Obtaining of Ultradispersed and Mesoporous Raw Products by Wet and Combined Methods

E A Trusova
Laboratory of Functional Ceramics, A.A. Baikov Institute of Metallurgy and Material Science RAS, 119991 Moscow, Russia
E-mail: trusova03@gmail.com

Abstract. The laboratory technology was developed for the obtaining of nano and submicron powders of II-VIII group metal oxide as well as composites based on mesoporous metal silicates, metal oxides or nanoscale colloidal silver. The optimal parameters of the nanoparticles synthesis: a qualitative and quantitative composition of the reaction mass and thermal treatment mode were determined. The developed approach allows to carry out synthesis of nano sized metal oxide particles with a reference size, to vary it in the range 10-130 nm with an accuracy of 20-30 nm. A distinctive feature of our method is environmental friendliness, efficiency, and simplicity of the technological realization.

1. Introduction
Currently, a breakthrough in field of creation fine-grained ceramic materials with improved mechanical strength, electrical, and other performance properties, first of all requires the development of a reliable ways to produce large quantities of nanostructured raw products, which include ultradispersed powders and mesoporous structure. Now although the great need for such materials the most methods of nanocrystalline materials manufacture are not suitable for the production of large quantities in industrial applications [1]. Wet methods of synthesis are very technologically promising for the large-scale fabrication of nanostructured raw materials for a broad purpose range.

The wet synthesis methods enable to control the nanostructures formation at the atomic and molecular level [2]. Sol-gel, template and microsuspension methods were used in the developed technology. The essence of the sol-gel method is the formation of highly dispersed colloidal sol particles coated with an organic shell of the first stage, the particles size can to reach a few tens of nanometers. Then evaporated sol was subjected to thermal treatment at 500°C and the resulting nanoparticles of metal oxides or composites based on them have been received [3]. Template method was used in obtaining mesoporous metal-silicates in which Al, Fe, Ge, Ni, Ti, Zr ions isomorphically substituted silicon ions in the SiO₂ structure [4]. Usually a polymer or dendrimer are used as templates in the traditional method [5, 6]. The low molecular weight organic compounds as hydrocarbons, N-containing or lower alcohols were used in the developed by us method. Oligomeric 3D template was formed in situ, and its structure determined the structure of the future silicate, its porosity, pore size, etc. This approach allows modeling the structure of the silicate by changing the composition of the organic component in the reaction mixture: co-solvents, surfactants, pH-regulators, ligands in the metal-source and metal nature, etc. The effective use of wet and cryo technological methods combination was shown by the example of Ni, Fe and Ce oxides [7].
Previously, we reported about separate results on the development of a modified sol-gel and template methods for fabricating of nanostructures [8-11] and using them to obtain the materials for various purposes [12, 13]. In this paper obtained results are generalized and the main approaches used for the development of technologies are presented. Also the possibility of the proposed technology is shown for the creation of new nanostructured raw products: ultradispersed powders and mesoporous structures of a wide range of purposes (figure 1).

![Diagram](image.png)

**Figure 1.** The possibility of wet methods for the production of raw materials of wide destination range

2. Experiment
Acetylacetonates, stearates, oxalates, palmitates, acetates and mineral salts (nitrates, sulfates, chlorides, carbonates) were used as the metals sources to produce initial solutions in deionization water. The concentration of the initial solutions was 0.01-0.62 M. Monoethanolamine (MEA), N,N-dimethyloktamine (DMOA), hexamethylenetetramine (HMTA) tetraethylammonium hydroxide (TEAH) at a molar ratio to metals 1-20 were used for complexation and sol stabilization. The resulting gel was thermal treated at 500-900°C for 1-3 h. The resulting powders were characterized by using a set of instrumental methods, including XRD (DRON-3M, Russia), TEM (LEO 912 ab_Omega Carl Zeiss), N₂-adsorbtion/desorbtion (NOVA 2200), particles size distribution was obtained using the diffusion aerosol spectrometer (AeroNanoTech, DAS 2702).

3. Discussion
3.1. Effect of the nature of the initial reagents and sol stabilizer on morphological characteristics of the obtained metal oxides
The II-VIII groups metal oxide powders with crystallite size from several to 120 nm and a specific surface area of 200 m²/g were obtained by varying the three process parameters: the metal-source, sol stabilizers and their molar ratio value of the metal (1-20). On the example of ZnO powders it has been shown that by using one and the same source of zinc, nitrate, the size of crystallites was controlled by substitution of N-containing reagent. Thus, the use of HMTA results in ZnO powder with a higher 3-40 times dispersion (figure 2a) than with use of DMOA. However, in the case of CeO₂ powders using of nitrate as the source as well as DMOA and TEAH for sol stabilization leads to obtaining of CeO₂ powders with similar particle size: 12.0 and 14.5 nm, respectively (figure 2b). The specific surface area of CeO₂ powder obtained by using DMOA was one and a half times larger than the sample
obtained with using TEAH: 91 and 61 m$^2$/g, respectively. Replacement DMOA on MEA caused an increase in the average crystallite size by 1.5-2 times (figure 2c).

**Figure 2.** Microphotos taken by use TEM: a – ZnO, obtained by use of HMTA, b – CeO$_2$, obtained by use of DMOA, c - CeO$_2$, obtained by use of MEA.

### 3.2. Solid solutions based on ZrO$_2$

Ultradispersed powders of solid solutions Y$_x$Zr$_{1-x}$O$_2$ (x = 0.25-0.75) and Ce$_x$Zr$_{1-x}$O$_2$ (x = 0.06-0.75) have been developed for fine-grained materials for microelectronics and endoprostheses. Thus, microporous Y$_{0.5}$Zr$_{0.5}$O$_{2-\delta}$ powder with a small portion of mesopores and surface area 105 m$^2$/g had an average crystallite size 2-4 nm, according to the XRD and TEM data (figure 3a). Microphoto obtained by dark field TEM shows that obtained powder consisted of discrete particles (figure 3b). Average crystallite size Ce$_{0.09}$Zr$_{0.91}$O$_2$ was 8 nm, according to XRD date, and the dark-field TEM photo showed that the particle size was not more than 12 nm (figure 3c). In all cases, the crystallite size of the solid solutions was almost 2-3 times less than the pure ZrO$_2$ (figure 3d).

### 3.3. Mesoporous systems

As already mentioned above, a number of mesoporous (pore size of 2-20 nm) metal silicates, where the metal ions (Al, Ge, Fe, Ni, Ti, Zr) isomorphically substitute Si$^{4+}$ ions in the SiO$_2$ lattice, were obtained by template method [14]. A number of composite systems based on Al-Ti-silicates were obtained as prospective models for the development of new catalysts and biomedical materials. Sulphided mesoporous system MoO$_3$/γ-Al$_2$O$_3$ and NiO-MoO$_3$/γ-Al$_2$O$_3$ with pore size of 10-20 nm, as well as CoO-MoO$_3$/Ti$_{0.03}$Si$_{0.97}$O$_2$ (H/Na-forms) with pore size 3-4 nm were tested in alcohols synthesis from CO and H$_2$, and provides access C$_1$+ alcohols at 16-20% [15]. Apparently, these composites can also be used as a base for the development of new low-temperature catalysts for alcohol synthesis.

Soft bactericidal action material was obtained by including of colloidal silver Ag$^0$ in the structure of mesoporous Al$_{0.25}$Si$_{0.75}$O$_{2.6}$ (figure 4). It can be seen that Ag$^0$-particles have a size 40-60 nm (figure 4a). When colloidal silver particles were the applied to mesoporous Al$_{0.25}$Si$_{0.75}$O$_{2.6}$ the dispersion of Ag$^0$-particles increased (figure 4b), apparently due to the impact of surface silicate. The obtained composite was tested for silver liberation dynamics in the model medium with a pH corresponding to human body pH. The curve shape (figure 4c) shows that the most intense Ag$^+$-emission in the physiological environment of silver occurs in the first few hours after the sample in the physiological environment, without causing tissue irritation. This composite can be considered as a model for the development on his basis clinical material for bandages, catheters and other materials of biomedical applications.

### 3.4. The variety of obtained ultradispersed and mesoporous systems and their purpose

On figure 5 list of developed ultrafine metal oxide powders for production of fine ceramic materials of wide application is shown. By simulating of qualitative and quantitative composition of the reaction mixture it can be controlled the particle size of the obtained metal oxide accurate within 10-

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20 nm, and thus, to form its physical properties. Thermal treatment conditions in every case are selected in accordance with the composition of the reaction mixture and the reference sizes of resulting metal oxide particles.

One of the major advantages of ultradispersed powders as raw materials for production of fine-grained ceramics is the ability to use a sintering temperature lower than for traditional ceramics. This size effect can be observed in the example of Bi$_2$O$_3$-ZnO ultradispersed powdery composite. On the Figure 6 it has been shown the presence of the triple junctions formed during the thermal treatment of the same composite at 550$^\circ$C, of 500-600$^\circ$C below the temperature at which the usually ceramics based on ZnO is sintered (1100-1300$^\circ$C). The use of ultradispersed powders to produce materials can not only save energy, but also to obtain a fine-grained ceramics, due to reduces the probability of recrystallization and grain consolidation.

**Figure 3.** Microphotos taken by use TEM ultradispersed powders: a and b - Y$_{0.5}$Zr$_{0.5}$O$_{2.4}$, c - Ce$_{0.09}$Zr$_{0.91}$O$_2$, d - ZrO$_2$. 
Figure 4. Microphotos taken by use TEM: a - colloidal silver Ag\(^0\), b - Ag\(^0\)/Al\(_{0.25}\)Si\(_{0.75}\)O\(_2\)-δ; c - curve of Ag\(^0\) emission in liquid medium

Figure 5. The resources of developed technology for producing of ultradispersed metal oxide powders - raw products for new functional materials

Figure 6. Microphoto obtained by using TEM: ultradispersed Bi\(_2\)O\(_3\)-ZnO powder composition was thermo treatment at 550°C. The formed triple junctions are circled with white circles
4. Conclusion
The laboratory technology was developed for the obtaining of nano and submicron powders of II-VIII group metal oxide as well as composites based on mesoporous metal silicates, metal oxides or nanoscale colloidal silver. The optimal parameters of the nanoparticles synthesis: a qualitative and quantitative composition of the reaction mass and thermal treatment mode were determined. The developed approach allows to carry out synthesis of nano sized metal oxide particles with a reference size, to vary it in the range 10-130 nm with an accuracy of 20-30 nm. A distinctive feature of our method is environmental friendliness, efficiency, and simplicity of the technological realization.

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