ISSN 0020-1685, Inorganic Materials, 2012, Vol. 48, No. 5, pp. 494–499. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.D. Yapryntsev, A.E. Baranchikov, N.N. Gubanova, V.K. Ivanov, Yu.D. Tret'yakov, 2012, published in Neorganicheskie Materialy, 2012, Vol. 48, No. 5, pp. 576–582.

Synthesis of Nanocrystalline ZrO_2 with Tailored Phase Composition and Microstructure under High-Power Sonication

A. D. Yapryntsev[a], **A. E. Baranchikov**[b], **N. N. Gubanova**[c], **V. K. Ivanov**[b], **and Yu. D. Tret'yakov**[a]

[a] *Moscow State University, Moscow, 119899 Russia*
[b] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
Leninskii pr. 31, Moscow, 119991 Russia
[c] *Konstantinov Institute of Nuclear Physics, Russian Academy of Sciences,*
Orlova Roshcha, Gatchina, Leningrad oblast, 188300 Russia

Received November 9, 2011

Abstract—The effect of sonication on the composition and properties of zirconia precipitated from aqueous zirconyl nitrate solutions at various pH values has been studied using thermal analysis, X-ray diffraction, and low-temperature nitrogen adsorption measurements. The results demonstrate that acoustic processing considerably reduces the content of sorbed ions in amorphous $ZrO_2 \cdot xH_2O$ gels and allows one to control the composition and microstructure of the nanocrystalline zirconia produced through thermal decomposition of the gels.

DOI: 10.1134/S0020168512050214

INTRODUCTION

One of the most promising approaches to the synthesis of inorganic materials in highly dispersed and nanoparticulate states is high-power sonication. In recent years, a number of studies have been concerned with the use of sonochemical techniques for the preparation of simple and complex nanoparticulate substances with tailored properties [1–3].

The mechanisms of sonochemical reactions in homogeneous liquids have been studied in sufficient detail. The results were systematized in terms of two main theories: hot spot theory [4] and local electrization of the surface of cavitation bubbles [5]. At the same time, the specifics of the physicochemical processes that take place in heterogeneous systems under high-power acoustic processing conditions are far less well understood. In particular, the effect of sonication on heterogeneous systems containing nanoparticles (e.g., sols) and on amorphous gels that result from the aggregation of colloidal particles has been studied little. The evolution of such systems in an acoustic field was studied using amorphous silica [6] and iron(III) hydroxide [7] as examples. The results indicate that ultrasonic processing increases the gelation rate and changes the mesostructure of the resulting gel (in particular, the density, particle size, aggregate size, and fractal characteristics of the surface).

The purpose of this work was to study the effect of sonication at various pH values of the medium on the thermal characteristics of amorphous hydrous zirconia and on the phase composition and microstructure of nanocrystalline zirconia hydrolysis products.

EXPERIMENTAL

Hydrous zirconia was prepared by slowly adding aqueous ammonia (2.7 M) to an aqueous 0.25 M solution of zirconyl nitrate, $ZrO(NO_3)_2$, with constant stirring, until the pH of the solution was 5.26, 7.17, or 8.99. The solution pH was monitored with a Crison GLP-22 pH meter, equipped with a multipurpose measuring electrode and thermocompensator. Precipitations were carried out in a thermostated cell. The temperature was maintained at $20 \pm 1°C$. In addition, $ZrO_2 \cdot xH_2O$ was precipitated in the same conditions but under sonication. The ultrasound source used was a Bandelin Sonopuls HD 3200 generator equipped with a submerged titanium waveguide. The ultrasound frequency was 20 kHz, and the effective acoustic power density was 35 W/cm^2.

After the precipitation, the resultant suspensions were vigorously stirred for an additional 15 min. The suspensions prepared under sonication were stirred in an ultrasonic field. Next, the precipitates were washed with distilled water several times, separated by centrifugation (8000 rpm), and air-dried at 50°C for 24 h.

The hydrous zirconia xerogels prepared at pH 5.26, 7.17, and 8.99 without sonication will be referred to as Z-5C, Z-7C, and Z-9C. The samples prepared under sonication will be designated Z-5US, Z-7US, and Z-9US.

The xerogels were annealed in air in a muffle furnace at 400, 500, 600, 700, and 800°C for 5 h.

The samples were characterized by thermogravimetry (TG) and differential thermal analysis (DTA) in air at temperatures from 20 to 1000°C using a Pyris

Diamond thermal analyzer (PerkinElmer). The heating rate was 10°C/min.

The phase composition of the samples was determined by X-ray diffraction (XRD) on a Rigaku D/MAX 2500 diffractometer (CuK_α radiation, scan rate of 2°2θ/min). Diffraction peaks were indexed using JCPDS PDF data. The crystallite size of zirconia was determined by the Scherrer formula:

$$D_{hkl} = \frac{K\lambda}{[\beta_{hkl}(2\theta) - s]\cos\theta}, \qquad (1)$$

where θ is the peak position, λ is the CuK_α X-ray wavelength (0.154056 nm), $\beta_{hkl}(2\theta)$ is the true physical broadening of the peak, and s is the instrumental broadening (0.1°). The Scherrer constant (K) was taken to be unity. To determine β, background-subtracted 111 and $\bar{1}11$ diffraction line profiles of monoclinic and 101 of tetragonal ZrO_2 were fitted with pseudo-Voigt functions.

The contents of the monoclinic (M-ZrO_2) and tetragonal (T-ZrO_2) zirconia polymorphs in our samples were evaluated from XRD data using relations reported by Toraya et al. [8].

Specific surface areas were determined by low-temperature nitrogen adsorption measurements with an ATX-6 analyzer (KATAKON, Russia). Prior to measurements, the samples were outgassed at 150°C in flowing dry helium for 30 min. The specific surface of the powders was evaluated using BET analysis (six points).

RESULTS AND DISCUSSION

The TG curves of the hydrous zirconia xerogels are presented in Fig. 1.

The weight loss curves of the control samples are seen to differ markedly in shape. In particular, the weight loss of the samples prepared in acid and neutral solutions (Z-5C and Z-7C) occurs in several steps. The first step (below 200°C) is the removal of sorbed water. The second step (200–400°C) is probably the decomposition of trace amounts of ammonium nitrate and nitrate-containing zirconium hydroxy compounds through high-temperature hydrolysis. The third decomposition step, with the highest rate at 440–445°C, is the complete removal of nitrates through pyrolysis in parallel with zirconia crystallization. Note that the decomposition of the nitrate-containing zirconium compounds is accompanied by an appreciable heat absorption.

The pyrolytic character of the high-temperature nitrate decomposition step is supported by the DTA curves in this temperature range (Fig. 1c). It can be seen that the exothermic zirconia crystallization process occurs concurrently with the endothermic decomposition process. As a result, the net heat effect of the process is insignificant in magnitude.

Consider now the TG curves of the samples prepared in the acid and neutral solutions (pH 5.26 and 7.17) under sonication (Fig. 1b). The key feature of these curves is that there is little or no weight loss during zirconia crystallization. This indicates that the amount of nitrate ions adsorbed on the surface of the particles forming in an ultrasonic field is considerably smaller than that in the control experiments.

The TG curves of the samples prepared in an alkaline solution (pH 8.99) with or without ultrasonic processing differ significantly from those of the samples obtained in the acid and neutral solutions. The DTA curve of the control sample shows no high-temperature nitrate decomposition step and is very similar to the DTA curve of the sample precipitated in the same conditions but under sonication. Also, there is no low-temperature ammonium nitrate decomposition step. These features lead us to conclude that there are few or no adsorbed nitrate ions in the corresponding samples, which fits well with the data on the variation of the phase composition of $ZrO_2 \cdot xH_2O$ with pH during synthesis [9].

Consider the phase compositions of the hydrous zirconia xerogels annealed at temperatures from 400 to 800°C. Heat treatment of $ZrO_2 \cdot nH_2O$ leads to zirconia crystallization in the form of the tetragonal and monoclinic phases. The phase composition of the annealing products is determined by the $ZrO_2 \cdot xH_2O$ xerogel preparation conditions. Figure 2 plots the percentage of tetragonal zirconia against annealing temperature. It can be seen that, at relatively low temperatures (up to 600°C), heat treatment of the xerogel precipitated in the alkaline solution without sonication produces no monoclinic ZrO_2, and the annealing product is phase-pure t-ZrO_2. Heat treatment of samples Z-5C and Z-7C, precipitated in the acid and neutral solutions leads to the formation of a mixture of t-ZrO_2 and m-ZrO_2 (containing 10–15% m-ZrO_2). The formation of monoclinic ZrO_2 during heat treatment of these samples and the absence of m-ZrO_2 in the annealing products of sample Z-9C (in the range 400–600°C) are consistent with a model for size stabilization of t-ZrO_2 [10–12], according to which metastable tetragonal zirconia can be obtained under ordinary conditions when its particle size is below 30 nm. Indeed, the particle sizes of the t-ZrO_2 produced by annealing samples Z-5C and Z-7C [evaluated using relation (1)] differ little and lie in the range 31–36 nm, whereas the particle size of the t-ZrO_2 obtained by annealing sample Z-9C at temperatures from 400 to 600°C is 24–25 nm (Fig. 3).

At the same time, all of the samples precipitated under sonication and heat-treated at temperatures from 400 to 600°C contain insignificant amounts of monoclinic ZrO_2.

Increasing the heat-treatment temperature to 700–800°C markedly increases the rate of the t-$ZrO_2 \rightarrow m$-ZrO_2 phase transition in the xerogels precipitated at pH 8.99 (Fig. 2). The monoclinic-ZrO_2 content of the

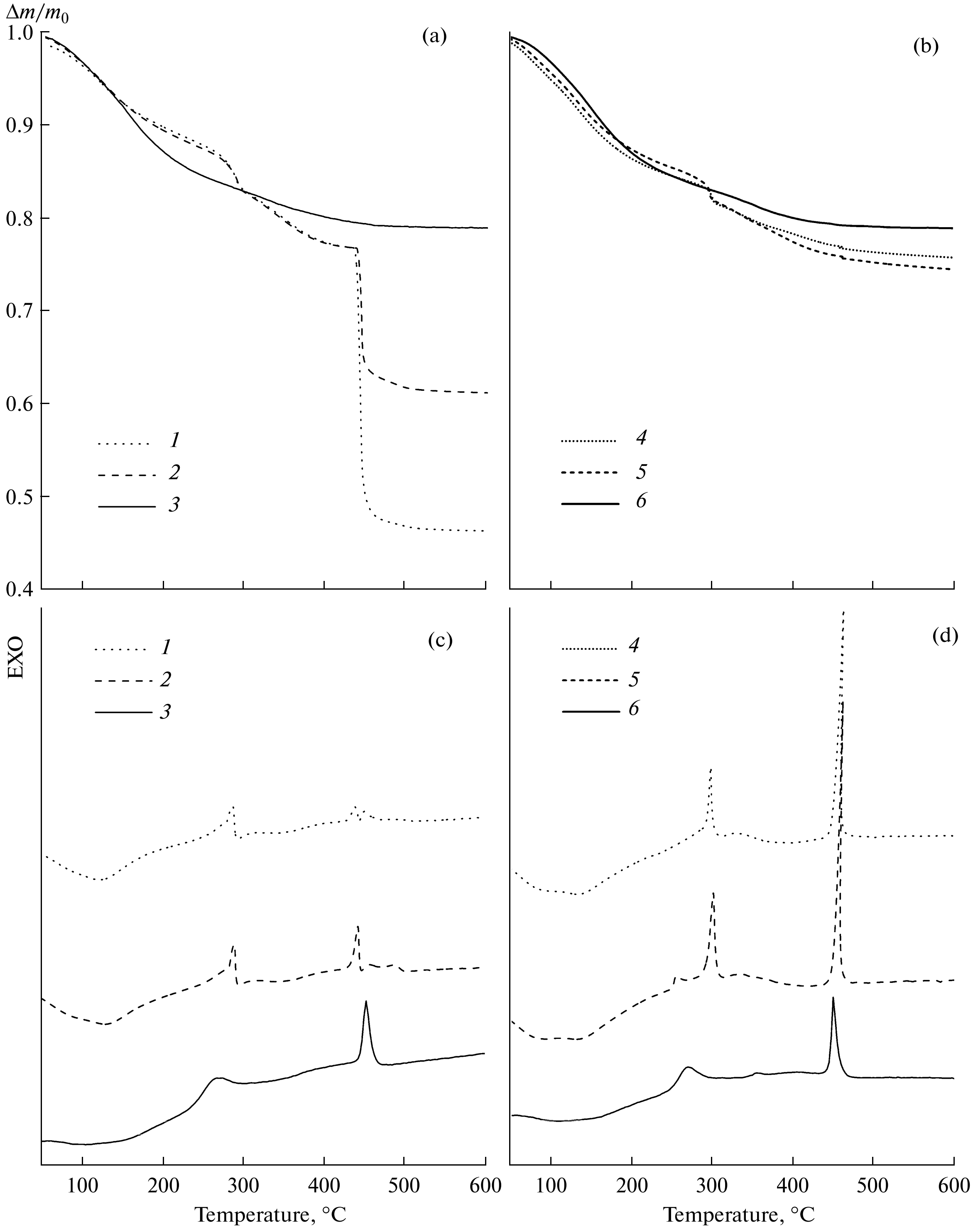

Fig. 1. (a, b) TG and (c, d) DTA curves of samples (*1*) Z-5C, (*2*) Z-7C, (*3*) Z-9C, (*4*) Z-5US, (*5*) Z-7US, and (*6*) Z-9US.

samples prepared under sonication considerably exceeds that of the control samples. In particular, after heat treatment of the as-prepared xerogels at 800°C for 5 h the degree of conversion was 33 and 12%, respectively. Note that the rate of the phase transformation in samples Z-5US and Z-7US was much lower than that in sample Z-9US. It seems likely that this was mainly due to the stabilization of the tetragonal phase by impurity ions and not to the size effect: the t-ZrO_2 particles in the samples prepared from xerogels

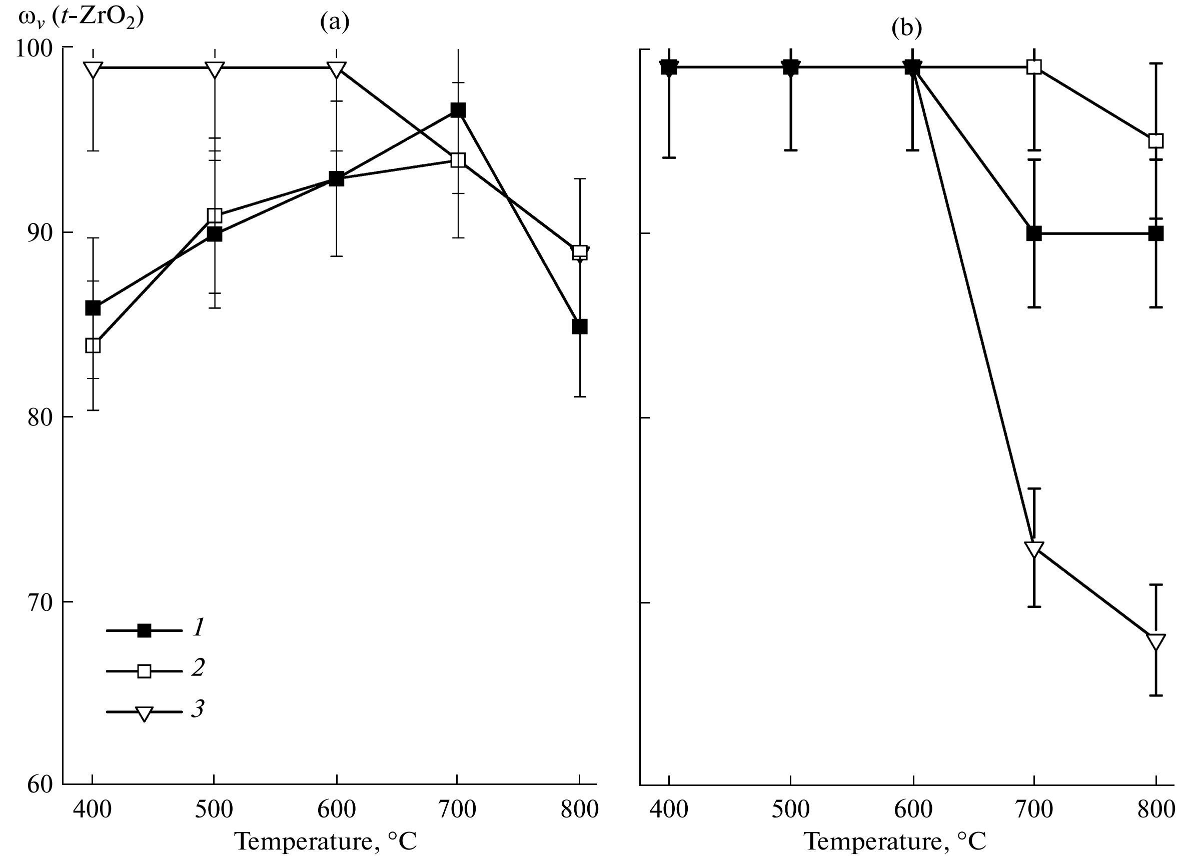

Fig. 2. Volume percent of tetragonal ZrO_2 as a function of annealing temperature for (a) the control samples precipitated at pH (*1*) 5.26, (*2*) 7.17, and (*3*) 8.99 and (b) the samples precipitated at the same solution pH values but under sonication.

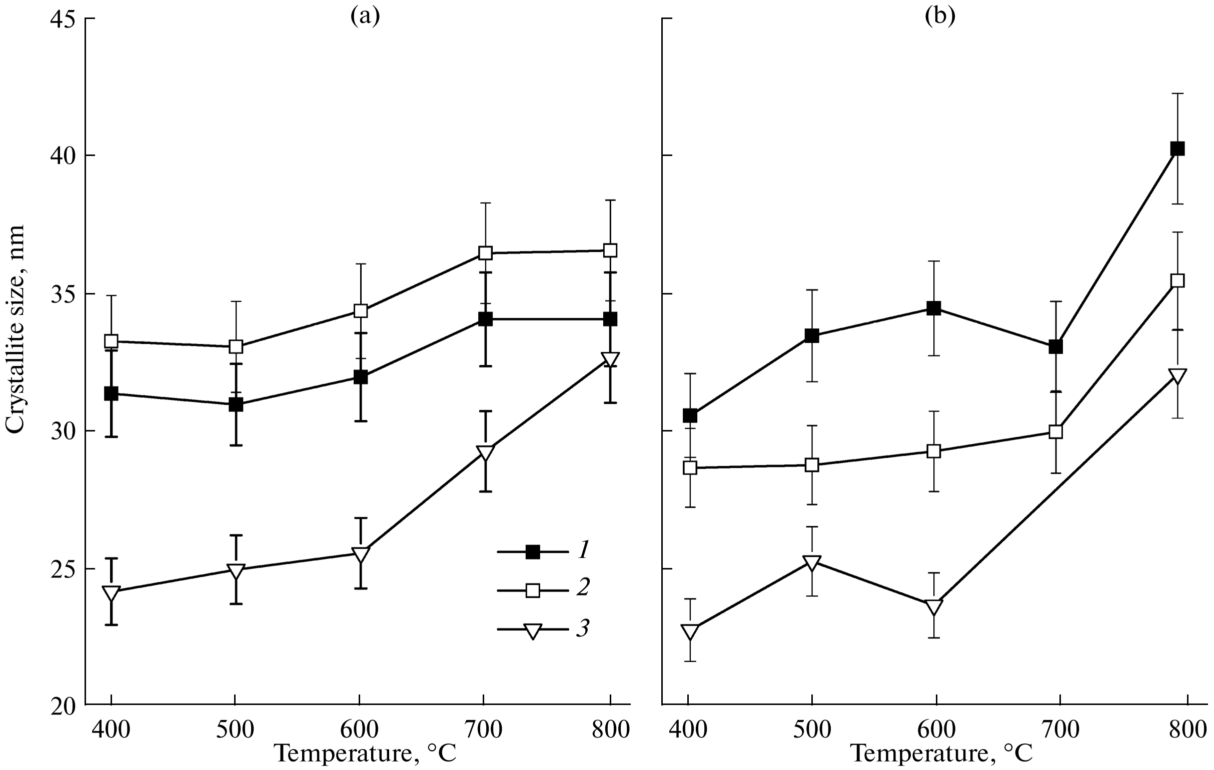

Fig. 3. Particle size of t-ZrO_2 as a function of annealing temperature for (a) the control samples precipitated at pH (*1*) 5.26, (*2*) 7.17, and (*3*) 8.99 and (b) the samples precipitated at the same solution pH values but under sonication.

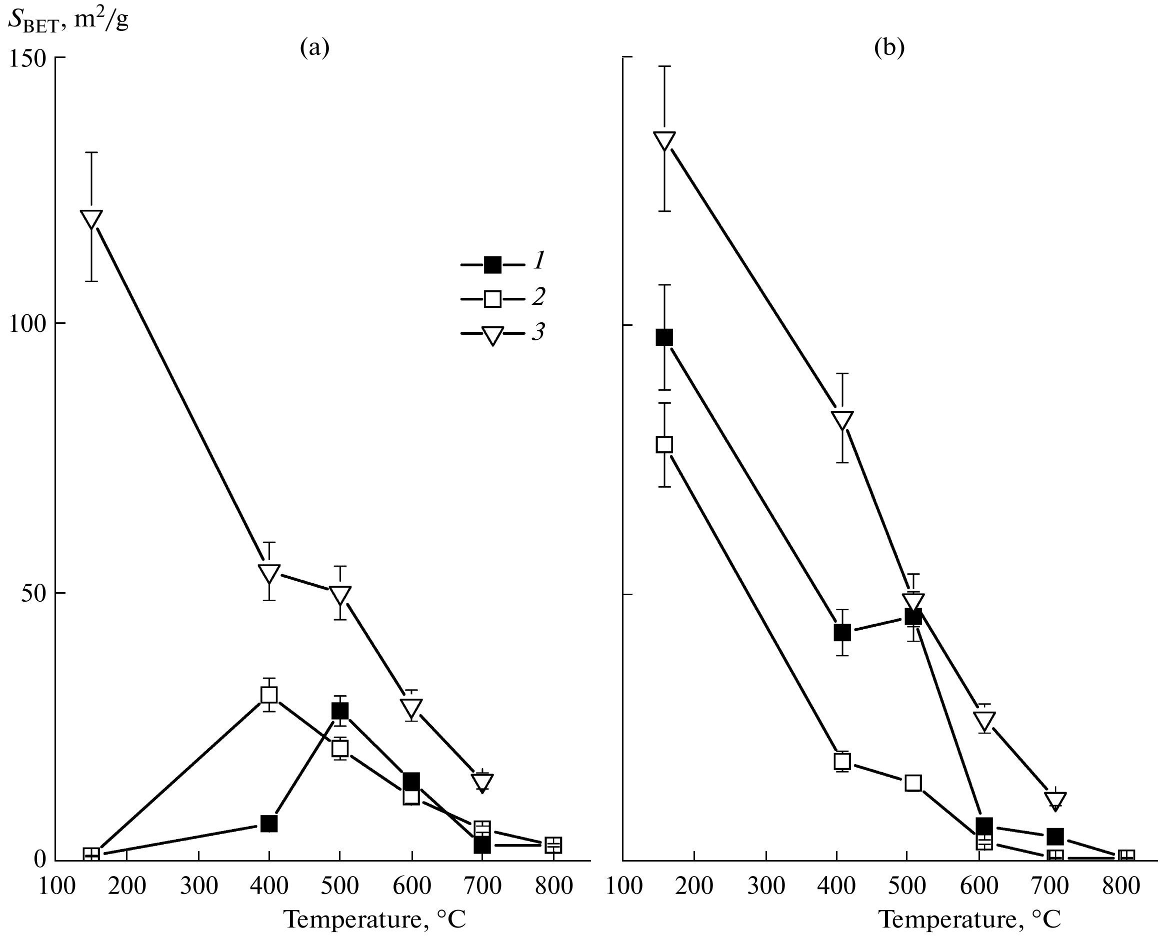

Fig. 4. Specific surface area as a function of annealing temperature for (a) the control zirconia samples precipitated at pH (*1*) 5.26, (*2*) 7.17, and (*3*) 8.99 and (b) the samples precipitated at the same solution pH values but under sonication.

Z-5US and Z-7US were larger than those in the samples obtained by annealing Z-9US (Fig. 3).

Consider now the low-temperature nitrogen adsorption data for the as-prepared hydrous zirconia xerogels and heat-treatment products (Fig. 4).

These data indicate that the specific surface area of the unannealed zirconia xerogels increases considerably with increasing solution pH. This correlates well with previous data of other groups [13–15] and ours [9]. In particular, it has been shown [16, 17] that the structure of solid zirconyl chloride corresponds to the formula $[Zr_4(OH)_8Cl_4 \cdot 16H_2O]4Cl \cdot 12H_2O$. According to small-angle X-ray scattering results, solutions also contain tetrameric planar complexes. In Clearfield's model [18], the interaction between the tetramers in the early stages of polymerization leads to the formation of an OH bridge pair in the plane of the zirconium atoms. Precipitation of gels from zirconium salt solutions by strong bases results in the formation of a so-called *A*-phase, which is commonly thought of as a two-dimensional disordered structure formed by tetramers. It is well known that acid hydrolysis has a higher rate in comparison with condensation, so the forming gels typically have a linear structure. With increasing pH, the polycondensation rate increases relative to the hydrolysis rate. As a consequence, the hydrous zirconia gels synthesized under alkaline conditions have a branched structure and large specific surface area.

The experimental data presented in Fig. 4 also lead us to conclude that sonication ensures a considerable increase in the specific surface area of the as-prepared xerogels. Clearly, this effect is related to the distinctive features of gel structure formation in an ultrasonic field: under active cavitation conditions, intense local liquid microflows and shock waves lead to the formation of gels with a looser structure, which have a larger specific surface area. Note also that the use of ultrasonic processing allows one to obtain hydrous zirconia gels with a larger specific surface area in acid solutions, in contrast to other techniques.

With increasing annealing temperature, the specific surface area of the powders decreases systematically, and the distinctions between the samples prepared from the xerogels precipitated with and without sonication vanish. Clearly, this is due to the collapse of pores through particle growth and coalescence of crystallites with the formation of monolithic structures.

Thus, the present results demonstrate that high-power sonication during hydrous zirconia precipitation allows one to tune the composition and microstructure of the resulting material. In particular, acoustic processing enables the preparation of xerogels containing much less impurities and having a considerably larger specific surface area (especially when synthesis is conducted at a relatively low solution pH).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 09-03-01067) and the RF Ministry of Education and Science (grant no. 14.740.11.0281).

REFERENCES

1. Gedanken, A., Using Sonochemistry for the Fabrication of Nanomaterials, *Ultrason. Sonochem,* 2004, vol. 11, pp. 47–55.
2. Suslick, K.S., Applications of Ultrasound to Materials Chemistry, *Ann. Rev. Mater. Sci.,* 1999, vol. 29, pp. 295–326.
3. Baranchikov, A.Ye., Ivanov, V.K., and Tretyakov, Yu.D., Sonochemical Synthesis of Inorganic Materials, *Russ. Chem. Rev.,* 2007, vol. 76, pp. 133–151.
4. Neppiras, E.A., Acoustic Cavitation, *Phys. Rep.,* 1980, vol. 61, pp. 159–251.
5. Margulis, M.A., Sonoluminescence, *Phys. Usp.,* 2000, vol. 43, pp. 259–282.
6. Donattiv, D.A., Vollet, D.R., Ibañez Ruiz, A., et al., Mass Fractal Characteristics of Silica Sonogels As Determined by Small-Angle X-Ray Scattering and Nitrogen Adsorption, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 2005, vol. 71, pp. 014 203–014 209.
7. Ivanov, V.K., Kopitsa, G.P., Sharikov, F.Yu., et al., Ultrasound-Induced Changes in Mesostructure of Amorphous Iron(III) Hydroxide Xerogels: A SANS Study, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 2010, vol. 81, paper 174 201.
8. Toraya, H., Yoshimura, M., and Somiya, S., Calibration Curve for Quantitative Analysis of the Monoclinic–Tetragonal ZrO_2 System by X-Ray Diffraction, *J. Am. Ceram. Soc.,* 1984, vol. 67, pp. C119–C121.
9. Ivanov, V.K., Kopitsa, G.P., Baranchikov, A.Ye., et al., Mesostructure, Fractal Properties and Thermal Decomposition of Hydrous Zirconia and Hafnia, *Russ. J. Inorg. Chem.,* 2009, vol. 54, no. 14, pp. 2091–2106.
10. Garvie, R.C., The Occurrence of Metastable Tetragonal Zirconia As a Crystallite Size Effect, *J. Phys. Chem.,* 1965, vol. 69, pp. 1238–1243.
11. Djurado, E., Bouvier, P., and Lucazeau, G., Crystallite Size Effect on the Tetragonal–Monoclinic Transition of Undoped Nanocrystalline Zirconia Studied by XRD and Raman Spectrometry, *J. Solid State Chem.,* 2000, vol. 149, pp. 399–407.
12. Shukla, S. and Seal, S., Thermodynamic Tetragonal Phase Stability in Sol–Gel Derived Nanodomains of Pure Zirconia, *J. Phys. Chem. B,* 2004, vol. 108, pp. 3395–3399.
13. Gavrilov, V.Yu. and Zenkovets, G.A., Formation of the Pore Structure of Zirconium Dioxide at the Stage of Gel Aging, *Kinet. Catal.,* 2000, vol. 41, pp. 561–565.
14. Stenina, I.A., Voropaeva, E.Yu., Veresov, A.G., et al., Effect of Precipitation pH and Heat Treatment on the Properties of Hydrous Zirconium Dioxide, *Russ. J. Inorg. Chem.,* 2008, vol. 53, p. 350.
15. Stenina, I.A., Voropaeva, E.Yu., Brueva, T.R., et al., Heat-Treatment Induced Evolution of the Morphology and Microstructure of Zirconia Prepared from Chloride Solutions, *Russ. J. Inorg. Chem.,* 2008, vol. 53, pp. 842–848.
16. Clearfield, A. and Vaughan, P.A., The Crystal Structure of Zirconyl Chloride Octahydrate and Zirconyl Bromide Octahydrate, *Acta Crystallogr.,* 1956, vol. 9, pp. 555–558.
17. Muha, G.M. and Vaughan, P.A., Structure of the Complex Ion in Aqueous Solutions of Zirconyl and Hafnyl Oxyhalides, *J. Chem. Phys.,* 1960, vol. 33, no. 1, pp. 194–199.
18. Clearfield, A., Structure Aspects of Zirconium Chemistry, *Rev. Pure Appl. Chem.,* 1964, vol. 14, pp. 91–108.