

Microemulsion water-in-oil (W/O) – microreactor for synthesis of ultrafine carbonate nanostructures

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Application of the water-in-oil (W/O) microemulsion system as a “microreactor” for synthesis of carbonate ultrafine nanostructures: In recent decades, microemulsions have been successfully used as reaction medium, allowing the realization of chemical reactions and the synthesis of various organic and inorganic nanoparticles. The aim of this work is to investigate the W/O microemulsion as an interesting alternative reaction medium for the formation and synthesis of ultrafine carbonate nanostructures. The nano-sized particles were obtained at various ratios of the phases forming the microemulsion and were studied by qualitative analysis and electron microscopy. By TEM to determine their shape, size and structure. Their sizes vary from 20 to 30 nm.

Key words: W/O microemulsion systems, particle synthesis, microreactor, carbonate nanostructures

INTRODUCTION

Nanotechnology is an interdisciplinary field combining organic and inorganic chemistry with physics, biology and materials science. Thus, it forms the subsequent scientific and technological revolution the results of which can already be seen in industry and living standards. The particles of nanometer size obey the laws of quantum physics so their mechanical, optical and electrical properties are entirely different. Based on their extraordinary properties, the nanoparticles and nanomaterials are becoming very important for microelectronics, catalysis, cosmetics, medicine, textile industry, corrosion protection, etc. (Fig.1) [1].

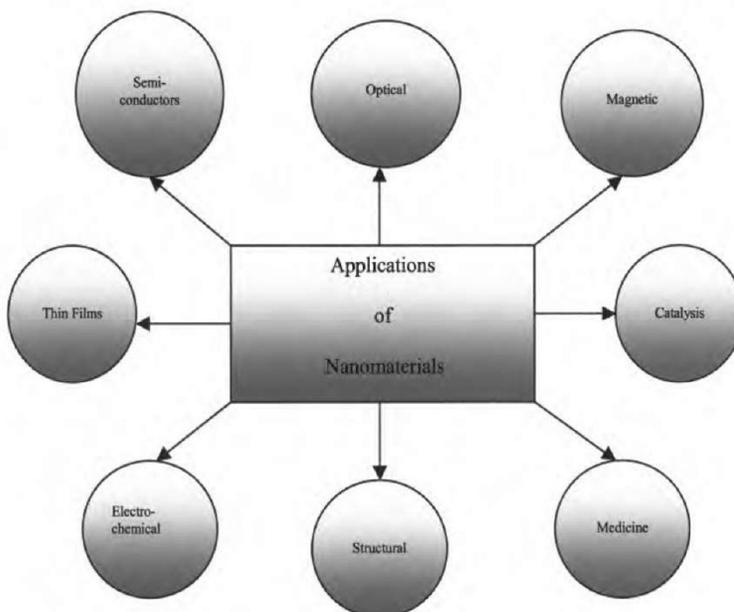


Figure 1. Applications of nanostructures.

In recent decades, microemulsions as certain kind of colloid dispersed systems are successfully used as reaction medium allowing realization of chemical reactions and synthesis of various organic and inorganic substances. With the development of the „new technology – nanotechnology”, this particular feature gradually obtained the label of a new approach to the preparation of nano-sized particles.

The water-in-oil microemulsion (W/O) can be regarded as specific microreactor which allows: realization of chemical reactions, synthesis of different by nature nanostructures and control synthesis parameters [2÷4].

The aim of the present work is to use W/O microemulsion system for synthesis and study on ultrafine carbonate nanostructures.

EXPERIMENTAL METHODS

The experimental method for preparation of ultrafine carbonate particle in reverse microemulsion system by the so called “method of reverse micelles” involves preparation of aqueous inorganic solutions ($\text{Ca}(\text{OH})_2$; $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) which are then kept in stationary conditions for one day. Generally, the initial concentration of the aqueous solutions was $C = 2 \cdot 10^{-2}$ mol/l as measured by volume-analytic titration.

The method for preparation of carbonate microstructures is based on the use of a single microemulsion system, namely the colloid dispersed system of W/O type: aqueous solution/n-hexane/Aerosol-OT. The corresponding alkali suspension is inorganic phase while the organic phase is n-hexane, with the inorganic microdrops being dispersed in the organic substance. The substances composing the three-component reverse microemulsion system are comparatively low by price, easily available and easily separable. The microemulsion samples were prepared by mixing with n-hexane and 0.01M solution of Aerosol-OT (AOT ($\text{C}_{20}\text{H}_{37}\text{NaO}_7\text{S}$)) in a glass reactor followed by addition of the particular inorganic solution.

The working volume of the W/O microemulsion prepared was 50 ml with the ratio organic to inorganic substances varying for the individual experiments. For all the experiments carried out, the reverse micelle solutions were obtained at ration of aqueous solution to surfactant ($R = [\text{Aqueous solution}]/[\text{AOT}] = 20$). The microemulsion system was stirred by magnetic stirrer for 60 min (t_1) at constant rotation speed of $n = 800 \text{ min}^{-1}$ and the experiments temperature was kept at $T = 25^\circ\text{C}$. The latter was kept constant since, as it is well known from literature, it does not have significant effect on the nano-sized product for the synthesis method used. The scheme of the installation for preparation of carbonate nanostructures has been described earlier [4].

Since the W/O emulsion formed contained only one of the components (the inorganic solution), the second component was introduced into the reactor as gas (CO_2). The gas bubbled at constant flow rate in the device for 60 min (t_2). In this case, the nanostructures were obtained by carbonization of the alkali suspension which resulted in chemical interaction between the gas and the inorganic solution. Thus, a chemical reaction occurred at $\text{pH} = 10$, the products of which are slightly soluble substances (CaCO_3 ; BaCO_3). A diagram of the experimental method is illustrated in Fig.2.

After each experiment for preparation of carbonate nanostructures, both the microemulsion phases were separated and they were analyzed to prove the presence of the corresponding carbonate. The distribution of metal ions in the two phases was determined complexometrically.

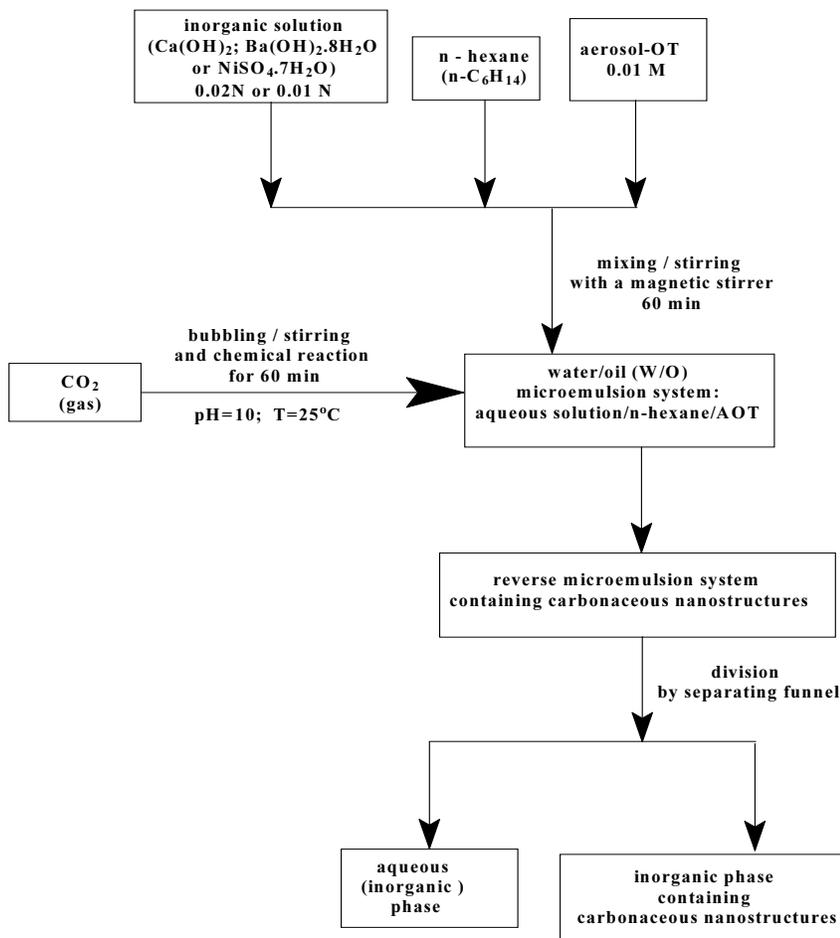
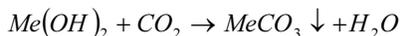


Figure 2. Diagram of the technology for synthesis of carbonate nanostructures in reverse (W/O) microemulsion system

RESULTS AND DISCUSSION

As a result of the method developed and the experiments carried out, solid carbonate nano-sized particles of CaCO₃ and BaCO₃ were synthesized. The nanostructures based on alkali carbonates were obtained by chemical reaction under microemulsion conditions, through carbonization of the corresponding inorganic solution. In the case W/O, the microemulsion was used as “microreactor” allowing the realization of chemical interaction and formation of nanoparticles. The summary equation of the chemical reaction taking place between the hydroxide (barium or calcium hydroxide) and CO₂ is as follows:



Where Me = Ca, Ba.

The organic and inorganic phases forming the reverse microemulsion system were subjected to qualitative analysis which showed the presence of the corresponding bonded

carbonate ions. The shape, size and dispersity of the nanostructures were determined by electron microscopy. TEM micrographs (TEM, "Opton" EM-10 B (Germany)) of the nano-sized CaCO_3 and BaCO_3 particles obtained are presented in Fig.3.

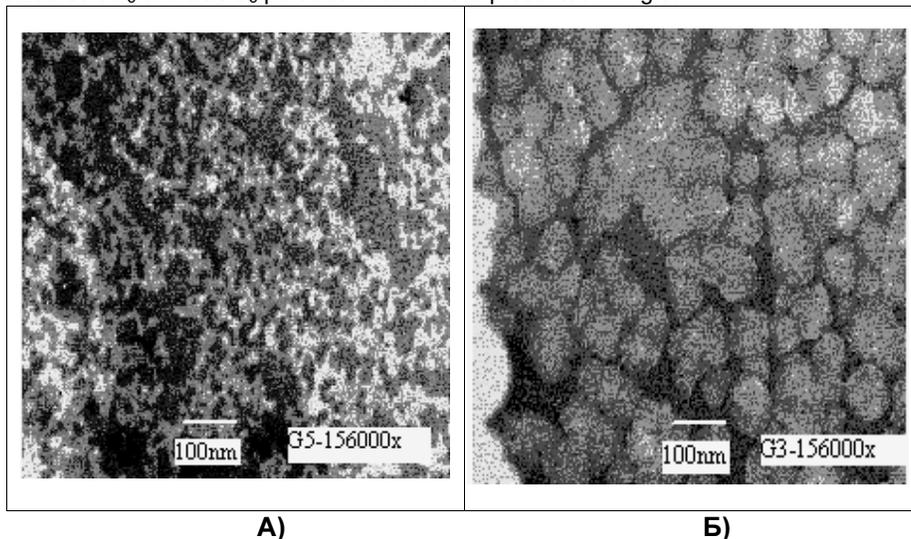


Figure 3. Electron microscopy photographs of TEM of nano-sized particles of BaCO_3 (A) and CaCO_3 (B) obtained in W/O microemulsion system (alkali solution/n- $\text{C}_6\text{H}_{14}/\text{C}_{20}\text{H}_{37}\text{NaO}_7\text{S}$) and the following reaction parameters: $C = 2.10^{-2} \text{ mol/l}$; $n = 800 \text{ min}^{-1}$; $t_1 = 60 \text{ min}$; $t_2 = 60 \text{ min}$; $R = [\text{H}_2\text{O}]/[\text{AOT}] = 20$; $T = 25^\circ\text{C}$; $d_{\text{op}} = 20 \div 30 \text{ nm}$.

The electron microscopy analysis carried out showed for each sample that the nanostructures synthesized were zero-dimensional, had narrow distribution by size, spherical shape and crystalline structure. Furthermore, they were observed both as individual particles and small agglomerates (3+4 particles). The photographs presented in Fig.3 indicate for spherical shape and sizes from 20 to 30 nm of the BaCO_3 and CaCO_3 nanoparticles obtained. The specific area ($A \text{ (m}^2/\text{kg)}$) of the barium carbonate nanoparticles obtained was calculated according to formulae reported in [5]. For the nanostructures sized 20÷30 nm, the values of A were from $6.82 \cdot 10^7$ to $4.55 \cdot 10^7 \text{ m}^2/\text{kg}$. The 20 nm particles had specific area of $6.82 \cdot 10^7 \text{ m}^2/\text{kg}$ while these sized 30 nm – $4.55 \cdot 10^7 \text{ m}^2/\text{kg}$. Therefore, the particles specific area decreased with the increase of their radius.

The results obtained confirmed the generally assumed opinion that the synthesis of nanostructures in microemulsion is preferred to the other approaches known, and the water-in-oil (W/O) microemulsion was successfully used as reaction medium allowing the realization of chemical reactions to obtain various organic and inorganic substances. While the two phases are observed to spontaneously separate in common emulsions, the behavior of microemulsions remains stable and they do not split. This can be explained with the microsize of the water drops which in our case was lower than 100 nm and, therefore, the microemulsion system used inorganic solution/n-hexane/AOT was isotropic and seemed optically transparent. Besides, the substance dissolved within the drops was small by quantity, i.e. the reagent concentration in the drop was very low ($C = 2.10^{-2} \text{ mol/l}$) so it could be expected to obtain great number of monodispersed nanoparticles. This once again sustains the advantages of the approach used and the nanosynthesis technology developed.

CONCLUSION

On the basis of the study carried out and the practical use of water-in-oil microemulsion system as special "microreactor" for synthesis of ultrafine carbonate nanostructures, the following conclusions can be drawn:

1. A method was developed, installation was designed according to this method and the process of preparation of carbonate nanostructures by microemulsion technique was studied. The little known variety of the microemulsion method of nanosynthesis was realized, namely: in the experiments, only one microemulsion system was used which was colloid dispersed system of the type water-in-oil (w/o) containing the components inorganic solution/n-hexane/Aerosol OT.

2. As a result of the experiments carried out, solid nano-sized particles of barium and calcium carbonate were synthesized. The nanostructures were obtained through a chemical reaction under microemulsion conditions at various mas' ratios of the phases forming the reverse microemulsion system.

3. Using the methods of electron microscopy (TEM), the nanoparticles obtained were identified and characterized. Their spherical shape, crystalline structure and narrow distribution by size (monodispersity) was proved in each sample. The BaCO₃ and CaCO₃ nanostructures had sizes from 20 to 30 nm. The results obtained from the present study confirmed the advantages of the method of nanosynthesis used.

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