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Combined SANS and SAXS study of the action of ultrasound on the structure of amorphous zirconia gels

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ABSTRACT

In the present work, we have studied for the first time the combined effect of both sonication and precipitation pH on the structure of amorphous zirconia gels synthesized from zirconium(IV) propoxide. The techniques of small-angle neutron and X-ray scattering (SANS and SAXS) and low temperature nitrogen adsorption provided the integral data on the changes in the microstructure and mesostructure of these materials caused by ultrasonic (US) treatment. Amorphous $ZrO_2 \cdot xH_2O$ synthesized under ultrasonic treatment was found to possess a very structured surface, characterized by the surface fractal dimension 2.9–3.0, compared to 2.3–2.5 for the non US-assisted synthesis, and it was also found to possess a higher specific surface area, while the sizes of the primary particles remain unchanged.

1. Introduction

The sonochemical approach is widely used for the synthesis of a great variety of advanced inorganic materials, including metal oxides and hydroxides, from solutions and suspensions [1–4], in hydrothermal media [5] and in solid phase [6,7]. The advantages of the ultrasound-assisted sol–gel technique over conventional routes of nanomaterials synthesis include shortening the synthesis duration due to faster hydrolysis, leading to more uniform particle size distribution, higher surface area, better thermal stability, and improved phase purity [4]. Examples of successful ultrasound-assisted sol–gel synthesis of metal oxide nanostructures include TiO_2 [8–10], ZnO [11–13], MoO_3 [14], In_2O_3 [15], ZrO_2 [16], SiO_2 [17–19], *etc.* It was shown that in a number of cases, sonochemically prepared materials demonstrate better characteristics than those synthesized by conventional methods. For example, nickel hydroxides obtained by ultrasonic-assisted techniques [20–23] possessed higher electrochemical performance. Similarly, layered double hydroxides obtained by an ultrasound-enhanced technique showed larger adsorption capacity for humic substances [24]. Recently, formation of high specific surface area porous adsorbents with the use of ultrasound was also reported [25,26].

When power ultrasound is introduced in the liquid-based media, absorbed acoustic energy gives rise to a number of physical effects, resulting in turbulent fluid movement in the vicinity of cavitational bubbles [27–29]. Near the phase boundary (e.g. solid–liquid interface), high speed microjets and shockwaves are formed [30]. Thus, acoustic treatment of suspensions consisting of relatively large particles, of which the size is comparable to the size of a collapsing cavitation bubble ($d > 0.5$–1 μm), can lead to several specific effects, including de-agglomeration, decrease of mean particle size, increase of the surface area, amorphization *etc.* [31–33]. Interestingly, cavitation bubble nucleation and collapse near the solid–liquid boundary is strongly dependent on a number of factors, including the wettability of the surface [34].

Zirconia and zirconia-based materials are of great importance because of the wide variety of their industrial applications (catalysts, oxygen-conducting materials *etc.*) [35–37]. The most convenient approach to synthesize these materials is based on the precipitation of amorphous hydrous zirconia gels in aqueous

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media using zirconium-containing precursors (e.g., zirconyl nitrate, zirconium alkoxides) and subsequent thermal or hydrothermal treatment of the resulting $ZrO_2 \cdot xH_2O$ gel [38,39]. The morphology and phase composition of such synthesized zirconia is, to a large extent, governed by the structure of the precursor gel, which in turn depends on the conditions of precipitation (e.g. composition, temperature, acidity of starting solution, *etc.*) [39–41]. For example, variation of precipitation pH changes the relative rates of the hydrolysis and condensation of zirconium-based clusters. The excess of alkali in the reaction media results in rapid hydrolysis and condensation, forming a branched metal oxy-hydroxide network. In particular, hydrous zirconia precipitated above the point of zero charge possesses a higher specific surface area and surface fractal dimension than when it is synthesized at low pH [39]. Similar behavior was shown for gels synthesized from zirconium isopropylate [41]. High surface fractal dimensions of amorphous hydrous zirconia obtained by the sol–gel route may, in some cases, remain unchanged, even after crystallization [42].

Recently, the application of ultrasound to the synthesis of zirconia-based materials has attracted certain interest. For example, it was established that ultrasonic cavitation disaggregates the agglomerates of zirconia colloidal particles, reduces the amount of physically and chemically bound water (as well as the amount of adsorbed ions), and leads to a notable increase in the specific surface area of zirconia amorphous samples [16,43]. Ultrasonically treated zirconia was shown to transform faster from the monoclinic to the tetragonal phase [44]. Obviously, these changes in the properties of zirconia are closely related to the effects of ultrasonication on the structure of amorphous hydrous zirconia formed during sonochemical-assisted precipitation, but these important structural aspects still remain virtually unstudied. Moreover, the corresponding experimental reports are contradictory. For instance, it was shown [45] that sonication increases the rate of linear polymeric clusters formation and notably decreases the gyration radius of ZrO_2 particles. Contrariwise, our later experiments [46,47] revealed the increase in the surface fractal dimension and in the size of individual particles in sonochemically prepared amorphous zirconia gels [47]. Up to now, studies on the fractal structure of gels forming under the action of ultrasound were conducted primarily for hydrous silica [48,49]. For example, Vollet et al. [49] have shown that ultrasound-stimulated wet silica gels possessed a lower fractal dimension than conventional ones. However, upon drying the former has shown a higher pore volume and specific surface area.

In the present work, we have studied for the first time the combined effect of both sonication and precipitation pH on the structure of amorphous zirconia gels precipitated from zirconium(IV) propoxide. Our investigation was primarily based on the use of small-angle neutron scattering (SANS) and X-ray scattering (SAXS), these being the most suitable methods for the structural study of amorphous materials. SANS, SAXS and low temperature nitrogen adsorption provided the integral data on the changes in the microstructure and mesostructure of these materials caused by ultrasonic treatment.

2. Experimental

2.1. Synthesis of samples

Hydrous zirconia xerogels were prepared as follows. First, nitric acid or aqueous ammonia was added to distilled water, giving 55 ml portions of solutions adjusted to pH 2.66, 5.46, 6.25, 8.26, 11.30. Then, 4 ml of 70 wt.% zirconium propoxide solution in propanol (Aldrich, 333,972) was added dropwise to each portion under constant stirring. The resulting precipitates have been stirred for 30 min, then thoroughly washed with distilled water and dried in air at 150 °C overnight.

Ultrasound-assisted synthesis was conducted according to a similar procedure. Starting solutions were adjusted to pH 5.46, 6.25, 8.26, 11.30, and sonicated using a Bandelin Sonopulse 3200 generator (titanium horn SH 213 G with TT13 tip) throughout the precipitation (15 min) and subsequent stirring (30 min) of resultant suspensions. The output ultrasonic specific power measured using a standard calorimetric technique [50,51] was equal to 13 ± 1 W/cm^2. The TT13 tip was immersed 10 mm below the surface of the solutions. To prevent overheating the whole process was conducted in a thermostated cell at 25 °C.

For the sake of clarity, hydrous zirconia xerogels synthesized from pH 2.66, 5.46, 6.25, 8.26, 11.30 solutions are hereafter named Z-2X, Z-5X, Z-6X, Z-8X, Z-11X, where X indicates whether the synthesis was ultrasonically assisted (X = U) or not (X = C).

2.2. Methods of analysis

2.2.1. Thermal analysis, XRD, low-temperature nitrogen adsorption and SEM study of the samples

Thermal analysis (TGA/DTA) was performed using a NETZSCH STA 409 PC/PG instrument in the temperature range 20–900 °C in air (heating rate $\beta = 10°$/min, platinum crucibles, ~30 mg samples). Mass-spectral data during thermal analysis were collected by QMS 403 C Aëolos.® X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX 2500 diffractometer (CuK_α radiation) over a 2θ range of 10–85° with an increment 0.02°/step at the rate of 2°/min. Low temperature nitrogen adsorption measurements were conducted using an ATX-6 analyzer (Katakon, Russia). Before the measurements the samples were outgassed at 150 °C for 30 min under a dry helium flow. Determination of the surface area was carried out by the 8-point Brunauer–Emmett–Teller (BET) method. The microstructure of powders was also studied using a Carl Zeiss NVision 40 scanning electron microscope with a Schottky field emission Gemini column, operated at 1 kV acceleration voltage.

2.2.2. Neutron and X-ray scattering measurements

The SANS experiment was performed at the "Yellow submarine" instrument of the BNC research reactor in Budapest (Hungary). The use of two neutrons wavelengths ($\lambda = 0.46$ and 1.2 nm), and two sample-to-detector distances (1.33 and 5.6 m) provided measurements in a wide momentum transfer range ($4.2 \cdot 10^{-2} < q < 3.8$ nm^{-1}, where: $q = 4\pi\lambda^{-1}\sin(\theta/2)$, θ is the scattering angle). The scattered neutrons were detected by a two-dimensional position-sensitive BF_3 gas detector (64×64 cells of 1 cm $\times$ 1 cm).

Samples of amorphous zirconia xerogels were placed in 1 mm thick quartz cells. Apparent density ρ_H of each sample was calculated as the mass of powder divided by its volume. The raw data were corrected using the standard procedures [52], taking into account the scattering from the set-up equipment and cell. The resulting 2D isotropic spectra were averaged azimuthally and their absolute values were determined by normalizing them to the incoherent scattering cross-section of water. All the measurements were done at room temperature. The BerSANS software [53] was used for data processing.

A small-angle X-ray scattering (SAXS) experiment was performed using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocused X-ray beam generator (Bede, Durham, UK) operating at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector with an active area diameter of 20 cm and 512×512 pixels (Gabriel design). An X-ray diode was put as a beamstop in the center of the detector. Measurements were conducted in a momentum