

Preparation of needle-like aragonite particles from calcium nitrate solution

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Abstract

Preparation of needle-like aragonite particles from calcium nitrate aqueous solutions was investigated in the temperature range 70 °C – 130 °C. Different additives recommended in literature as substances influencing morphology of aragonite crystals were tested. It was found that the studied system is so complex that all parameters (concentration of reagents, temperature, rate of mixing), not only the presence of surface active substances influence the process of nucleation and crystal growth. The highest yield of aragonite was obtained in the system H₂O – Ca(NO₃)₂ – CO₂ at 70 °C with no admixture of organic substances.

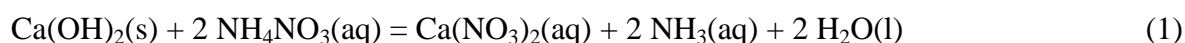
Keywords: aragonite, precipitated calcium carbonate, calcium nitrate

Introduction

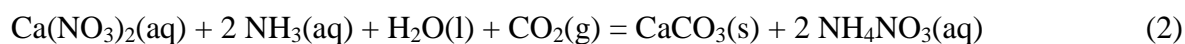
Precipitated calcium carbonate is widely used in many branches of industry. Each application requires different properties of calcium carbonate, such as crystal structure, size and shape of particles, purity, etc. In paper industry, needle-like aragonite is used in surface treatment of papers. Diameter of the aragonite needles has to be tenths of micrometer and length about 1 μm. There are many papers dealing with this subject (Feng et al. 2007, Lee et al. 2009, Park et al. 2008, Wang et al. 2006, Wang et al. 1999, Xiang et al. 2002, Yu et al. 2004). They describe importance of metastable phases and limits of stability of different crystallographic modifications of calcium carbonate (Elfil and Roques 2001, Elfil and Roques 2004). Many papers are also devoted to the influence of organic substances on the formation of specific phases of calcium carbonate (Feng et al. 2007, Lee et al. 2009, Park et al. 2008, Wang et al. 2006, Wang et al. 1999, Xiang et al. 2002, Yu et al. 2004). In industry, lime, calcium hydrate,

calcium chloride or calcium sulfate are often used for preparation of precipitated calcium carbonate. Source of carbonate anion is most commonly CO₂, but Na₂CO₃ or (NH₄)₂CO₃ can be used as well.

In this paper we will describe the preparation of needle-like aragonite particles from calcium nitrate. In industrial scale, calcium nitrate can be prepared in different ways – from limestone, dolomite or from waste calcium hydrate. In the later case, aqueous solution of calcium nitrate is formed by the reaction of calcium hydrate with ammonium nitrate.



In the next step calcium carbonate precipitates according to the reaction scheme:



Ammonium nitrate is returned back to the process. We applied this idea to the preparation of calcium nitrate from waste lime from the production of acetylene from calcium acetylide.

However, in the laboratory experiments reported in this paper we used higher purity (“pro analysis”, “purum”) reagents. The aim is to prepare needle-like aragonite crystals which could be applied in paper industry.

Experimental

The following chemicals were used: Ca(NO₃)₂·4H₂O, purum, Mikrochem; NH₄OH (26 wt % NH₃, p.a.), Mikrochem; CO₂ (gas cylinder), Messer. Several reagent grade substances were used as admixture influencing crystallization of calcium carbonate: maleic acid, malic acid, o-phthalic acid, imidodiacetic acid, diglycolic acid (98 %), DL-aspartic acid (99 %), sodium stearate, polyethylene glycol (Mn 600); Sigma Aldrich, Fluka.

On the basis of literature data (Gmelins 1961) and our preliminary experiments, the precipitation reaction was carried out at three temperatures: 70 °C, 110 °C, and 130 °C. In this temperature range and for concentrations of reagents used, aragonite phase of calcium carbonate is formed. The experiments at the temperatures higher than 100 °C were carried out in a pressure reactor (Parr 4842).

In the case of experiments carried out at 70 °C, CO₂ was introduced to the 15 wt % Ca(NO₃)₂ aqueous solution (150 ml) through glass frit (S3). Excess of NH₄OH was 10 wt %. When an organic admixture was added, its concentration was 1 wt % to product. The reaction

vessel was kept in a thermostat at 70 °C and the solution was mixed by a magnetic stirrer (400 rpm). The amount of CO₂ gas was measured by a gas flowmeter.

The experiments in the pressure reactor were carried out at 110 °C and 130 °C. 100 ml of solution was used and pressure of CO₂ at the beginning of experiment was 0.6 MPa. Because the reaction (2) is exothermic, the temperature increased by 8 °C in 5 min. After next ten minutes the temperature slowly dropped to a constant value, which was considered as the end of the reaction. Precipitated CaCO₃ was filtered and washed by distilled water. Application in paper industry requires concentrated suspension of aragonite needles. This suspension was also used for scanning microscopy. For X-ray analysis, the samples were dried at 50 °C. Powder X-ray analysis (STADI P, STOE) and SEM (Tesla BS 300 with digital unit Tescan) were used to characterize the product. Content of crystallographic phases of CaCO₃ in samples was determined on the basis of X-ray diffraction. It can be estimated that the error is about 5 %. From an extensive set of SEM pictures only a few of them are shown here for illustration. The other can be obtained from authors on the request.

In this paper, the following abbreviations are used for organic substances:

Me – maleic acid; M – malic acid; Ph – phthalic acid; IDA – iminodiacetic acid; SNa – sodium stearate; DG – diglycolic acid; PEG – polyethylene glycol; DLA – DL-aspartic acid.

Crystallographic phases of calcium carbonates are denoted as follows:

A – aragonite; V – vaterite; C – calcite.

For the description of shape of crystals, following symbols are used: P – prism; S – spheres; D – discs; N – rods (needles); R – rosette. Dominant structure is printed in bold.

Results and Discussion

Preparation of CaCO₃ at 70 °C

The results of the experiments carried out at 70 °C are summarized in Table 1. It can be seen that the admixtures of organic substances remarkably effect crystallographic phase in which CaCO₃ crystallizes. When maleic acid was added, only vaterite was formed. In other cases all stable crystallographic phases of CaCO₃ were present in different ratios. An influence of organic additives is described in many papers (Lee et al. 2009, Park et al. 2008, Wang et al. 2006, Xiang et al. 2002). Organic dicarboxylic acids work as a template of nucleation. Organic molecules adsorb Ca²⁺ ions and become nucleation centres for CaCO₃ phase. Which phase is created depends on the layout and distance between two carboxylic groups.

From X-ray analysis it follows that the highest amount of aragonite (71 %) was formed when 1 % of polyethylene glycol was added. The admixture of sodium stearate resulted in the formation of 45 % of aragonite. However, aragonite was formed also when no organic admixtures were used (36 %). As can be seen from scanning electron microscopy (SEM) (Fig. 1), different crystallographic phases of calcium carbonate have different shape. Vaterite forms empty spheres or discs, calcite forms cubes and aragonite forms needles.

Table 1. Influence of the addition of organic substances (1 wt %) on the crystal structure and shape of precipitated calcium carbonate; temperature 70 °C.

No.	Admixture	C [%]	A [%]	V [%]	Shape	Size [μm]
1	-	64	36	-	N, P	1 – 8
2	Me	-	-	100	D, G	2 – 12
3	M	64	10	26	D, G, P	1 – 6
4	Ph	60	-	40	D, P	1 – 5
5	IDA	94	6	-	P, N, R	1 – 10
6	DG	80	20	-	P, N	< 5
7	SNa	55	45	-	N, R, P	1 – 5
8	PEG	29	71	-	N, P	0.5 – 10

Preparation of CaCO₃ in pressure reactor at 110 °C

Table 2 summarizes phase composition of CaCO₃ prepared at 110 °C. It follows that temperature has remarkable effect on the formation of specific crystallographic forms of CaCO₃. (In this case CO₂ filled up over the level of liquid and it dissolved in the solution. Thus mixing of reagents was different from that reported above.) In almost all cases (with exception of sample 11) the product of precipitation contained only mixture of aragonite and calcite in different ratio. The highest yield of aragonite (74 %) was achieved when no organic admixture was used. SEM of prepared samples (Fig. 2) confirms this conclusion. The higher is the content of aragonite the higher is the percentage of needle-like crystals in the sample. When diglycolic acid was used as the admixture, also plate-like crystals of calcium carbonate were formed (see Fig. 2). They have probably crystallographic structure of calcite.

As mentioned in the introduction, literature (Lee et al. 2009, Park et al. 2008, Wang et al. 2006, Xiang et al. 2002) describes influence of several admixtures on the crystallographic

structure and shape of precipitated CaCO_3 . Our results do not always confirm conclusions of the literature. This, however, has been also the experience of other authors (Feng et al. 2007). As can be seen, the highest yield of aragonite as the desired phase was obtained for the system containing no admixtures of organic substances. This means that also other parameters (temperature, rate of mixing, concentration of calcium cations, partial pressure of CO_2) influence formation of specific crystallographic form of CaCO_3 . Moreover, most results in the cited literature were obtained by precipitation of CaCO_3 from $\text{Ca}(\text{OH})_2$ suspension in which calcium cations have a low solubility and pH is constant during reaction.

Table 2. Influence of the addition of organic substances (1 wt %) on the crystal structure and shape of precipitated calcium carbonate; temperature 110 °C.

No.	Admixture	A [%]	C [%]	Shape	Size [μm]
9	-	74	26	N, P	0.5 – 5
10	SNa	18	87	P, N	0.5 – 3
11	DG	9	91*	D, P	~ 2
12	DLA	16	84	P, R, N	0.5 – 20

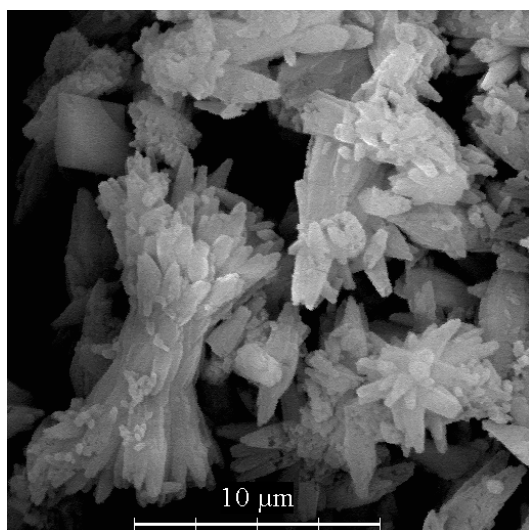
*The value 91 corresponds to the sum of two phases C+V

Preparation of CaCO_3 in a pressure reactor at 130 °C

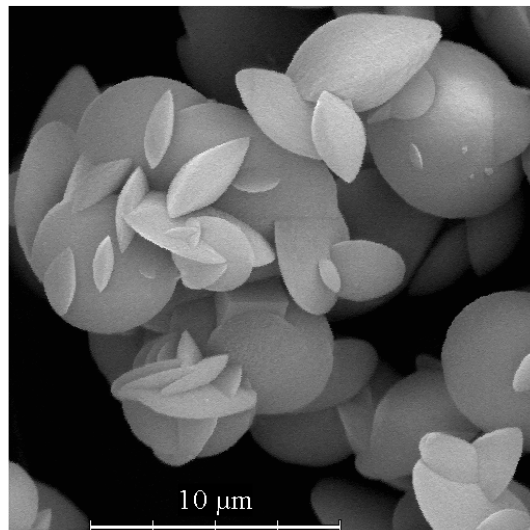
Table 3 summarizes phase composition of CaCO_3 prepared at 130 °C. It can be seen that the content of aragonite in samples prepared without any admixture of organic substance increased up to 80 %. However, also size of crystals increased twice in comparison with lower temperatures, which is not a desired effect. This experiment also confirmed that the addition of the admixture of organic acid does not generally contribute to the increase of aragonite in precipitated calcium carbonate.

Table 3. Influence of the addition of organic substances (1 wt %) on the crystal structure and shape of precipitated calcium carbonate; temperature 130 °C.

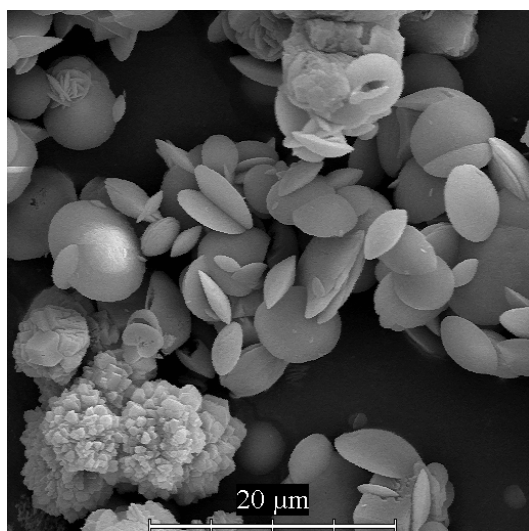
No.	Admixture	A [%]	C [%]	Shape	Size [μm]
13	-	20	80	N, P	1 – 6
14	DG	18	82	N, P	1 – 20
15	PEG	18	82	N, P	1 – 15



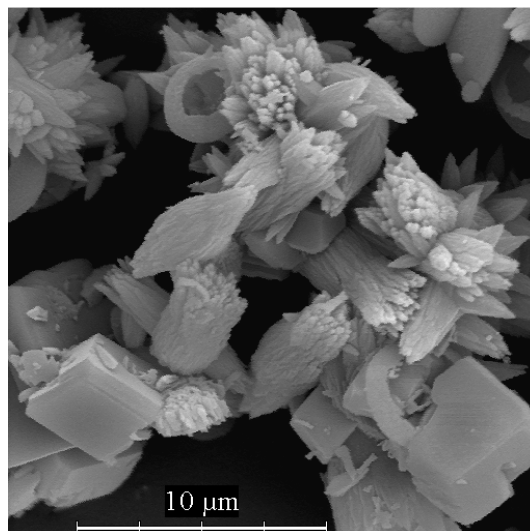
No admixture, 70 °C



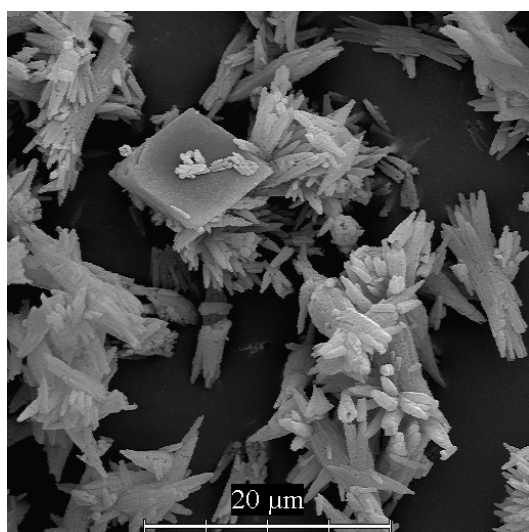
Maleic acid, 70 °C



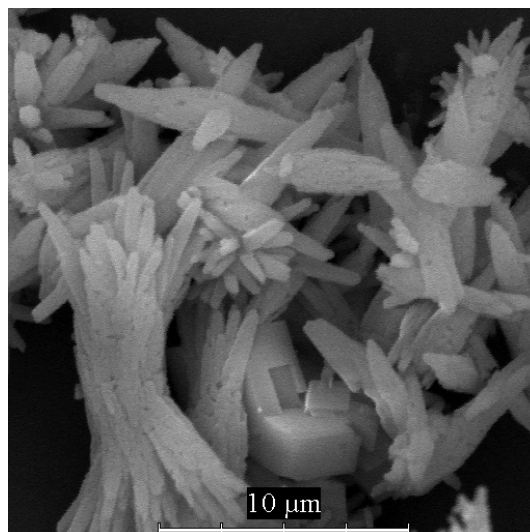
Malic acid, 70 °C



Diglycolic acid, 70 °C

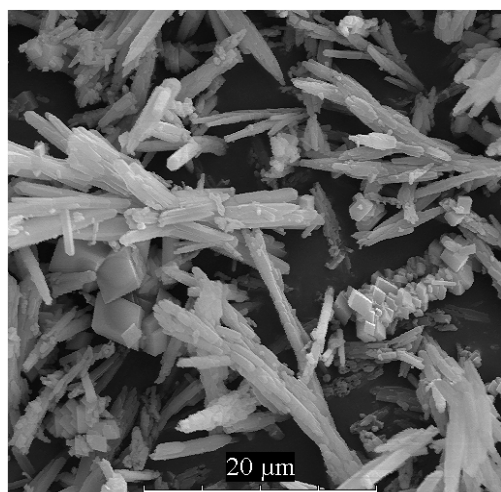


Sodium stearate, 70 °C

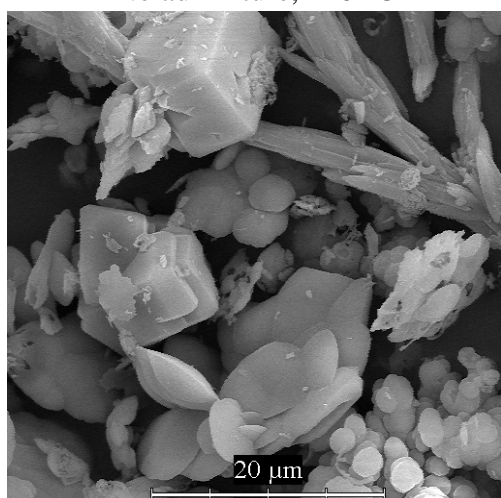


Polyethylen glycol, 70 °C

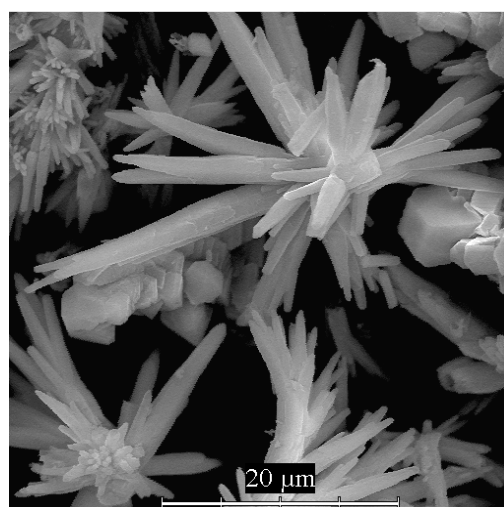
Fig. 1. SEM of CaCO_3 particles prepared at 70 °C; the effect of 1 wt % of admixture.



No admixture, 110 °C

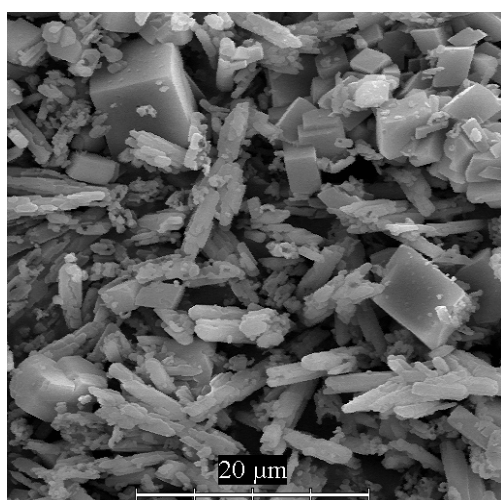


Diglycolic acid, 110 °C

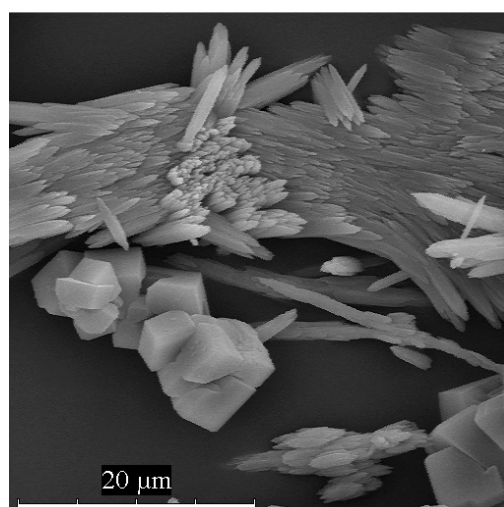


DL-Aspartic acid, 110 °C

Fig. 2. SEM of CaCO_3 particles prepared at 110 °C; the effect of 1 wt % of admixture.



No admixture, 130 °C



Diglycolic acid, 130 °C

Fig. 3. SEM of CaCO_3 particles prepared at 130 °C; the effect of 1 wt % of admixture.

Conclusion

Based on the literature data we prepared needle-like aragonite from calcium nitrate. We found that the influence of admixture of organic substances often influences morphology of calcium carbonate in different way than that described in literature. From the point of view of preparation of needle-like aragonite, the best result was achieved when the system contained no organic admixtures and the precipitation was carried out at 70 °C. Besides temperature and concentration of calcium nitrate, partial pressure of CO₂ plays very important role at the synthesis. Also pH of the reaction mixture is of great importance. Achieved results served as a base for construction of a continuous reactor for preparation of needle-like aragonite. The experimental work is in progress.

Acknowledgement

This work was supported by the project VMSP-P-0088-09 and by the Slovak Research and Development Agency under contract No. APVV-0203-07.

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