

EFFECT OF HYDROTHERMAL SYNTHESIS CONDITIONS ON THE MORPHOLOGY OF ZrO_2 NANOPARTICLES

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Nanoparticles based on ZrO_2 in the form of spheres, cylinders and agglomerates in the form of hollow microspheres were obtained. It is shown that the main factor influencing on the formation of nanostructures based on zirconium dioxide under hydrothermal conditions is the chemical prehistory of the starting materials. The possibility of varying the synthetic parameters to obtain a zirconia-based material with high porosity and specific surface area was shown.

Keywords: nanoparticles, hydrothermal synthesis, zirconia.

1. Introduction

Analysis of the size, morphology and structural characteristics of nanoparticles shows that they are highly dependent on the method and conditions of their production [1-3]. Moreover, even within the same method changing the synthetic parameters can lead to a significant change in the characteristics of the resulting nanostructures. One such method is hydrothermal synthesis. This method, as shown in [2, 4-6], allows one to obtain weakly agglomerated nanoparticles with different chemical composition and narrow particle size distribution. Through a wide range of variable parameters (chemical prehistory of the starting materials, pressure, temperature, time, chemical composition of hydrothermal solutions) nanostructures with desired the dispersion, morphology and structure can be obtained [7-11]. However, the existing differences in the results of various researchers [2, 4-12] does not allow one to predict the possibility of obtaining nanoparticles with specified characteristics, which leads to the need for a comprehensive study and the establishment of the influence of prehistory and chemical parameters of hydrothermal treatment on the formation of nanoparticles.

In that regard, this article examines the influence of the method by which the initial zirconium hydroxide was obtained and the conditions of its subsequent hydrothermal treatment on the size, structure and shape of the formed nanostructures.

2. Experiment

The following were used as the starting materials for hydrothermal treatment:

- (1) Zirconium hydroxide was obtained by precipitation from a solution of 1M ZrOCl_2 with 12M NH_4OH . The precipitate was then washed with distilled water until a negative reaction to Cl^- ions and neutral pH ($\text{pH} \approx 7$) and dried at 100°C .

- (2) Zirconium hydroxide was obtained by adding ZrOCl_2 to a 0.5 M solution of NaOH. The precipitate wasn't washed from the neutralization reaction products, however, subjected to sonication ($\nu = 3.5$ kHz) for 30 minutes with continuous mechanical stirring.
- (3) The suspension obtained by dissolving ZrOCl_2 in an ethanol-HCl mixture with the addition of $(\text{NH}_2)_2\text{CO}$ to adjust the pH. The ratio of $\text{C}_2\text{H}_5\text{OH}:\text{HCl}$ in the mixture was 3:2.

Hydrothermal treatment was performed in a steel autoclave with a teflon vial from 160–240 °C for 4–72 hours. Distilled water solutions of either NaOH or an acid-alcohol mixture were used as the hydrothermal solution.

To determine the elemental composition of the hydrothermal treatment products, we used the method of energy dispersive X-ray analysis (EDX) (electron microscope Hitachi S-570, equipped with a microprobe system Bruker Quantax 200).

In the case of ZrO_2 based nanostructures, the chemical composition of the post hydrothermal synthesis medium was determined using the Fourier AVANCE-400 NMR spectrometer (Bruker, Germany) with an operating frequency for ^1H : 400 MHz. ^1H NMR spectra of hydrothermal solution in heavy water D_2O was obtained at $T = 298$ K in a single-pulse method with a suppressed water signal.

The phase composition of the samples was determined by X-ray diffraction analysis on a Shimadzu XRD-7000 diffractometer ($\text{CuK}\alpha$ - radiation).

The crystallite size was calculated by X-ray diffraction line broadening samples using Scherrer's formula. The particle size was determined by analysis of the results obtained by transmission electron microscopy (Tesla BS-500 U = 90 kV).

The specific surface area values for ZrO_2 nanoparticles of different composition, size and morphology were determined on the Micromeritics ASAP 2020 analyzer (USA) by removing the nitrogen adsorption isotherms at 77 K.

3. Results and discussion

According to X-ray analysis of composition 1, treated at 240 °C for 4 hours using a distilled water hydrothermal solution leads to the formation of predominantly tetragonal ZrO_2 nanoparticles with a size of coherent scattering area (CSA), about 20 nm (Fig. 1a). Analysis of the electron microscopy data indicated that the formed nanoparticles were close to spherical with a narrow size distribution (Fig. 1.b). These results were consistent with the results of articles [12-14].

Hydrothermal treatment of composition 2 was conducted at 200 °C for 24–72 hours. A solution of NaOH was used as the hydrothermal solution. Based on X-ray diffraction and electron microscopy data, it can be concluded that changing the feed preparation process and the chemical composition of the hydrothermal solution leads to some changes in the flow processes of dehydration and crystallization under hydrothermal conditions.

Hydrothermal treatment of composition 2 at 240 °C for 24 h resulted in a rather broad peak in the X-ray diffraction pattern corresponding to 100% reflex of *t*- ZrO_2 , against which, relatively narrow maxima of *m*- ZrO_2 were recorded (Fig. 2a).

According to results of a SEM study, the sample contains two types of particles. One can be characterized as rod shaped (Fig. 2b) particles having diameter of 50 nm and length of 100 nm and other as considerably smaller particles with close to spherical morphology.

When hydrothermal treatment was increased from 24 to 48 and 72 hours, the intensity of *t*- ZrO_2 peaks for composition 2 considerably decreased (Fig. 2a). Herewith, it should be

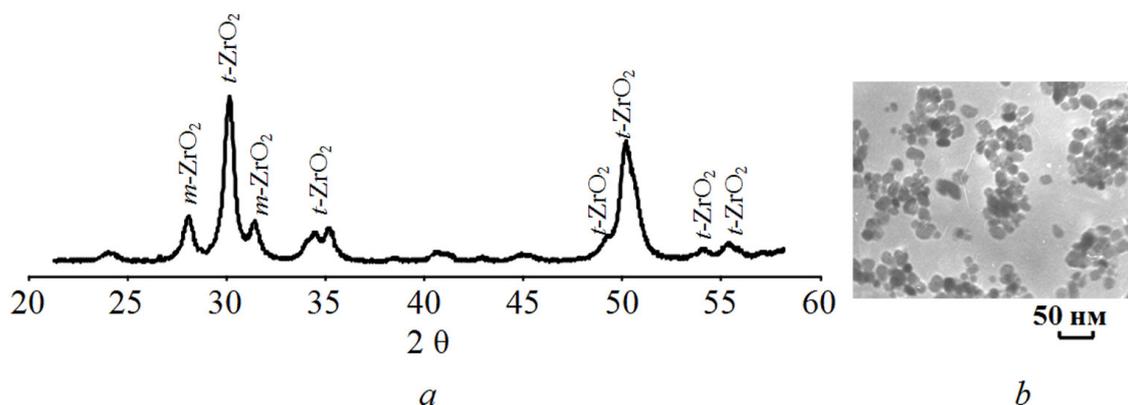


FIG. 1. X-ray diffraction pattern and photomicrograph of nanoparticles based on ZrO_2 , obtained by hydrothermal treatment of composition 1

noted that because of the lack of a discernible change in the width of peaks for monoclinic as well as cubic zirconia, one can argue that the size of the formed crystallites was constant.

However, the results of the SEM study showed not only an increase in the quantity of the ZrO_2 particles in the form of rods, apparently with monoclinic crystalline structure, but also in their length, which average 200 nm, while at the same time, the diameter of rods didn't change appreciably.

As was reported in papers [12, 15], the use of distilled water as the hydrothermal solution at the same temperature didn't lead to a noticeable change in the shape and structure of the zirconia nanoparticles, even in the case of prior ultrasonic treatment of the initial suspension and increasing the hydrothermal treatment duration to 72 hours. Additionally, it was shown [13] that the direct addition of sodium hydroxide or chloride to the hydrothermal solution also didn't drastically change the shape and size of zirconia nanoparticles in comparison with distilled water.

Results of an EDX study showed that the hydrothermal synthesis product of composition 2 contained a noticeable quantity of sodium (about 5 mol. %), but at the same time, in samples obtained from compositions 1 and 3, those impurities were not found.

Seemingly, in this case, because sodium hydroxide was used at the generating stage of the $[\text{Zr}(\text{OH})_2 \cdot 4\text{H}_2\text{O}]_4^{2+}(\text{OH})_8^-$ hydroxo-complex, its role in the formation of zirconia nanoparticles with one or another crystallite structure was previously noted [12, 14], sodium ions are kept in a zirconia nanoparticle structure, thus stabilizing the tetragonal phase in a manner similar to water molecules as has been shown previously [15]. Herein, analysis of obtained data showed that formation of monoclinic phase occurs not because of $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$ crystalline phase transition, but because of a recrystallization process. In other words, the use of NaOH as a hydrothermal solution provides pH value, which is enough to activate dilution of $t\text{-ZrO}_2$ nanoparticles, stabilized by impurity ions, with size of coherent scattering region about 10 nm and subsequent crystallization of thermodynamically stable $m\text{-ZrO}_2$ in the form of rods.

The hydrothermal treatment of composition 3, which is a high temperature hydrolysis of ZrOCl_2 in an acid-alcohol medium, was carried out at 160°C over 24 hours. According to X-ray diffraction line broadening analysis, the obtained zirconia particles have size of coherent scattering region of about 5 nm (Fig. 3a).

In this case, SEM images showed the formation of hollow spheres in the range of 300–700 nm with wall thickness of approximately 50 nm (Fig. 3b).

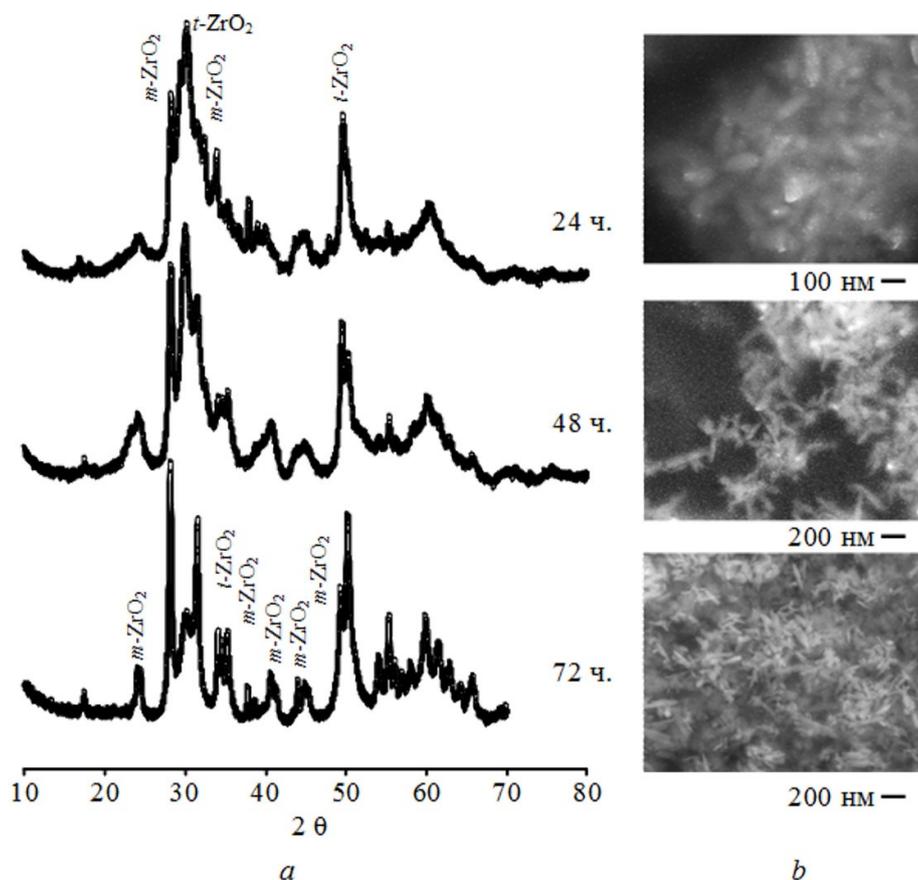


FIG. 2. X-ray diffraction pattern and photomicrograph of nanoparticles based on ZrO_2 , obtained by hydrothermal treatment of composition 2

Apparently in this case, the observed hollow microspheres are agglomerates, consisting of $m\text{-ZrO}_2$ crystallites with average size of about 5 nm. Analysis of the specific surface area, which amounts $140 \text{ m}^2/\text{g}$, confirmed this fact. At the same time, the specific surface area of zirconia nanoparticles, produced by hydrothermal treatment of composition 1, is only $85 \text{ m}^2/\text{g}$.

NMR spectral analysis of the hydrothermal solution after heat treatment (Fig. 4) indicated the presence of two quartets at 3.5 ppm region assigned to CH_2 groups of ethanol and diethyl ether, the signals at 4.2 ppm and 1.0 ppm assigned to HDO and CH_3 groups of ethanol and ether. Furthermore, the presence of a small amount of ammonium ions, which apparently could be formed by decomposition of urea during hydrothermal treatment was shown by the signal at 7.0 ppm

It can be assumed that in this case the formation of the observed structure occurs by a template synthesis mechanism. That is, ethanol in the presence of concentrated hydrochloric acid at elevated temperature dehydrates to form an ether, which, due to the low solubility in the mixed solution of ethanol and water, may exist in the form of oil droplets in the solution [10]. When the temperature is raised urea located in the initial mixture slowly reacts with water to form NH_4OH and CO_2 , which leads to higher pH and as a consequence hydrolysis of ZrOCl_2 on the oil drop-aqueous solution interface.

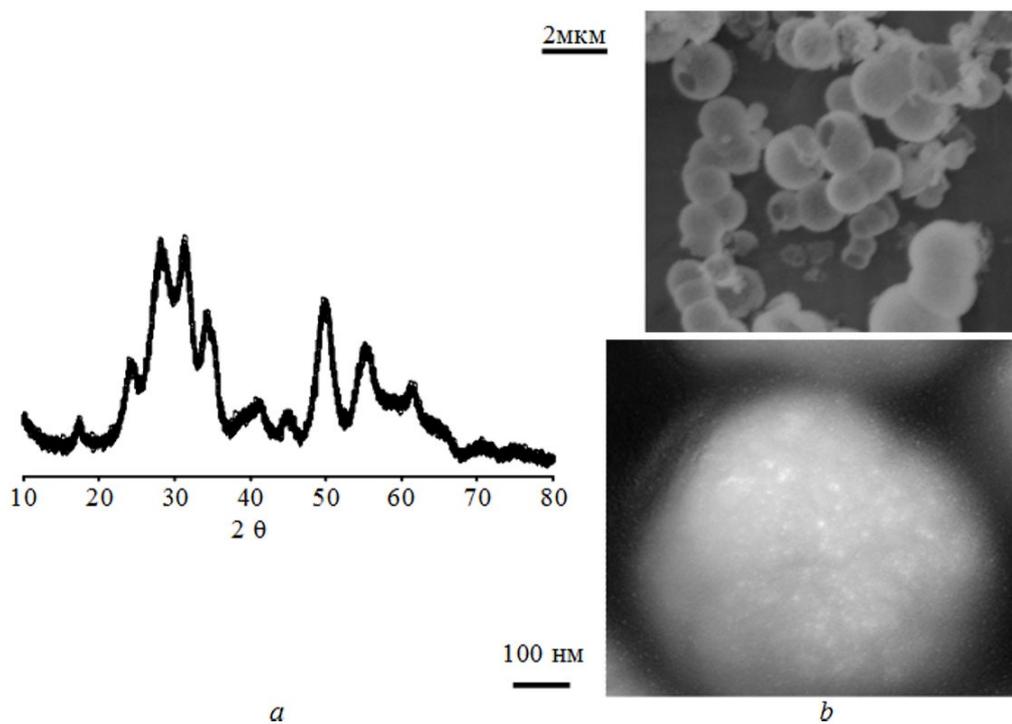


FIG. 3. X-ray diffraction pattern and photomicrograph of nanoparticles based on ZrO_2 , obtained by hydrothermal treatment of composition 3

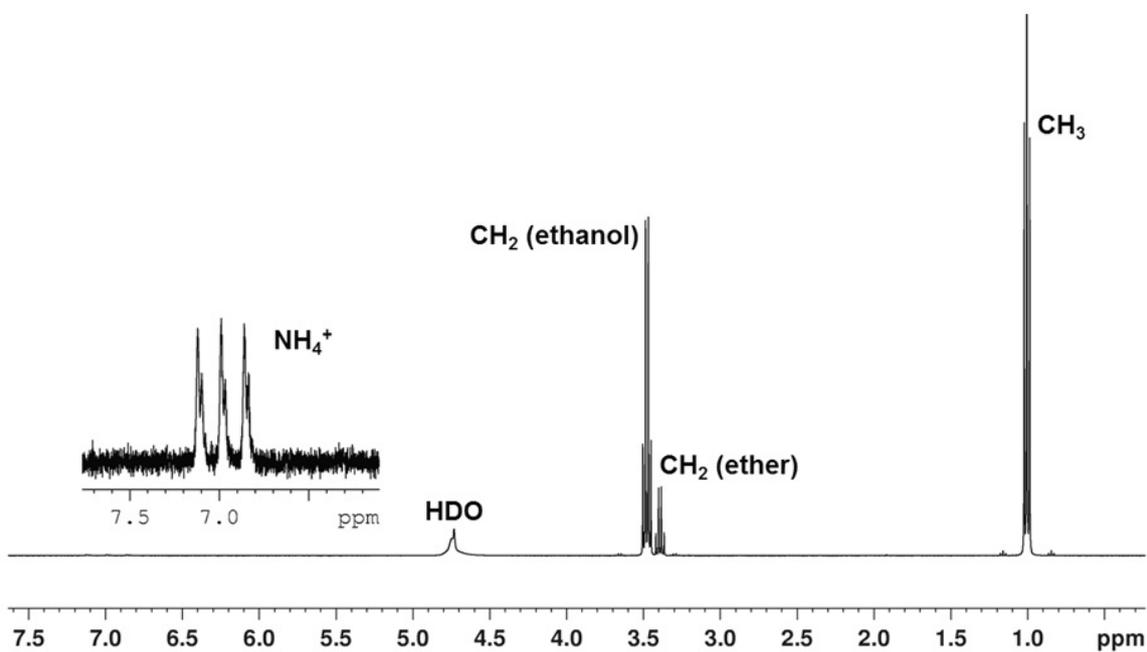


FIG. 4. NMR spectrum of hydrothermal solution after heat treatment of composition 3

4. Conclusions

Thus, on the basis of these data, it can be concluded that the main factor contributing to the formation of nanostructures based on zirconium dioxide under hydrothermal conditions is the prehistory of the starting materials.

This work has shown that it is possible to vary synthetic parameters to obtain a zirconia-based materials with high porosity and a specific surface area, which is promising for the generation of nanoparticles for use as nanoreactors, catalyst or catalyst carrier, adsorbent, etc.

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