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ИЗСЛЕДВАНЕ ВЛИЯНИЕТО НА КОНЦЕНТРАЦИЯТА НА НАЧАЛНИТЕ РАЗТВОРИ ПРИ СИНТЕЗА НА МОНОДИСПЕРСНИ НАНОЧАСТИЦИ ОТ $BaCO_3$ В ОБРАТНА МИКРОЕМУЛСИОННА СИСТЕМА

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A STUDY THE EFFECT OF THE CONCENTRATION OF THE INITIAL SOLUTIONS OF REAGENTS IN THE SYNTHESIS OF MONODISPERSED NANO-SIZED PARTICLES OF $BaCO_3$ IN A REVERSE MICROEMULSION SYSTEM

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ABSTRACT

The use of microemulsion systems in industrial technology requires investigation of a number of parameters of the synthesis to find the most appropriate reaction conditions for control and regulation of particle size. The aim of the present paper is to study the effect of the concentration of the initial solutions of reagents in the synthesis of monodispersed nano-sized particles of $BaCO_3$ in a reverse microemulsion system. The nanoparticles present in the organic phase were identified by TEM to determine their shape, size and structure. The effect of the initial $Ba(OH)_2.8H_2O$ concentration on the diameter of the spherical particles obtained was studied. The smallest sized particles (d = 8 nm) was observed at initial concentration of $Ba(OH)_2.8H_2O$ – 6.10^{-2} mol/l.
Key words: *reverse (W/O) microemulsion system, particle synthsis, nanoparticles, barium carbonate*

INTRODUCTION

The recent rapid development of "nanotechnology" provided opportunities to design materials with improved properties – so called "nano-materials"- and study new phenomena in substances. Due to their unusual properties, the nanostructures became quite important in a number of fields (microelectronics, biomedicine, catalysis, cosmetics, corrosion, pharmaceutical, ceramic and glass industries, etc.) [1-6].

Microemulsions are known to be an alternative reaction medium for preparation of fine monodispersed colloid particles [1, 7-12]. The WATER/OIL (W/O) microemulsion can be regarded as special microreactor where controlled chemical reactions can be carried out to obtain ultradispersed particles of desired size and shape [1, 7]. To use microemulsion systems on industrial scale, a number of parameters of the synthesis should be studied to find the best reaction conditions allowing control and regulation of particle properties [8-11].

The aim of the present paper is to study the effects of the physico-chemical conditions on the synthesis of monodispersed nanosized $BaCO_3$ particles in reverse microemulsion system.

MATERIALS AND METHODS

The synthesis of ultrafine $BaCO_3$ particles was carried out in an installation containing glass reactor with stirrer. Its design and performance have been described earlier [1, 7].

The experimental methods involve preparation of aqueous solutions of $Ba(OH)_2.8H_2O$ with different normalities and determination of their concentration by volume - analytic titration. The microemulsion used was a colloid - dispersed system of water/oil type (W/O). The aqueous solution of $Ba(OH)_2.8H_2O$ was the inorganic phase and n-hexane was the organic phase (oil). The inorganic microdrops are distributed in the organic medium. The working volume of the microemulsion (50 ml) and the ratio between the inorganic and organic phases ($V_1/V_2 = 1/3$) were selected on the basis of earlier experiments [1, 7]. Since the W/O microemulsion contained one of the reagents, the other was fed into the reactor in gaseous form (CO_2) at constant flow. The reaction conditions and the inorganic phase concentrations used for the synthesis of $BaCO_3$ particles were:

- initial concentration of $Ba(OH)_2.8H_2O$ ($C.10^{-2}$) – 2, 6, 8, 10, 20 mol / l;
- stirring speed (n) – 800 min^{-1};
- time for mixing the two phases (without chemical reaction) (t_1) – 60 min;
- time for mixing and chemical reaction (t_2) – 60 min;
- total process time (t_3) – 120 min.

The stirring speed and phase stirring time were selected on the basis of preliminary experiments aimed at preparation of nano-sized particles with minimal size [1, 7]. The distribution of barium ions in both phases was measured complexonometrically after each experiment.

RESULTS AND DISCUSSION

A series of experiments on synthesis of nano-sized $BaCO_3$ particles were carried out. Due to the "dynamic process" of mass transfer [10, 11], chemical reaction takes place in the microemulsion drops to produce the slightly soluble compound $BaCO_3$. Here, the microdrop can be regarded as "microreactor" where the new phase formed. Within the drop, the probable chemistry of the process can be described as follows:

$$Ba(OH)_2 \leftrightarrow Ba^{2+} + 2OH^- \quad \textbf{(I)}$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad \textbf{(II)}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad \textbf{(III)}$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad \textbf{(IV)}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad \textbf{(V)}$$

$$Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3 \downarrow \quad \textbf{(VI)}$$

The size of the forming particles is limited by the size of the microdrops and the internal hydrodynamics and their shape is supposed to follow the shape of the drops [10, 11]. The probable physical model of the process of formation of nano-sized carbonate particles in reverse microemulsion medium has been described in an earlier publication. The studies carried out have shown that the nanostructures are formed mainly in the organic phase [1, 7]. The nano-sized $BaCO_3$ particles residing in the organic phase were identified by electron microscopy. Their shape, size and structure were determined using TEM. The effect of the initial concentration on the diameter of the spherical nanoparfticles obtained is illustrated in Fig.1. It shows the dependence of the average diameter of the spheres on the initial concentration of $Ba(OH)_2.8H_2O$ - (ln d = f(ln C)):

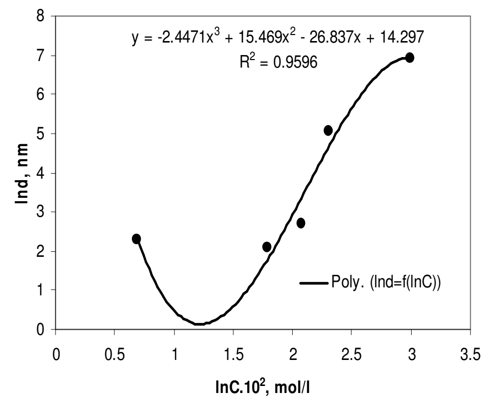
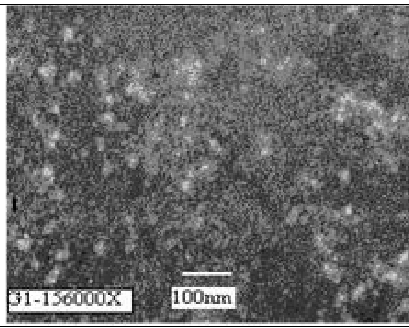


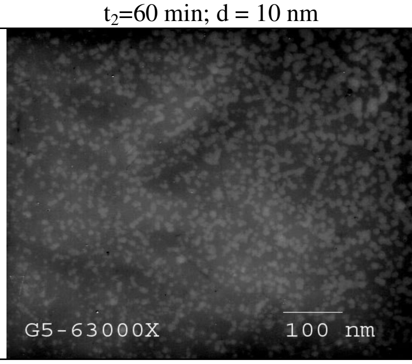
Fig. 1. Dependence of nano-particles size on the initial concentration of the inorganic phase ($Ba(OH)_2.8H_2O$) at t_1 =; t_2 =, and n = const.

As can be seen, the increase of concentration has diverse effect: particle size decreased up to concentration $C_{(Ba(OH)2.8H2O)}$ =6.10^{-2} mol/l and above this concentration increased linearly. Besides, the increase of concentration by an order gave particles with size by three orders bigger. The dependence observed is strongly non-linear which suggests that the initial concentration of the inorganic solution has significant effect on the size of the end product.

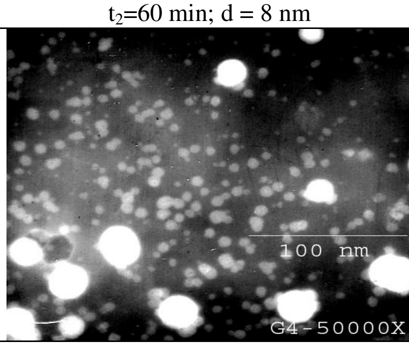
TEM micrographs of ultrafine particles formed in the organic phase are shown in Fig.2. They differ according to the initial concentration of $Ba(OH)_2.8H_2O$ aqueous solution. TEM resolution allows to observe the nanoparticles shape and arrangement, as well as to measure their size. It can be seen that the samples are composed of numerous microstructures with average size from 10 to 1000 nm depending in the inorganic phase initial concentration. In all the samples studied, the particles had spherical shape and they were observed as single particles or small aggregates (3-4 particles). The micrograph data suggest uniformity of particles size, i.e. monodispersity of the solid phase. The lowest diameter (d = 8 nm) had the particles obtained at initial concentration $C_{(Ba(OH)2.8H2O)}$ = 6.10^{-2} mol/l, provided the same other experimental conditions.



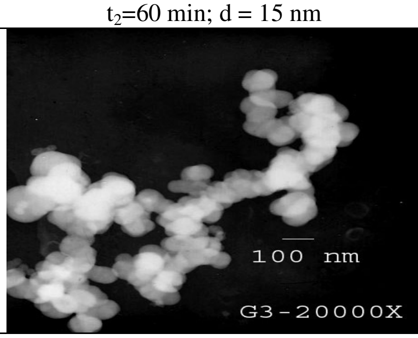
No. 1
$Ba(OH)_2.8H_2O$ – 30 ml; $n\text{-}C_6H_{14}$ – 20 ml
$C=2.10^{-2}$ mol/l; $n=800$ min^{-1}; $t_1=60$ min;
$t_2=60$ min; d = 10 nm



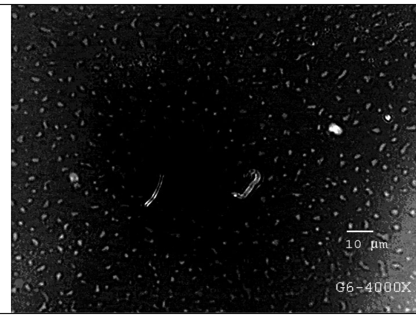
No. 2
$Ba(OH)_2.8H_2O$ – 30 ml; $n\text{-}C_6H_{14}$ – 20 ml
$C=6.10^{-2}$ mol/l; $n=800$ min^{-1}; $t_1=60$ min;
$t_2=60$ min; d = 8 nm



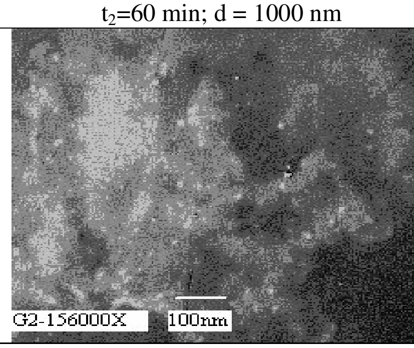
No. 3
$Ba(OH)_2.8H_2O$ – 30 ml; $n\text{-}C_6H_{14}$ – 20 ml
$C=8.10^{-2}$ mol/l; $n=800$ min^{-1}; $t_1=60$ min;
$t_2=60$ min; d = 15 nm



No. 4
$Ba(OH)_2.8H_2O$ – 30 ml; $n\text{-}C_6H_{14}$ – 20 ml
$C=10.10^{-2}$ mol/l; $n=800$ min^{-1}; $t_1=60$ min;
$t_2=60$ min; d = 160 nm



No. 5
$Ba(OH)_2.8H_2O$ – 30 ml; $n\text{-}C_6H_{14}$ – 20 ml
$C=20.10^{-2}$ mol/l; $n=800$ min^{-1}; $t_1=60$ min;
$t_2=60$ min; d = 1000 nm



No. 6
$Ba(OH)_2.8H_2O$ – 30 ml; $n\text{-}C_6H_{14}$ – 20 ml
$C=2.10^{-2}$ mol/l; $n=800$ min^{-1}; $t_1=60$ min;
$t_2=60$min; d = 10 nm

Fig. 2. TEM micrographs of nano-sized $BaCO_3$ particles obtained in reverse microemulsion system.

Fig.2 shows also an electron micrograph (No.6) of a sample obtained at $C_{(Ba(OH)2.8H2O)} = 2.10^{-2}$ mol/l, which was taken at low exposition. Here, "fog" was observed which could be attributed to initial formation of particles nuclei. Their initial size was hard to determine with the available apparatus. Further irradiation of such samples gave the pattern shown in Fig.2 (No.1) the nanoparticle size can be clearly seen. Such phenomenon has been observed by other authors, too [12].

One of the basic parameters characterizing the nanoparticles is their specific area which can be determined by the expression [7, 13]:

$$A = 4\pi r^2 N, \quad m^2/kg \qquad \textbf{(1)}$$

Where:

A – specific area, m^2/kg; r – particle radius, m; N – number of particles per unit mass which can be calcuklated by the formula.

$$N = \frac{1}{\frac{4}{3}\pi . r^3 . \rho} \qquad \textbf{(2)}$$

The values of A (m^2/kg) calculated for the nanoparticles synthesized are presented in table 1.

Table 1. Some physical characteristics of $BaCO_3$ nano-sized particles

№	$C_{(Ba(OH)2.8H2O)}$. 10^2, mol/l	d, nm	$N.10^{-18}$	$A.10^{-4}$, m^2/kg
1	2	10	439	13,8
2	6	8	858	17,8
3	8	15	130	9,2
4	10	160	0,107	0,862
5	20	1000	0,00044	0,138

The data in table 1 show that the number of particles per unit mass and their specific area decreased with the increase of their size. This decrease was quite high for small change in nanoparticles size. In double logarithmic coordinates, the dependence lnA = f(lnd) can be written as: $\ln A = -3{,}9765\ln(d) + 15{,}196$, at $R^2 = 0{,}9852$. The relationship between the specific area of the nanoparticles and the initial concentration of the inorganic solution from which they were formed is shown in Fig.3. Again, strong nonlinearity of the effect of $C_{(Ba(OH)2.8H2O)}$ (mol/l) on nanostructures specific area A(m^2/kg). At certain concentration, the probable maximum (Fig.3) coincides with the minimum of nanoparticles size (Fig.1).

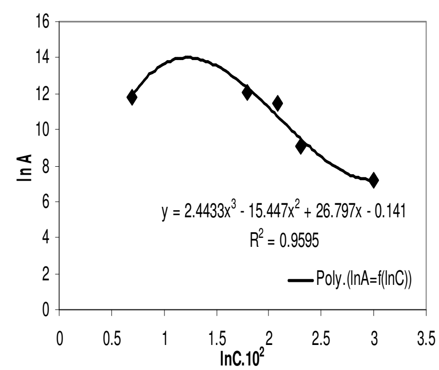


Fig. 3. Dependence of the $BaCO_3$ nano-particles specific area (A (m^2/kg)) on the inorganic phase initial concentration ($C_{Ba(OH)2.8H2O}$ (mol/l).

CONCLUSIONS

1. The process of preparation of carbonate nano-sized particles by chemical reaction under microemulsion conditions was studied.

2. Ultrafine $BaCO_3$ particles wer synthesized by the method of reverse micelles. They were characterized by electron microscopy (TEM). Their shape was proved to be spherical and the distribution of the particles by size was quite narrow (monodispersity) in each experiment. Ths is an advantage of the method used.

3. The effect of the inorganic phase initial concentration (aqueous solution of $Ba(OH)_2.8H_2O$) on the size of the nanostructures obtained was studied, keeping the other reaction conditions at constant values.

4. The average diameter of the nano-sized particles obtained was the lowest (d = 8 nm) at initial concentration of $Ba(OH)_2.8H_2O$ – 6.10^{-2} mol/l.

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