Precipitation of Nanostructured Copper Oxalate: Substructure and Growth Mechanism

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The possibility of controlling materials properties by tailoring their substructure at the nanometer scale is a current topic of great interest. To do so, a fundamental understanding of the growth mechanism is of key importance and an analytical challenge as nanostructured materials are often produced by precipitation methods at high supersaturations where formation kinetics are fast. The current study focuses on the precipitation of copper oxalate, which has been previously shown to produce self-assembled ordered nanostructered particles with the promise of being able to tailor this nanometer substructure. In the current study we investigate in detail the growth mechanism and kinetics of precipitation by using in-situ particle size measurement or by stopping the reaction at various stages and using ex-situ methods. Combining the ex-situ methods of highresolution scanning electron microscopy, transmission electron microscopy, and X-ray powder diffraction along with the in-situ methods, we were able to follow the growth process from 2 min to 2 weeks. The results in the 2-30 min period lead to the proposal of a core-shell growth model with a poorly ordered core and a well-structured shell of nanosized crystallites (50-70 nm), adding support to the brick-by-brick model previously proposed for this phase of particle growth. Particle evolution over long periods up to 2 weeks show a ripening which produces lens-shaped particles that eliminate the "high" surface energy faces observed in the earlier stages of growth. A more complete growth mechanism for copper oxalate precipitation at moderate supersaturations is proposed similar to recent findings for other self-assembled nanostructured particles.

Introduction

The synthesis of tailored particles of specific size, structure, and morphology is a key factor in the further development of new materials in fields as diverse as catalysis, medicine, electronics, ceramics, pigments, and cosmetics.¹ Although micrometersized particles with various morphologies, such as spheres, rods, and cubes, can be obtained by the use of controlled precipitation conditions in the presence of additives,² the synthesis of such particles using the self-assembly of nanosized building blocks is still a challenge.³ This bottom-up approach provides a way to use the unique physical properties of the nanoscale primary particles to tune the physical and chemical properties of materials.⁴ By controlling the distance between the assembled particles, additional effects such as magnetic coupling can be achieved.⁴

In many cases presented in the literature, spherical particles are produced by chemical precipitation routes and the polycrystalline particles consist of randomly oriented nanocrystallites.^{5,6} Besides these spherical particles several examples of ordered assemblies of the primary particles exist. Particles showing such behavior are (NH₄)₃PW₁₂O₄₀,⁷ α -Fe₂O₃,⁸ barium sulfate,⁹ barium chromate,¹⁰ and copper and cobalt oxalates.^{11,12} The presence of additives seems to contribute greatly to the self-assembly,¹³ and hydrophobic/hydrophilic interactions are often cited as being the driving forces.⁹ In precipitation routes supersaturation, *S*, during the early stages is usually high as the electrical double layer is compressed and hence electrostatic repulsive barriers are low. This is expected to lead to the randomly oriented polycrystalline particles. Particles in a lower ionic strength solution may re-align themselves into a lower free energy state of the system before being fixed into place.¹⁴ Penn and Banfield have shown that some materials grow by an oriented attachment which is directed by the crystallographic structure to minimize the total free energy of the system,¹⁵ leading to either single crystals or well-organized nanostructures. Such growth mechanisms via aggregation or self-assembly are not often understood in detail, and to fully exploit nanostructured materials and to tailor their structures for novel applications, a better understanding of the growth mechanisms is needed.

For precipitation routes S plays an important role in the nucleus formation and the growth mechanism. For batch precipitation, used in most laboratory and exploratory work including the present study, S varies with time as the reactants create a solid phase. Different growth mechanisms may result from this changing state of S, as illustrated in Figure 1 for classical crystal growth, where different mechanisms dominate depending on S and the crystal size, r.

Point Z in Figure 1 is located in a region corresponding to an arbitrary initial S. The dotted line represents the "life history" of the crystals during their growth, the crystals moving along this path in the direction of the arrow. Very small crystals are formed in the beginning of precipitation and start growing. Although their size rapidly increases, S remains almost constant because the mass of solute deposited on the crystals is very small. A line almost parallel to the size axis therefore represents the initial portion of the life history. With increasing crystal size, the mass deposited on the crystals increases and S begins to fall. In this region, the precipitation process is represented by a curve. In the last stage of precipitation S decreases to its final value but the crystal size changes little, as here a large amount of mass is required to produce even a small increase in

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Figure 1. Precipitation map for BaSO₄. Controlling growth mechanism in the individual regions are as follow: (A) mononuclear or convection; (B) polynuclear or convection; (C) convection; (D) mononuclear or screw dislocation; (E) polynuclear or screw dislocation; (F) polynuclear; (G) diffusion; (H) mononuclear.¹⁶

crystal size. Therefore in this final stage the life history curve is almost parallel to the *S* axis. Thus during the course of their growth, crystals can pass through a number of regions representing different controlling mechanisms. Thus growth strongly depends on the structure of the material, the properties of the solution, the nature of the interface between crystals, and the surrounding solution and will be just as important for selfassembled or aggregation dominated growth of nanosized primary particles as for crystal growth by molecular attachment.¹⁷

Metal oxalates are interesting candidates for nanostructured particle synthesis. Besides the possibility to precipitate nonspherical nanostructured particles, the metal oxalates can be transformed to oxides or metals without losing the ordered structure.¹⁸ Copper oxalate has been shown to be ordered selfassembled particles with nanosized crystallites (20-70 nm), and a brick-by-brick growth mechanism was proposed.¹¹ The copper oxalate particle morphology can be modified using hydroxypropyl methylcellulose (HPMC) from a cushionlike morphology without polymer through cubes to elongated particles as the polymer concentration is increased. Also as the polymer concentration increases, the size of the primary particles decreases, and they become more elongated. The anisotropic shape is linked with a specific growth in the 001 direction attributed to a specific adsorption onto certain crystallographic faces. From the anisotropic nature of the crystal structure, ¹⁹ the crystallites and particles are expected to show two distinct types of surface either hydrophobic (ϵ) or hydrophilic (α).

In the final product, the amount of the adsorbed polymer corresponds to the geometrical external ϵ surfaces. This indicates that the particle assembly is governed by a dynamic mechanism of polymer adsorption and desorption. The transmission electron microscopy (TEM) results obtained for the nanostructures material showed an alignment of the nanocrystals parallel to the 110 direction, parallel to the stacking of the ...Cu(C₂O₄)... ribbons perpendicular to each other¹⁹ within the crystal structure. The above observations led the authors to propose the brick-by-brick growth mechanism. However all the measurements were made in ex-situ conditions on the final precipitate.¹¹ In the current study the kinetics and growth mechanism of copper oxalate precipitation have been studied in more

detail. We used high-resolution scanning electron microscopy (HRSEM) to investigate precipitates after the reaction was stopped for different aging times. Also in-situ particle size distributions measured by laser diffraction (PSD) were used follow the later stages of the particle growth. Complementary techniques were used to investigate the internal structure in detail such as cross-section transmission electron microscopy (TEM) and X-ray diffraction. Also the solution chemistry has been considered using a previously developed thermodynamic model.²⁰ With the information from these measurements a modified growth mechanism is proposed.

Experimental Section

Synthesis. All chemicals used were of analytical grade or highest purity available. Copper oxalate precipitates investigated throughout the present work was prepared as follows:

$$Cu^{2+} + 2NO_3^{2-} + 2Na^+ + C_2O_4^{2-} \leftrightarrow CuC_2O_4 \downarrow +$$

2(Na⁺ + NO₃⁻) (1)

The reactants, copper nitrate trihydrate (Merck 1.02753, p.a.) and sodium oxalate (Merck 1.06557, p.a.) were used without purification. The precipitates were prepared using 0.01 M solutions; both solutions were filtered through a 0.2 μ m membrane (RCN) before carrying out the precipitation experiments to avoid possible dust. A more detailed description of particle synthesis can be found elsewhere.^{11,18} The value of the initial supersaturation²⁰ is of the order of $S_r = \log(P_s/K_s)^{1/x} = 0.70$, where P_s is the ionic product, K_s is the solubility constant at 25 °C, and x is the number of the ionic species involved for the dissolution process (here assumed to be 2). For the reaction described in eq 1 cushionlike particles are formed. Cube shape particles were also investigated—prepared by adding 0.005 g/L HPMC 100 to the copper nitrate solution.¹¹

Particle Characterization. *Microscopy.* The evolution of the particle morphology from the initial stage of formation toward the final stage of precipitation was followed by filtration through 20 nm ceramic membrane (Whatmann) for different reaction times (2, 8, 12, 15, 30, and 60 min and 2 weeks). The samples on the ceramic membrane were investigated using HRSEM XL 30-FEG Sirion (FEI, Eindhoven, The Netherlands) operating at 3 kV, with a working distance of 5 mm and a spot size of 3. The samples were analyzed without any further special treatment such as gold coating, to avoid visual artifacts.

Copper oxalate particles with both cushionlike and cubic morphology were analyzed using cross-section TEM. The crosssection was obtained by ultramicrotomy. The dry powder of copper oxalate with cubic or cushion morphology was embedded in an epoxy resin matrix of Agar100, dodecenyl succinic anhydride (DDSA), methyl nadic anhydride (MNA), and 2,4,6tris(dimethylaminomethyl)phenol (DMP 30). The mixture of the resin and powder was put in a drier at 60 °C during 12 h for the polymerization. Then the block was cut in a dry environment at room temperature with a 35° Diatom diamond knife (radius of 5 nm) mounted on Reichert-Jung Ultracut E ultramicrotom. The thickness of the cross-section was of the range of 80 nm. The particle structures were studied on a Philips CM 200 TEM operating at 200 kV at room temperature.

For atomic force microscopy (AFM), we used a Park Instrument Autoprobe CP (0.6 μ m Ultralever SiN; contact mode, force of 1–2 nN). The samples under investigation were placed on a ceramic membrane and coated with a thin film of gold.

Particle Size Distribution. Measurements of the particle size evolution of copper oxalate precipitates without HPMC have



Figure 2. (a) pH evolution as a function of time with the points A–D corresponding to filtration time and HRSEM analyses; (b) reaction yield evolution with the time of precipitation from pH measurements and a thermodynamic model.

 TABLE 1: Optical Parameters Used for Copper Oxalate for

 PSD Evolution Using Laser Diffraction

devices	refractive index	refractive index	refractive index
	(CuC ₂ O ₄)	(CuC ₂ O ₄)	H ₂ O
Mastersizer S	real part 1.77	imaginary part 0.01	1.33

been carried out in-situ by laser diffraction (Malvern Mastersizer S). The total volume of the cell is about 100 mL, and the 300 mm lens used probes in a PSD range from 50 nm to 100 μ m. Before starting the measurements with the two reactant solutions of copper nitrate and sodium oxalate, a background was measured. The background measurement was carried out using decarbonated water that had been filtered through a 20 nm ceramic membrane to avoid possible dust and bubbles. A 50 mL aliquot of each reactant solution (at a concentration of 0.01 M) was injected within 20 s and then circulated at 1400 rpm. The data were collected every minute up to 25 min and then at 30, 45, and 60 min. To transform these types of measurements from diffraction patterns into PSDs, the optical data for the copper oxalate were not found in the literature and were thus determined by comparing several techniques, namely, imaging analysis, photo centrifugation, and laser diffraction.¹⁸ The optical data are reported in Table 1.

X-ray Diffraction. The diffraction patterns have been collected using an X-Pert Philips with copper radiation, wavelength λ (Cu K α_1) = 0.1506 nm, U = 50 kV, and I = 40 mA. Samples were rotated in order to minimize textural effects, in a range of 20–90°. XRD was used in order to determine the phase under investigation and then to estimate the coherent crystalline domain or crystallite size, from line broadening using the following Scherer eq 2

$$l = \frac{K\lambda}{B\cos(\theta)} \tag{2}$$

where λ is the wavelength of the X-ray source (nm), *B* is the line width at half of the maximum intensity (radians), Θ is the diffraction angle, *l* is the average diameter of the crystallites (nm), and *K* is a factor related to the crystallite shape, which is assumed to be 0.89.²² Some powder diffractograms have been fitted using TOPAS 2000 software that takes into consideration the crystallographic parameters. JCPDS files used for the copper oxalate identification is 21-0297, and the theoretical density of copper oxalate is 3500 kg/m³.

Particles Density. The particle density measurement has been carried out by helium pycnometry (Microline 380 Micrometrics). Before the measurement the powder under investigation was thermally treated at 85 $^{\circ}$ C, for 4 h under air to eliminate possible adsorbed water on particles surfaces. For each sample 10 measurements were carried out.



Figure 3. HRSEM micrographs of copper oxalate particles as a function of precipitation time at high and low magnification after (a) 2 min, (b) 8 min, (c) 12 min, (d) 30 min, and (e) 2 weeks.

Results

HRSEM Analysis. The particle evolution was followed as a function of reaction time by stopping the precipitation process by filtration through 20 nm ceramic membranes. Figure 2a shows the pH evolution with time for the copper oxalate precipitation, and it is indicated where the reaction was stopped for HRSEM analysis. Figure 2b shows the precipitation yield calculated from the pH evolution using a thermodynamic model.²⁰



Figure 4. (a) Topography of a typical particle with an aging time of 2 min measured with atomic force microscopy; (b) 3D view of typical particle under construction.

Samples collected after 2, 5, 8, 12, 30, 60, and 40 230 min (2 weeks) were analyzed using HRSEM and are shown in Figure 3 at low and high magnification.

The pH evolution of copper oxalate precipitation was unexpected from the thermodynamic calculations if the only solid-phase assumed to precipitate was copper oxalate.²⁰ The precipitation analysis was consequently split into two parts, before and after 2 min, the point at which the pH stops increasing and starts to decrease. From the thermodynamic simulation the increasing part corresponds to copper oxalate precipitation. The second part of the pH evolution, a slow decrease, could only be explained by the precipitation of a minor (0.4 wt %) secondary-phase malachite, the copper hydroxy carbonate. The carbonate comes from CO₂ in ambient air.

After 2 min the HRSEM micrographs show particles around 500 nm under "construction" with steps and kinks the same size as the crystallite size measured by XRD. These particles under construction are surrounded by nanoparticles with a size under 100 nm, supporting the brick-by-brick growth mechanism previously proposed for copper oxalate and also seen for other systems.²³ The micrographs with aging times of 12 min show a broad range of particle sizes; some around $1 \,\mu$ m, some around 200 nm, and some nearer 50 nm. After 12 min the small particles were much reduced in frequency and rarely observed, again coherent with the hypothesis that growth by aggregation dominates in this period. The particles then grow to sizes of $1-3 \mu m$ between 15 and 60 min. These cushionlike particles show two large surfaces (α) and four small surfaces (ϵ) (Figure 3c), which were shown previously to be linked to the anisotropic nature of the crystallographic structure of copper oxalate.¹¹ After 12 min the larger surfaces have a rough appearance, while the four lateral ϵ surfaces appear smoother. This is even more accentuated after 30 min with a very smooth lateral surface (Figure 2d), suggesting the nanocrystallite building

blocks have been cemented together with the remaining solute as the reaction approaches the equilibrium state. After 2 weeks the morphology has continued to evolve and the smaller surfaces have more or less disappeared and show only the two large surfaces, suggesting a ripening or slow growth process (Figure 2e). These last stages (60 min to 2 weeks) could be expected from the residual copper oxalate supersaturation predicted by the solubility simulation (S = 0.40 after 30 min).

Although we have presented here more evidence for the selfassembly of nanostructure particles via the brick-by-brick mechanism, to further confirm the proposed mechanism, a direct link between the kinetics and observed particle size distribution and substructure using a population balance approach is still needed. This is currently under investigation using a recently developed approach (by Testino et al.), which was successful in describing the growth of nanostructured barium titanate.¹⁷

AFM Analysis. Particles under construction with an aging time of 2 min have been analyzed in detail by AFM in order to determine the height and width of the growth steps and compare them to the XRD crystallite size measurement. Figure 3 shows a typical particle measured by AFM with an aging time of 2 min. The steps of particles under construction are clearly visible. The height and the width of the steps measured for several particles are summarized in Table 2. The measurements were made with an experimental error of 10 nm, which corresponds to the radius of the instrument pointer.

For copper oxalate precipitated under similar conditions, with 30 min aging time, the crystallite size was found to be 70 nm in the 110 direction and 50 nm in the 001 direction.¹¹ The height of the step measured by AFM has the same order of magnitude as, or is close to an integer multiple of, the XRD crystallite size (70 nm). These steps and their correspondence with the XRD line broadening crystallite size add significant weight to the brick-by-brick growth mechanism.

TABLE 2: Dimension of the Particles and of Their Corresponding Step Size Determined by Atomic Force Microscopy^a

	particle			step		
particle no.	length (nm)	width (nm) $w =$ width d_{001}	height (nm) $h =$ height d_{110}	length (nm)	width (nm) $w =$ width d_{001}	height (nm) $h =$ height d_{110}
1	1000	700	280	420	360	$73(1)^{b}$
2	1300	780	450	800	380	214 (3)
3	1100	927	505	710	650	287 (4)
4	1530	1225	275	760	900	210 (3)
5	1000	875	280	500	448	145 (2)

^a Measurements were made with a precision of ± 10 nm. ^b Integer value no. of 70 nm units making up the step height.



Figure 5. Copper oxalate TEM cross-section-cushion morphology: (a) diffraction patterns for micrograph b; (c) diffraction patterns for micrograph d.



Figure 6. Copper oxalate TEM cross-sections—cubic morphology: (a) diffraction patterns from the particle core; (b) image of particle core; (c) diffraction pattern of outer region; (d) image of outer region showing larger crystallites at the surface of the cubic copper oxalate particles.

TEM Cross-Section. The copper oxalate particles were investigated by TEM cross-section to observe their internal structure (Figure 5). It was very difficult to decide which region of the cushion-shaped particle was being sampled because of the damage or random orientation of the cross-section during sample preparation. Previous results on cubic copper oxalate showed an order in the 110 direction.¹¹ Therefore cross-section

TEM was carried out on cubic copper oxalate formed with the addition of HMPC,^{11,23} and the results are shown in Figure 6. The cubic shape of the particles made it much easier to identify which region of the particle was being imaged in the TEM. The central region of the particles shows rings in the electron diffraction pattern which were indexed as copper oxalate, indicating a random orientation between the crystallites. The



Figure 7. Particles size distribution of copper oxalate as a function of time for two repeated experiments.

TABLE 3: Particle Size Distribution Data in AqueousSolution Determined by Laser Diffraction as a Function ofTime (Span = $(D_{v90} - D_{v10})/D_{v50}$

time (min)	$D_{ m v10}~(\mu{ m m})$	$D_{\rm v50}(\mu{ m m})$	$D_{\rm v90}(\mu{ m m})$	span
15	0.59	1.10	2.45	1.68
17.5	0.70	1.23	2.74	1.51
20	0.22	1.14	2.73	2.19
22	0.26	0.95	2.53	2.38
30	0.78	1.23	2.05	1.02
45	0.98	1.76	3.05	1.17
60	1.05	2.00	3.72	1.32

electron diffraction patterns from the outer regions show sharp dots with minor broadening indicative of a strong alignment between the primary particles or crystallites. From indexation of the diffraction pattern this alignment is in the 110 direction parallel to the CuC₂O₄ ribbon axis of the crystal structure. The earlier brick-by-brick mechanism assumed very good alignment throughout the interior of the particle; here we see more of a core-shell structure as seen recently for cobalt oxalate.²³ The poor order observed from the TEM cross-section suggested a certain degree of porosity may be present in this zone. This is confirmed by the density measurements, which showed an internal porosity of 14%, i.e., a density of 3 g/cm³ instead of 3.5 g/cm³ as calculated from the crystallographic structure. The outermost layer in Figure 6d shows larger crystallites than the zone just beneath the surface where the diffraction was made. This may be due the ripening discussed in the HRSEM section.

Particle Size Distribution. *Evolution.* All the results presented above were made on ex-situ samples at the end of precipitation or for the intermediate times (HRSEM) in static conditions. These techniques do not give a real time evolution of the precipitation reaction. Therefore in-situ PSD measurements were made using laser diffraction. The results are shown in Figure 7 and summarized in Table 3.



Figure 8. Particle size evolution of copper oxalate versus time for d_{v10} (μ m) for two different runs.



Figure 9. SEM images for copper oxalate precipitation with an aging time of 23 min: (a) particles with a size less than 200 nm; (b) a large distribution of "primary" particles, particles under construction, and well formed cushion-shaped particles.

Before 12-15 min it was not possible to detect the formation of particles, the scattered light intensity being too low. This is perhaps due to two contributing factors, a low particle volume concentration (solid/liquid = 0.004) and the low scattering coefficient for particles less than 100 nm which are expected to be most numerous in the initial stages of precipitation.²⁵ After 15 min, particles larger than 500 nm are detected and a d_{v50} at around 1 μ m is measured. The particles then increase in size to a $d_{v50} = 1.23 \ \mu m$ (Figure 7, 17.5 min). After 20 min the PSD shows a significant decrease with small particles under 200 nm being detected (Table 3). This transition takes place during a short period of about 5 min, when the smaller particles are detected and then the growth process continues and the d_{v50} increases again. A plot of d_{v10} as a function of time shows this decrease in size very clearly for two different precipitation experiments (Figure 8). The phenomenon is reproducible, but the exact time at which the smaller particles appear is not the same in all cases. This is probably due to difficulties in reproducing mixing in the laser diffraction cell of 100 mL. This sudden appearance of a second population of fine particles smaller than 500 nm is indicative of a second nucleation event. The smallest size that can be measured in these conditions, using laser diffraction is 50 nm.

To confirm this production of small particles, 250 μ L of suspension was filtered through 20 nm ceramic membranes and then analyzed using HRSEM. Figure 9 shows particles with an aging time of 23 min. Three types of particles can be seen, one with a size less than 200 nm (which look like random aggregates of primary particles), a second population under construction (100–500 nm), and a third population of well-formed particles (1500 nm).

Attempts to follow the very early stages of precipitation nucleation and growth were made using the small-angle X-ray scattering (SAXS) technique.²⁵ Unfortunately the supersaturation had to be increased from 0.70 to 1.22 (the concentration was increased 5 times from 0.005 to 0.025 M after mixing) to produce a solid content accessible by the SAXS method. For these conditions of higher supersaturation, the first particles were



Figure 10. Schematic representation of the precipitation mechanism of copper oxalate formation from the initial stage to final particle as a function of time and supersaturation: (a) early stages of nucleation and primary particle growth; (b) evolution between 1 and 5 min showing the random core and the beginning of the ordered self-asssembly; (c) evolution from 5 min to 2 weeks with a cross-section of the final particles—with a possible increase of supersaturation leading to a second nucleation event during the ordered assembly period (*E*).

detected in the time range of milliseconds, they then grew quickly, and after 25 s the intensity of scattering remains constant. This means that the particles reached a size greater than 100 nm after the first 25 s. These experiments are in general agreement with the thermodynamic simulation of the pH evolution (Figure 2), where the majority of the copper oxalate (73%) precipitates in less than 2 min²⁰ but did not allow us to follow the PSD evolution at early times. At this higher supersaturation



Figure 11. Schematic representation of the variation of system free energy as the supersaturation and hence ionic strength decrease during the batch precipitation reaction (high ionic strength at early times < 2 min, low ionic strength > 2 min).

the particle morphology becomes almost spherical with randomly oriented crystallites throughout the particle as seen in earlier studies on copper oxalate.¹¹ The crystallite sizes also decrease for precipitates aged for 30 min from 50 nm for the cushion morphology (0.005M) to 27 nm for the spherical morphology (0.025M) for the 110 reflection.

Discussion

The mechanism of copper oxalate particles assembly proposed previously¹¹ starts with a simple fast burst of nucleation, growth of crystallites by molecular attachment, and then growth by self-ordered aggregation. The above results suggest that more than one process may take place at the same time, and the formation of copper oxalate involves a more complicated mechanism. Each of the processes of nucleation, growth by molecular attachment, or growth by aggregation may be influenced by the distribution and concentration evolution of ions and complexes in the precipitating system. This will be discussed below, incorporating information from thermodynamic solubility simulation.²⁰

Proposed Growth Mechanism. Figure 10 shows a schematic representation of a modified growth mechanism for copper oxalate precipitation at a low level of supersaturation $S_r < 1.00$. Just after the two reactants come in contact, the supersaturation produces a burst of nucleation in a time of milliseconds, as suggested from the SAXS results²⁵ (point A, Figure 10). The total system energy decreases quickly represented by the chemical potential change; i.e., supersaturation decreases the nuclei grow (point B, Figure 10), and then particles begin to agglomerate. The large number density of particles initially induces a high collision frequency and with a relatively high ionic concentration of around 0.005 M, giving a thin electric double layer and low colloidal stability, leading to a random agglomeration of the particles (point C, Figure 10). When the particles aggregate in a random fashion by simple contact, little change in the total system energy would be expected, as they would have an open porosity, i.e., no reduction of surface area per unit volume. This open structure for the random organization of the particles is supported by the presence of an internal porosity of about 14% from pycnometry analysis and also from the TEM crosssection study.

As particle number density and collision frequency decrease, the particles then start to aggregate in a more ordered behavior, brick-by-brick eliminating the solution—solid interface to minimize the system free energy. This more ordered attachment may be helped by the decrease in the overall ionic strength (decreasing supersaturation), which would increase the electric double layer thickness from 3 nm (0.005 M) to 5.7 nm after



Figure 12. SEM micrographs of partially dissolved copper oxalate cubic particles showing the core-shell structure proposed in the modified growth model.

30 min (0.001 45 M, from the thermodynamic model²⁰). This could produce a local potential minimum, E_1 , Figure 11, which attaches the primary particle to the larger particles but allows rotation to find the global energy minimum E_3 , i.e., crystallographically well-aligned. In the earlier random agglomeration the local attractive potential is too deep, E_2 , to allow rotation and alignment. When primary particles attach in an ordered fashion, the ions that were in the electric double layer will be released into solution. Interparticle potential calculations have not been made because no Hamaker constant for copper oxalate could be found.

When a significant quantity of "ordered" attachment has taken place, the "released" ions may be numerous enough to increase the supersaturation and induce a second nucleation event—as modeled and proposed for nanoparticle aggregation by Nomura et al.²⁶ This behavior corresponds to point E in Figure 10. In the in-situ PSD measurements an apparent second nucleation event between 12 and 20 min was also observed. This is coherent with the above discussion of ordered aggregation between 2 and 20 min and the electron microscopy observations. Finally to move toward the equilibrium state of the system, the particles continue to aggregate and the free particle surfaces is further eliminated.

After 30 min of precipitation the particles reach a size of around $2 \,\mu m$ (Figure 2d). The TEM cross-section for the particles with an aging time of 60 min showed larger crystallites at the surface than in the core (Figure 6d are the cubes after 60 min aging). This outer layer, formed from 2 to 3 layers of crystallites, is assumed to be due to a ripening process or continued crystal growth by molecular attachment from the residual supersaturation (Figure 2). During the development of the particles, once they have taken on the cushion shape, the four small lateral ϵ surfaces decrease in relative importance compared to the two large basal surfaces. Particles with an aging time of 2 weeks, point F (Figure 10), are larger in size (5 μ m), and the morphology has developed from cushions to lenses (Figure 2 d,e). The four small ϵ surfaces of the cushionlike particles have vanished, and the particles are made up from the two large curved surfaces. The elimination of the smaller edge faces is both coherent with a slow desaturation or ripening and their "high energy"-hydrophobic nature. Further supporting evidence for the core-shell structure is illustrated in Figure 12, where SEM micrographs of partially dissolved particles (under controlled conditions¹⁸) are presented. The substructure shows the dense outer layer (more difficult to dissolve) and an ordered layer which has been significantly dissolved. The inner core

shows very poor order. The dissolution process does not necessarily mimic the crystallization process, but the regions are very coherent with the proposed model.

The proposed model can also qualitatively accommodate the change in the particle morphology from cushions to spheres for higher levels of supersaturation ($S_r > 1.00$) used in the SAXS experiments. The number of primary particles per unit volume increases significantly if we assume that each crystallite comes from a single nucleation event. For the cushion morphology we would have an initial number density around 6×10^{16} (particles/dm³) and for the spherical morphology around 8 \times 10²⁰ (particles/dm³.) The mean separation between particles decrease from around 1000 nm to around 90 nm, and thus the collision frequency increases. Also with the higher concentrations (0.025 M) the electrical double layer would also be highly compressed (around 1.3 nm). So at the higher S_r the period of the random aggregation, seen at the core of the low- S_r precipitates, would be expected to last for much longer times and the local potential minimum E_2 is too deep to allow particle reorientation before more particles are attached. Thus particles aggregate as spheres to minimize the volume consistent with the proposed growth model.

Conclusions

In the present paper we have investigated, using both in-situ and ex-situ methods, copper oxalate precipitation from the early stages of precipitation to the final nanostructured particles. The growth mechanism has been shown to be more complex than the simple nucleation, growth, and brick-by-brick self-assembly mechanism previously proposed. The mechanism can be described in four stages: (i) initial nucleation and growth of primary particles; (ii) rapid aggregation to give a core of randomly oriented primary particles or crystallites; (iii) a period of ordered attachment of crystallites giving an inner shell of well-aligned nanocrystals; (iv) a slow approach toward equilibrium with the solution where high-energy surfaces are eliminated and an outer shell of larger well-cemented crystallites envelopes the particles. A qualitative mechanism describing the four stages has been described using knowledge of the supersaturation and solution evolution from a previously developed thermodynamic model, adding weight to the direct microscopic observations.

The two different regimes of aggregation, a random organization followed by well-aligned crystallites, were supported by both HRSEM and TEM cross-section imaging combined with

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electron diffraction. The specific organization evoked a second nucleation event, supported by in-situ PSD measurement and ex-situ microscopy, both showing bimodal particle distributions. For intermediate times (2–30 min) the measurements generally confirm the previously proposed brick-by-brick agglomeration mechanism producing a cushionlike morphology. After 2 weeks a disk- or lenslike morphology with only two curved surfaces indicates an equilibrium form has been achieved.

The experimental approach of using a small well-mixed batch reactor, following PSD evolution in-situ and using highresolution SEM and TEM cross-section, ex-situ for specific time intervals has been successful in further elucidating the growth mechanism of copper oxalate. With knowledge of this growth mechanism better control over such nanostructured particles can be envisaged, although further work on the early stages and population balance modeling to further confirm the kinetic aspects should prove fruitful. Such detailed approaches should allow us to approach the ultimate goal of being able to design and tailor structures on the nanometer scale—a key issue in current materials science.

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