Synthesis and study of a well crystallized $CaCO_3$ vaterite showing a new habitus

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Synthetic $CaCO_3$ vaterite obtained by classical routes consists of shapeless particles. However, owing to their small size (50 nm), the particles tend to agglomerate strongly, thus resulting in spherical packs of 3 μm average diameter. Transmission electron microscopy studies of isolated particles are therefore very difficult to achieve without submitting these aggregates to treatments that could affect their structural and textural features. We have synthesized pure vaterite particles which do not exhibit this agglomeration phenomenon but present a clearly defined habitus (size, shape, texture). It is therefore possible to prepare microcrystalline monolithic hexagonal platelets of vaterite in the micrometre range that exhibit very good crystallinity. In addition, we have carried out an IR study of this pure vaterite and an assignment of the different absorption bands is proposed, in comparison with the two other $CaCO_3$ modifications.

Calcium carbonate exists in three distinct crystallographic varieties. The least stable form, vaterite, is generally synthesized by direct precipitation.[1] This form crystallizes in either an orthorhombic[2] or a hexagonal cell.[3] In general, these particles do not show very well defined morphologies and they agglutinate to form spherical aggregates.[1] The second form, aragonite, is obtained by hydrolysis of a trichloroacetate salt,[4] by the mixing of boiling solutions of a calcium salt with an alkali-metal carbonate[5] or by bubbling CO_2 through different solutions such as aq. $Ca(OH)_2$.[6,7] This variety crystallizes in the orthorhombic system and the corresponding particles appear in the form of polyhedral sticks (40 μm length, 3 μm diameter). Finally, the stable form, calcite, crystallizes in the trigonal system[8] and is obtained by direct precipitation. In this case, the particles appear as foliated cubes of diameter 10 μm.[7]

Some groups have reported the possibility of synthesizing vaterite by modifying the initial synthesis method of calcite.[9,10] In parallel, by modifying the synthesis method of aragonite proposed by Rao and Yoganarasimhan,[4] we prepared pure vaterite with a very high crystallinity and a quite specific habit.

Method of synthesis

Calcium carbonate in the calcite form (Prolabo, 5 g) was dissolved in an aqueous solution of 17 g of trichloroacetic acid (Prolabo). The slightly acidic solution was then filtered and the surfactant hydroxyethylidene-1,1-phosphonic acid (HEDP, Aldrich) was added to the solution. The HEDP concentration in the solution was about 10^{-8} mol dm^{-3}. The solution thus obtained was heated under reflux at 95 °C. An ultrasonic processor horn (Vibracell VC 375) was immersed in the solution during the heating step. The reaction was stopped as soon as the solution became slightly milky. After filtration, the precipitate was washed with doubly deionised water. Finally, the recovered white solid powder was dried at room temperature for 24 h.

Characterization

X-Ray diffraction study

The X-ray diffraction patterns were collected on a Philips PW 1710 diffractometer (Cu-Kα back monochromator). Careful evaluation of the peak positions was carried out with a fitting program available in the PC software DIFFRAC-AT, and least-square refinements from observed data with the computer programs DICVOL91[11] and NBS*AIDS83.[12]

The XRD pattern of synthetic vaterite (Fig. 1) is very similar to the patterns of vaterite samples prepared *via* classical routes. Since the cell parameters were known approximately,[3] a least-squares refinement from the observed data was carried out which led to the figures of merit[13,14] $M_{15}=13.8$ and $F_{15}=9.5$ (0.025, 63) for cell parameters $a=7.169(4)$, $c=16.98(1)$ Å and space group $P6_3/mmc$. The XRD data are listed in Table 1.

Electron microscopy studies

In order to carry out scanning electron microscopy studies, the samples were coated with a thin gold film. The electron micrographs were taken with a Philips SEM 505 scanning electron microscope operating at an accelerating voltage of 30 kV. For transmission electron microscopy studies, the samples were dispersed in butan-1-ol under ultrasonic waves and then deposited on a carbon film supported by a copper grid. The microscope used was a JEOL 200CX operating at 200 kV.

Scanning electron microscopy. The vaterite obtained in this work is shown in Fig. 2 together with, for comparison, the morphology of the classical vaterite composed of agglomerates which consist of small elemental grains that are not easily dispersible [Fig. 2(*a*)]. The vaterite synthesized by the new method appears as hexagonal platelets of 1–2 μm in diameter

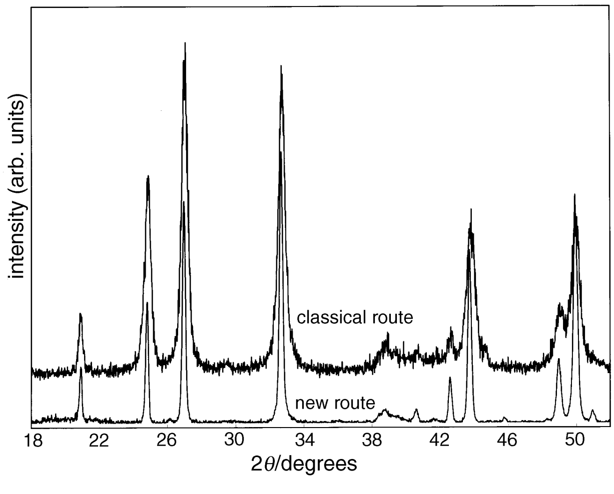

Fig. 1 XRD pattern of different synthetic vaterites

Table 1 XRD data for vaterite synthesized by the new route

h	k	l	d_{obs}/Å	$2\theta_{obs}$/degrees	$2\theta_{calc}$/degrees	$\Delta 2\theta$/degrees	I_{obs}
0	0	4	4.254	20.866	20.911	−0.044	20
1	1	0	3.591	24.775	24.821	−0.046	43
1	1	2	3.307	26.940	26.980	−0.040	81
1	1	4	2.741	32.646	32.673	−0.027	100
2	1	1	2.327	38.669	38.708	−0.039	6
2	0	5	2.287	39.373	39.293	0.081	<1
1	1	6	2.223	40.555	40.585	−0.030	6
2	1	3	2.167	41.640	41.633	0.007	2
0	0	8	2.122	42.565	42.561	0.004	17
3	0	0	2.070	43.697	43.707	−0.010	64
3	0	4	1.860	48.923	48.927	−0.004	25
1	1	8	1.826	49.906	49.896	0.010	84
2	2	0	1.792	50.924	50.912	0.012	5
2	0	8	1.752	52.165	52.165	0.000	2
2	2	4	1.650	55.644	55.622	0.021	22

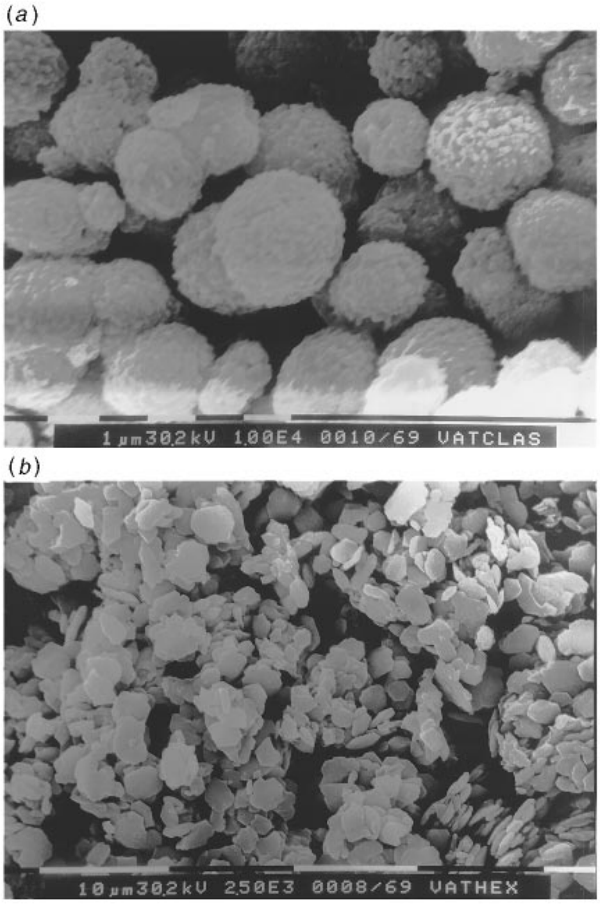

Fig. 2 Morphology of vaterite (*a*) prepared by the classical route; (*b*) prepared by the new route

and 0.5 μm in thickness [Fig. 2(*b*)]. These particles do not aggregate like those obtained from classical methods, thus making possible their characterization by transmission electron microscopy.

Transmission electron microscopy. For vaterite prepared by the classical route, it is impossible to obtain a clear single-crystal electron diffraction pattern. Ultrasonic treatment is not able to desegregate the small particles (Fig. 3). Moreover, mechanical treatments are prohibited in this case since grinding is known to induce phase transitions in the calcium carbonate system.[15]

The electron diffraction pattern observed on an isolated particle prepared with our method shows hexagonal symmetry [Fig. 4(*a*)]. The diffraction spots are points, indicating that the particles are monocrystalline and monolithic. According to the indexation of the electron diffraction pattern, using the X-ray results, the particles are lying on the (001) plane. No extra spots, indicating the presence of other polymorphic varieties or the transition from vaterite to calcite, are observed. The corresponding TEM image [Fig. 4(*b*)] shows the hexagonal platelet shape of the particles. This particle shape is similar to the single-crystal shape studied by Meyer.[3] The thickness of the particles was too large (5000 Å) to obtain sufficient contrast to enable a study of the synthetic vaterite by HREM.

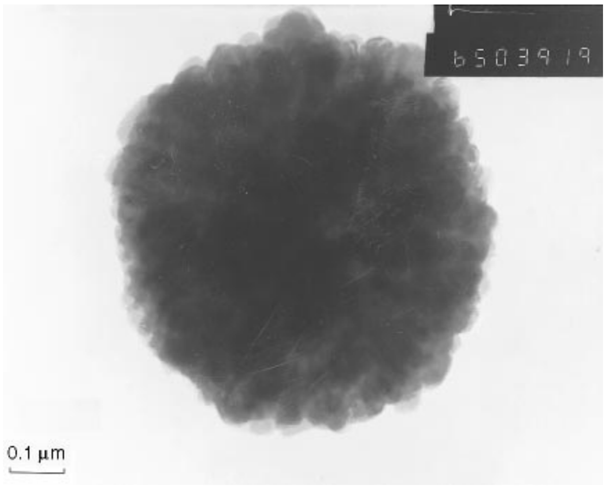

Fig. 3 TEM image of 'classical' vaterite after ultrasonic treatment

IR study

IR studies were carried out at room temperature with a Nicolet FFT 510 spectrophotometer running in transmission mode. Samples of vaterite were dispersed in a dried KBr matrix and pressed into solid discs. We were unable to find any published vaterite IR data. The absorption bands of the different crystallographic varieties are listed in Table 2.

We note an important displacement of the ν_4 band (Fig. 5), which seems to be characteristic of the vaterite form. In contrast, the vaterite ν_1 and ν_2 bands are similar to the corresponding calcite and aragonite bands.

Discussion

We have reported the synthesis of the last stable form of calcium carbonate by a combination of physical means (ultrasonic waves) and chemical means (surfactant). Such methods have been employed during a study of the effect of diphosphonates on the precipitation of calcite in aqueous solutions.[9]

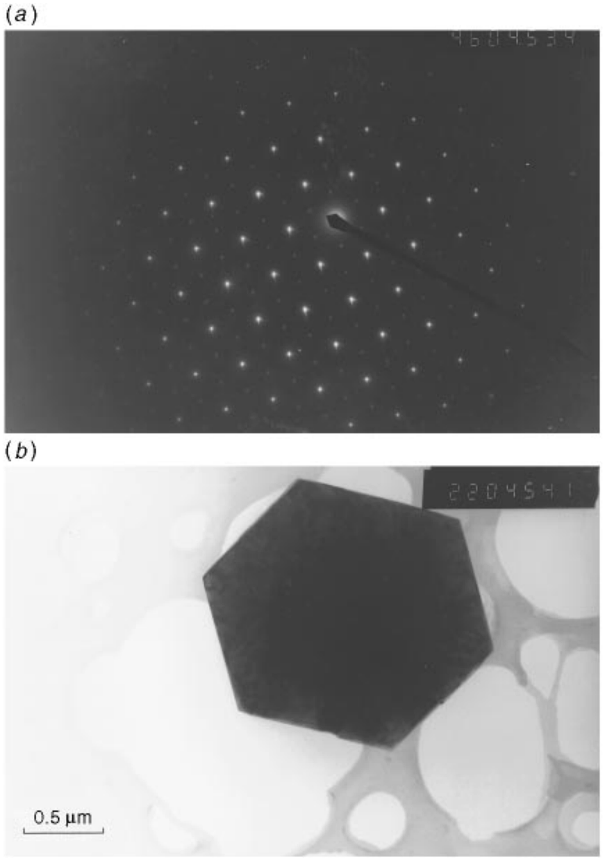

Fig. 4 (*a*) SAED realized on an isolated particle prepared *via* the new method. (*b*) TEM image of an isolated particle prepared *via* the new method.

Table 2 Assignment of the IR absorption bands of the three different calcium carbonates

	IR absorption band		
	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_4/cm^{-1}
vaterite[a]	1087	877	745
aragonite[b]	1080	866	706
calcite[b]	1080	879	706

[a]Experimental data (this work). [b]Ref. 16.

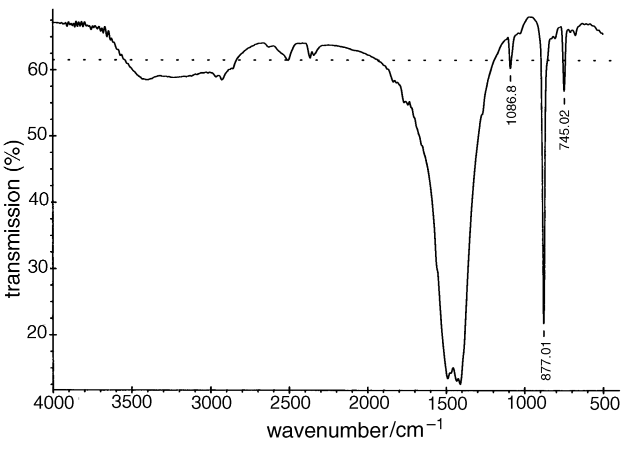

Fig. 5 IR spectrum of vaterite (new process)

Indeed, the HEDP caused a significant reduction in the rate of calcite formation. Moreover, the addition of this surfactant to the reaction medium also results in the stabilization of the initially metastable vaterite. In our studies, we have shown that by using a derived synthesis method for the metastable aragonite, it is possible to obtain similar results.

In general, the use of ultrasonic waves decreases the sizes of particles and makes the synthesis of some products easier. Cavitation effects induce the stirring of the medium, prevent agglomeration and thus allow the formation of regularly shaped particles.

In this synthesis of calcium carbonate, HEDP plays the dual role of surfactant and stabilizing agent. A surfactant acts as a surface-active species, preventing the agglomeration of particles and modifying the growth stage. In our case, this surfactant reduces the growth in some crystallographic directions, creating sharp edges and the hexagonal form of the platelets. A HEDP concentration of 10^{-8} mol dm^{-3} prevents the agglomeration of particles but does not stop the growth stage. Indeed, the particles observed are larger than those obtained by the classical route. If the concentration is $>10^{-7}$ mol dm^{-3}, the obtained product is a mixture of small unfaceted vaterite particles together with sticks of aragonite (Fig. 6), and if the concentration is $<10^{-8}$ mol dm^{-3}, the product is pure aragonite (Fig. 7). It is therefore very important to adjust the quantity of surfactant to direct the product of the reaction and thus to obtain pure vaterite.

HEDP is well known to stabilize the vaterite form of calcium carbonate. In the literature, vaterite stabilized by HEDP from the calcite synthesis method is obtained as 'spherulitic formations'[10] and is therefore not easily characterisable by trans-

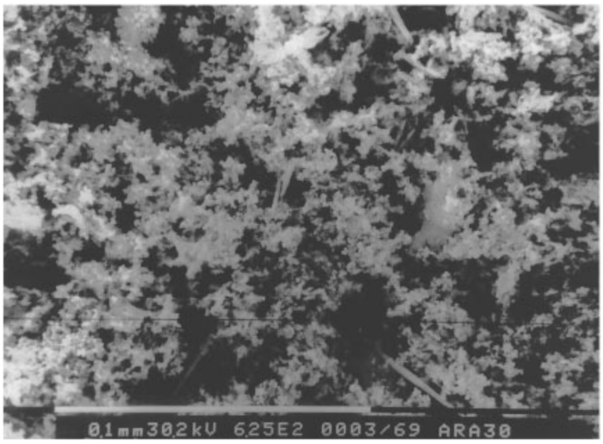

Fig. 6 SEM image of the product obtained with a HEDP concentration $>10^{-7}$ mol dm^{-3} (vaterite + aragonite)

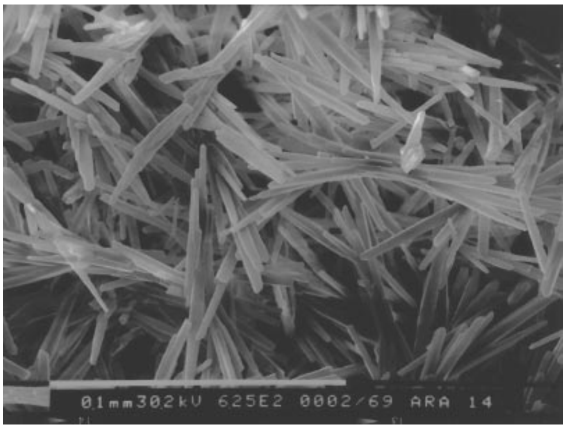

Fig. 7 SEM image of the product obtained with a HEDP concentration $<10^{-8}$ mol dm^{-3} (aragonite)

Table 3 Comparison of the X-ray diffraction pattern intensities for vaterite

	peak intensity (%)	
d_{obs}/Å	new route	classical route
4.254	20	20
3.591	43	34
3.307	80	100
2.741	100	95
2.327	6	11
2.287	<1	9
2.223	6	9
2.167	2	<1
2.122	17	15
2.070	64	48
1.860	25	22
1.826	84	49
1.792	5	
1.752	2	
1.650	22	

mission electron microscopy. The vaterite obtained from our derived aragonite method of synthesis does not exhibit this spherical shape. Moreover, if the quantity of polyphosphate is $>10^{-7}$ mol dm^{-3}, the presence of aragonite in the mixture indicates that HEDP does not stabilize only the vaterite form. In this case, HEDP is only a crystal-growth poison. This fact may be explained by the following hypothesis: in the case of calcite formation reported in the literature, the initial seed of calcium carbonate in the medium is in the vaterite form, and if HEDP is added, the vaterite form continues to grow and there is no transition from vaterite to the calcite form. In the case of the modified Rao method, the initial seed without HEDP must be a mixture of the two metastable forms. Without addition of polyphosphate, the vaterite seeds transform to aragonite. The use of HEDP in the appropriate proportion allows the precipitation of only the initial vaterite seeds. The use of too much surfactant decreases the sizes of the particles but does not stop the transformation of vaterite to aragonite.

The change in the morphology of the particles should lead to the appearance of preferential orientations that should be observed on the X-ray powder diffraction patterns. In fact, vaterite which grows in spherical clusters of particles (*e.g.* which must show all the crystallographic directions) now crystallizes in hexagonal platelets on the (001) plane. Therefore, the (00*l*) Bragg peaks should be higher in intensity, but we do not observe this feature (Fig. 1). Comparison of the X-ray diffraction peak intensities for the different synthetic vaterite batches does not show a significant change in the Bragg peak intensities (Table 3). To explain this fact, we must base our argument on the SEM results rather than on the TEM results. Indeed, from a morphological point of view, although the particles of the new synthetic vaterite show a specific shape and lie individually on the (001) plane [Fig. 4(*b*)], a set of particles describes all the crystallographic directions [Fig. 2(*b*)] as in the case of vaterite prepared by the classical route. Since the particles describe all the crystallographic directions, we do not observe any preferential orientation and the X-ray powder diffraction intensities are quite similar in both cases.

Conclusions

The combined effects of ultrasonic waves and polyphosphate allow us, by modifying an initial aragonite method of synthesis, to obtain pure vaterite showing a new specific morphology (hexagonal platelets). Indeed, a hexagonal symmetry of particles has been observed with other carbonates (*e.g.* lead carbonate). Moreover, we have shown that this change in morphology does not alter the reflection intensities on the X-ray diffraction patterns. The platelets are too thick to obtain contrast on a HREM image. However, further studies have been undertaken to decrease the platelet thickness while preserving their well defined hexagonal morphology.

References

1 P. Davies, D. Dollimore and G. R. Heal, *J. Thermal Anal.*, 1978, **13**, 473.
2 R. W. G. Wyckoff, *Crystal Struct.*, 1964, **2**, 364.
3 H. J. Meyer, *Z. Kristallogr.*, 1969, **128**, 183.
4 M. S. Rao and S. R. Yoganarasimham, *Am. Mineral.*, 1965, **50**, 1489.
5 R. B. Gammage and D. R. Glasson, *J. Colloid Interface Sci.*, 1976, **55**, 396.
6 Y. Kitano, K. Park and D. W. Hood, *J. Geophys. Res.*, 1962, **67**, 4873.
7 A. Girou, *Génèse Expérimentale et Naturelle des Carbonates de Calcium (étude bibliographique)*, Institut Français du Pétrole, 1975.
8 J. Bernard, *Nouv. Traité Chim. Minér.*, 1958, **4**, 514.
9 A. G. Xyla and P. G. Koutsoukos, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 1477.
10 A. G. Xyla, E. K. Giannimaras and P. G. Koutsoukos, *Colloids Surf.*, 1991, **53**, 241.
11 A. Boultif and D. Louër, *J. Appl. Crystallogr.*, 1991, **24**, 987.
12 A. D. Mighell, C. R. Hubbard and J. K. Stählick, NBS*AIDS80: a FORTRAN Program for Crystallographic Data Evaluation, *Natl. Bur. Stand. (USA)*, Tech. Note 1141, 1981. [NBS*AIDS83 is an expanded version of NBS*AIDS80].
13 P. M. de Wolff, *J. Appl. Crystallogr.*, 1968, **1**, 108.
14 G. S. Smith and R. L. Snyder, *J. Appl. Crystallogr.*, 1979, **12**, 60.
15 G. Martinez, J. Morales and G. Munuera, *J. Colloid Interface Sci.*, 1980, **81**, 500.
16 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1964.

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