Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

SYNTHESIS OF SUPER FINE ARAGONITE-TYPE CALCIUM CARBONATE BY PRECIPITATION IN ULTRASONIC FIELD

C.D. Mateescu [a], M. Mocioi [b], C.Sarbu [a], F. Branzoi [c]

[a] *National Institute for Materials Physics ,105 bis Atomistilor str., Magurele, Romania*
[b] *University Politehnica Bucharest, 313 Splaiul Independentei str., Bucharest, Romania*
[c] *Institute of Physical Chemistry, Bucharest, Romania*

1. Summary

Aragonite, the high pressure polymorph of calcium carbonate, was synthesized by liquid-liquid reaction, at low temperature, in ultrasonic field in the presence of organic additives. In the presence of alcohols, rod-like crystals with nanometer size diameters were formed. The material is quite pure and the particle size distribution is uniform.

Keywords: calcium carbonate, aragonite, ultrasonic field, additives, alcohols

2. Extended abstract

The synthesis of calcium carbonate with submicron dimensions and specific morphology by a simple route, at low temperatures, is interesting due to the possible applications of this material in new fields like biotechnology. Properties like purity, morphology, dimensions and grain size distribution, porosity, aggregation degree must be carefully controlled.

There are three stable polymorphs of calcium carbonate: rhombohedral calcite, needle or rod like aragonite and spherical vaterite.

The synthesis of calcium carbonate by precipitation in liquid-liquid reaction depends on many parameters as supersaturation, pH, temperature, reaction time, agitation speed, feeding order of the reacting solutions, the nature and the presence/absence of the additives. Usually a mixture of the three polymorphs is formed.

The aim of this work was to develop an aragonite type calcium carbonate with uniform particle size distribution and submicron dimensions by precipitation in liquid-liquid reaction using as starting reagents 0.1M solutions of calcium nitrate and potassium or sodium carbonate :

$$Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3$$
$$Ca(NO_3)_2 + Na_2CO_3 = CaCO_3 + 2NaNO_3$$

The synthesis was carried out in a batch reactor placed in an ultrasonic field of 45 kHz. The optimum acoustic amplitude was established at 50% of the full amplitude of the ultrasonic device.

The influence of several additives as Tween 20, AOT as growth inhibitors and alcohols as precipitation agents was investigated.

Other parameters, like pH, temperature, reaction time and feeding order were also varied.

All samples were examined by FT-IR spectroscopy, optical and electron microscopy and grain size distribution.

In ultrasonic field aragonite developed in the absence of any additive at pH > 9. At pH=7 calcite was formed. The particles mean diameter was in the range of several microns. The grain size distribution shows the presence of two particles populations, one with submicron dimensions and one in the micron range. The material was impurified with vaterite and calcite.

In the presence of Tween 20 or AOT as growth inhibitors the formation of aragonite is also dependent of pH which must be adjusted at 9-10. The material is a mixture of calcium carbonate polymorphs but aragonite is predominant. The mean particle size is still in the range of microns as recorded by laser granulometer but many nanometer size particles of aragonite are present among large crystals of calcite as determined by electron diffraction microscopy and transmission electron microscopy.

Replacing the surfactants with an alcohol as precipitation agent, in ultrasonic field, aragonite develops at 50°C and pH = 7. We studied the influence of methanol, ethanol and 2-propanol. We varied the feeding order of the reactants and we started with Na_2CO_3 or K_2CO_3. In all cases, independent of the nature of the alcohol, rod like crystals of aragonite are formed (figure 1c). Laser granulometer measurements shows that the particles mean size is 1.0 -1.3 µm (figure 1b) but TEM microscopy images shows that the rods diameter is smaller than 100 nm (figure 1c), their lengths getting to 2-3µm. The material is quite pure as results from the FT-IR spectra (figure 1a).

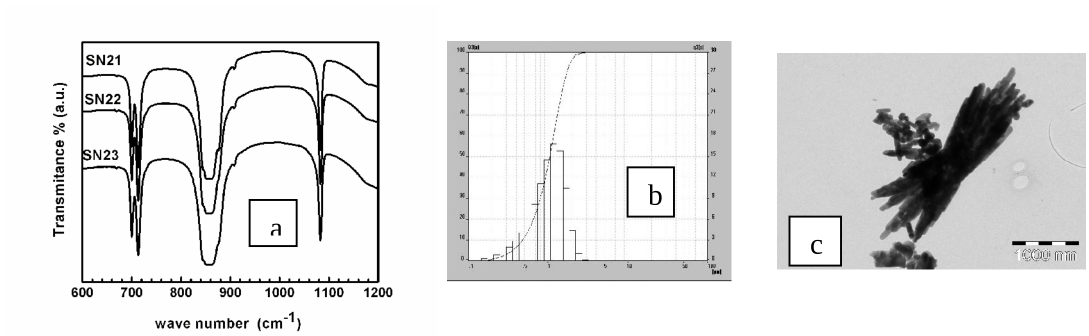

Figure1a. FT-IR spectra for aragonite precipitated in ethanol (SN 21), 2- propanol (SN 22) and methanol (SN23). Figure 1b. Particle size distribution characteristic for aragonite precipitated in alcohols. Figure 1c. TEM image of a bundle of aragonite rod like crystals.

This research established a simple method to synthesize super-fine, rod like aragonite by liquid-liquid reaction at low temperature. Ultrasonic field is the main factor determining the precipitate morphology. Alcohols prove to be more efficient than other additives in decreasing the particles sizes.