show the carbonatation process inside the suspension. Besides, we have determined the structural parameters of the $Ca(OH)_2$ crystals in aqueous suspensions synthesized by the two different methods, in terms of cell parameters, atomic coordinates, interatomic distances and bond angles, Debye-Waller factors, preferred orientation of crystallites and average grain dimension. We have used the pseudo-Voigt profile function of Thompson, Cox and Hastings [9] in order to fit the peak shapes. The instrumental contribution to peak broadening was determined measuring a diffraction pattern of a LaB6 sample in the same geometry of the samples [10].

SR-X ray diffraction patterns for samples **A** and **B**, refined with Rietveld method, have been reported in **Figure 3** as an example of the quality of the refinement that can be appreciated from the spectra-difference (in blue) between the measured spectra (in red) and the calculated spectra (in black); the green lines indicate the Bragg reflections. The most intense peaks have been indexed and we observed that only the $Ca(OH)_2$ crystalline phase is stably present in suspension, with the main Bragg reflection attributed to (101) peak (d_{101} = 1.33 Å) and it can be described in the space group P-3 ml.

In **Table 2**, structural results have been reported, considering the comparison between samples **A** and **B**, respectively. In particular, cell volumes in sample **B** ap-peared smaller respect to those relative to sample **A**; this result can be explained considering that the addition of surfactant tends to favor, in aqueous suspension, smaller calcium hydroxide cell volume. As concerns Ca-O and O-H distances and bond angles, they were not influenced by the synthesis method.



(a)



(b)

Figure 3. SR-X ray diffraction patterns refined with Rietveld method; (a) sample A; (b) sample B. The difference between the measured spectra (red line) and the calculated ones (black line) is reported in blue line; the green lines indicate Bragg reflection.

Finally, by Rietveld analysis [7] we have also determined the average apparent size for each considered sample. Calculating, for each reflection, the coherent domain size, we have found average values of 147.6 (1) nm (sample **A**) and 92.94 (4) nm (sample **B**), showing sub

Table 2. Cell parameters and volume, interatomic distances and bond angles of $Ca(OH)_2$ particles in aqueous suspendsion, synthesized without and with the addition of the surfactant.

	Sample **A**	Sample **B**
a (Å)	3.599 (1)	3.588 (1)
b (Å)	3.599 (1)	3.588 (1)
c (Å)	4.917 (3)	4.906 (3)
Volume	55.16 (4)	54.69 (4)
Ca-O distance (Å)	2.5 (1)	2.43 (8)
O-H distance (Å)	1.9 (3)	1.9 (2)
O-Ca-O angle (˚)	94 (4)	95 (3)
H-Ô-H angle (˚)	33 (1)	37 (9)

microcrystalline phases, in particular for the sample synthesized by the addition of surfactant.

4. Conclusions

The present work was focused on a new synthesis of $Ca(OH)_2$ nanoparticles, in aqueous suspensions, by adding a surfactant agent in the initial reactants, so obtaining very small particles easily and reducing drastically the time needful for preparation. We have studied $Ca(OH)_2$ nanoparticles, synthesized in our laboratory, in terms of structural and morphological features, by means of X-Ray diffraction powder (XRD) and by transmission electron microscopy (TEM). The $Ca(OH)_2$ nanoparticles, studied also in terms of the carbonatation process by XRD, appeared crystalline, hexagonally plated and regularly shaped, with dimensions ranging from 300 nm to 30 nm or less.

By means of synchrotron radiation (SR-XRD) we have studied the structure of the $Ca(OH)_2$ nanoparticles directly in aqueous suspension. From Rietveld refinement of SR-X ray diffraction data, we have found that the addition of surfactant during the synthesis tends to reduce the cell volumes of $Ca(OH)_2$ particles in aqueous suspension.

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