

P-8: Effect of High Intensity Ultrasound on the Mesostructure of Amorphous Hydrated Metal Oxides

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We report structural changes in amorphous hydrated zirconia, iron (III) hydroxide and chromium oxyhydroxide xerogels caused by high intensity ultrasonic treatment. We have established that sonication greatly affects the mesostructure of amorphous xerogels, namely results in increase in their homogeneity, surface fractal dimension, and also changes in sizes of aggregates of primary particles and their aggregates.

1. Introduction

Specific physical and chemical effects taking place during sonication of liquids arise mostly from acoustic cavitation, i.e. formation of vapour-gas microbubbles and their further oscillations and collapse. The mechanism of sonochemical reactions in homogeneous liquids is well studied and summarized in the frames of two major theories, namely, hot spot theory (Neppiras, 1980) and the theory of local electrization (Margulis, 2000).

In turn, information on the specific action of high intensity ultrasound on heterogeneous systems (mainly liquid-solid systems) is still rather poor. It is generally accepted that the collapse of cavitation bubbles in the vicinity of the phase boundary (e.g. solid-liquid interface) occurs asymmetrically, thus it is affected by shockwaves and local microjets of liquid. Acoustic treatment of suspensions consisting of relatively large particles ($d > 0.5\text{--}1\ \mu\text{m}$) leads to several specific effects including de-agglomeration, decrease of mean particle size, increase of the surface area, etc. Investigations concerning the influence of sonication on heterogeneous systems (for instance, sols and gels) consisting of substantially smaller particles were performed on a quite limited number of systems, including xerogels of zirconia (Chaumont et al., 1992) and silica (Barrera-Solano et al., 1992; Donatti et al., 2005). It was established that ultrasonication leads to the increase of the rate of gel formation and to changes in the mesostructure (e.g. density, size of monomers and size of aggregates) of hydrogels, xerogels and aerogels. Nevertheless the effect of ultrasonication on such systems is to be studied more thorough.

In view of this circumstance the present work aims to analyze the influence of high intensity ultrasound on the mesostructure and fractal structure of amorphous transition metal hydroxides xerogels.

2. Experimental

Typical synthetic procedure included precipitation of hydrous oxides from aqueous solution of corresponding metal salt by addition of aqueous ammonia under sonication performed using Bandelin Sonopuls HD 3200 generator operated at 20 kHz. To prevent uncontrollable rise of the temperature due to dissipation of acoustic energy the precipitation process was always conducted in the thermostated cell. Some experiments included precipitation from solutions of metal salts having various concentrations (0.1–1.0 M), and in some cases precipitation was performed at various pH (5–9). All hydrous oxides were also precipitated under the same conditions but without ultrasonic treatment. As synthesized hydrated gels were centrifuged and washed several times with distilled water. Gels were further dried in air at 60°C overnight to produce xerogels. As prepared samples of hydrated zirconia and chromium oxyhydroxide were further annealed at 200–800°C for 5 h. Fe(OH)₃ samples were treated hydrothermally at 160°C for 5 h.

Our investigation was primarily based on the use of small-angle neutron scattering method (SANS) which is widely used in the study of nuclear and magnetic inhomogeneities in various amorphous materials (Kopitsa et al., 2007). Structural changes in hydrous oxides caused by ultrasonication were also corroborated by means of X-ray diffraction, low-temperature nitrogen adsorption, heat-flux calorimetry, thermal analysis and electron microscopy.

3. Results and discussion

Analysis of SANS data shows that the mesostructure of iron hydroxide xerogels depends notably on the concentration of initial iron(III) nitrate solutions. It can be clearly seen that the increase of the concentration leads to decrease of clusters size and, on the contrary, to the increase of primary particles size. The second conclusion arising from these data is that the increase of the concentration also results in the significant increase of surface fractal

dimension of aggregates. Thus we can conclude that homogeneity of xerogels falls with the increase of concentration of an initial solution. Ultrasonic treatment leads to the growth of the size R_c of aggregates of primary particles. In the case of concentrated solutions ultrasonication results also in notable increase of fractal dimension (D_s) of a resulting xerogel. Analysis of heat flux calorimetry data indicates that ultrasonic treatment of iron(III) hydroxide gel results in formation of a noticeably more homogeneous sample which is decomposed autocatalytically in one definite stage. Such a conclusion is in a good agreement with the results of SANS measurements confirming the same changes in the mesostructure. For all the samples obtained by hydrothermal treatment of sonicated iron hydroxide xerogels mean particle sizes are notably larger than for control ones. This fact can also be considered as an additional argument in favor of a higher homogeneity of ultrasonicated xerogel samples.

Similar results were obtained for hydrated zirconia xerogels. Increase in the concentration of starting zirconium oxynitrate solution results in an increase in the SANS intensity, indicating a decrease in the nuclear density homogeneity of corresponding xerogels. In the case of control samples dependence of SANS intensity upon the concentration of starting solution is much more pronounced than in case of ultrasonicated gels. Thus application of ultrasound diminishes this effect so that nuclear homogeneity of samples synthesized from different starting solutions is practically identical. Surface fractal dimension of hydrated zirconia xerogels depends upon both concentration of starting zirconium oxynitrate solution and conditions of synthesis (application of ultrasound). In general increase in concentration results in increase of surface fractal dimension. Effect of ultrasonication on the surface fractal dimension of xerogels synthesized from 0.25 and 1.00 mole·L⁻¹ solutions is negligible. On the other hand, application of ultrasound results in notable growth of D_s in xerogels obtained from 0.10 mole·L⁻¹ solution. Application of ultrasound during synthesis of hydrated zirconia results in notable changes in phase composition of resulting nanocrystalline ZrO₂. Volume fraction of metastable tetragonal zirconia is higher for the samples obtained under sonication over all the concentration range.

In most cases hydrated zirconia precipitated in alkaline and neutral media contain notable amount of adsorbed ions (for instance, NO₃⁻). We have demonstrated that under ultrasonication amount of nitrate ions adsorbed on the surface of hydrated zirconia particles is considerably smaller than that in the control experiments. Moreover we can conclude that sonication ensures a considerable increase in the specific surface area of the as prepared xerogels. Increase of specific surface area was also shown for chromium oxhydroxide xerogels. Note also that the use of ultrasonic processing allows one to obtain hydrous zirconia gels with a larger specific surface area (70–80 m²·g⁻¹) in acid media, that is hardly to achieve by other techniques.

Thus, basing on the results obtained we can conclude that sonication leads to the increase of homogeneity of xerogels in mesoscopic range and to the increase of the size of aggregates of primary particles as well as to the increase of the surface fractal dimension. It was also established that ultrasonically-induced changes in mesostructure of xerogels greatly affect their subsequent transformation into nanocrystalline oxides under hydrothermal conditions or thermal treatment.

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