

Synthesis of zirconia colloidal dispersions by forced hydrolysis

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Abstract: Different zirconia colloidal dispersions (sols) were prepared from zirconyl oxynitrate and zirconyl oxychloride solutions by forced hydrolysis. Vigorously stirred acidic solutions of these salts were refluxed at 102 °C for 24 h. Characterization of the obtained sols (pH, solid phase content, crystal structure) was performed by potentiometric, XRD, TGA/DTA and SEM measurements. The prepared sols contained almost spherical monoclinic hydrated zirconia particles 7–10 nm in diameter.

Keywords: zirconia sol, colloidal dispersion, forced hydrolyses, SEM, TGA/DTA.

INTRODUCTION

Ultrafine zirconia (ZrO₂) particles have wide applications in the production of advanced ceramics,¹ dense films, ultrafiltration membranes,² catalysts, adsorbents,³ chromatography packing materials,⁴ pigments, cosmetics, *etc.* The potential use of nanosized zirconia in the fabrication of dense ceramics is based on its unique set of properties, such as high refractivity, corrosion resistance, mechanical strength, fracture toughness, and ion conduction. These properties are based on the high quality of nanoscaled zirconia powders with respect to chemical purity, crystallinity, homogeneity, controlled state of agglomeration and particle size distribution, as well as low production costs. Several methods have been reported for the production of ultrafine zirconia particles: sol–gel processing *via* hydrolysis and condensation of zirconium alkoxides,⁵ forced hydrolysis of zirconium inorganic salt solutions,^{1,6–12} forced hydrolysis *via* microwave heating,^{13,14} precipitation from solutions of inorganic salts or alkoxide complexes,¹⁵ hydrothermal and plasma decomposition methods,¹⁶ microemulsion and electrodispersion techniques combined with precipitation reactions,¹⁷ combustion synthesis, and electric explosion and oxidation of zirconium metal wires.¹

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The sol–gel route, in which gels may be produced from metal oxide sols obtained by hydrolysis and condensation of metal alkoxides or inorganic salts, has advantages over conventional techniques due to the chemical purity of the precursors and homogeneity of the gels. The disadvantage of this process is, however, the fact that metal alkoxides are inflammable and expensive. On the other hand, forced hydrolysis of inorganic salt solutions provides an especially promising chemical precipitation route for large-scale production of nanosized hydrous zirconia sols because this approach uses inexpensive inorganic salts as starting materials and has relatively simple, low energy heating requirements to induce homogeneous precipitation in inorganic zirconyl salt solutions.¹⁸ Clearfield¹⁶ pointed out that heating/boiling (refluxing) or otherwise aging of zirconyl salt solutions promotes hydrolytic polymerization (among tetramer species) and induces the formation of crystalline hydrous zirconia.

The characteristics of the final hydrous zirconia sols are dependent on the experimental conditions, including pH, temperature, concentration of reactants, nature of anions, and stirring and aging time.¹⁹ Although there are disagreements in the literature, a slow process at extreme pH values favors the tetragonal structure while rapid precipitation leads to amorphous precipitates or monoclinic phase formation (the latter being promoted by heating).⁴ The pH also affects the size of the hydrous zirconia particles. The average secondary particle size of hydrous zirconia increases with increasing H^+ ion concentration, attaining a maximum of 200 nm at an H^+ ion concentration of 0.44 mol dm^{-3} . A further increase in the H^+ ion concentration causes a decrease in the average particle size.^{11,12} The final particle size increases with increasing initial $ZrOCl_2$ concentration to a certain maximum size (about 250 nm). Further increasing of the $ZrOCl_2$ concentration results in smaller ZrO_2 particles. The optimum $ZrOCl_2$ concentration, at which nanometric particles (< 100 nm) can be produced at a reasonable production rate and zirconia content in the sol, is approximately 0.5 to 1 mol dm^{-3} . The temperature near the boiling point of $ZrOCl_2$ solution affects the induction period of particle formation causing a slight difference in the final particle size.¹ A microwave oven provides uniform and rapid heating without stirring.¹⁴ Addition of certain anions (e.g. SO_4^{2-}) changes the shape of the hydrous zirconia particles. Blesa *et al.*⁷ produced spherical hydrous zirconia particles by heating a solution containing $ZrOCl_2$, K_2SO_4 and HCl. After an induction period (from 20 h to several days, depending on the zirconyl salt concentration), the zirconia particle size increases and reaches a plateau.¹

Vesteghem *et al.*²⁰ obtained zirconia sols from zirconium oxyacetate solutions by hydrolysis at temperature above $150 \text{ }^\circ\text{C}$. Colloidal dispersions were prepared by aggregation of zirconia crystallites, the size of which changed from 5 to 15 nm under hydrothermal conditions. For zirconium oxyacetate concentration higher than 0.5 mol dm^{-3} , dense aggregates of monoclinic ZrO_2 crystallites were obtained. A tetragonal to monoclinic transformation was observed with increased isothermal

times at zirconium concentrations below 0.5 mol dm^{-3} .

The aim of this work was to investigate the effect of the initial pH value as well as the types and concentration of the zirconyl salt on the characteristics (crystallinity, particle shape and size, final sol pH, and solid phase content) of the synthesized hydrous zirconia sols.

EXPERIMENTAL

The starting materials used in this study were zirconium oxychloride octahydrate (Merck, p.a. grade), zirconium oxynitrate (Merck, p. a. grade), hydrochloric acid (35 % HCl, Lachema, p. a. grade), and nitric acid (63 % HNO₃, p. a. grade). Distilled water was used to prepare the acid solutions. Zirconyl salt solutions were prepared by dissolving the required amount of zirconyl salt in 200 ml of the corresponding acid solution.

Hydrous zirconia sols were prepared by the following procedure: 500 ml of HNO₃ or HCl solution (concentration 0.01 or 0.05 mol dm⁻³) were prepared by diluting the concentrated acids. Three hundred milliliters of the required acid solution was heated at the boiling point (102 °C) under reflux, and then 200 ml of the required zirconyl salt in the same acid solution were added dropwise. The final concentration of zirconyl salt was in the range from 0.012 to 0.065 mol dm⁻³. After addition of the zirconyl salt solution, the boiling solution was continuously stirred (160 r/min). The starting zirconyl salt solution turned into a milk-white sol of hydrous zirconia after 24 h.

Hydrolysis, during the hydrothermal treatment, of zirconium oxychloride and zirconium oxynitrate was incomplete. Non-hydrolyzed zirconium oxychloride or zirconium oxynitrate was removed from the prepared sols by ultrafiltration. The washing with distilled water was continued until a negative reaction on chloride or nitrate ions in permeate was obtained. The ultrafiltration was carried out in a stirred cell with an Amicon Diaflo PM 10 type membrane.

The solid phase content in the sol was determined gravimetrically and the sol pH was measured by a combination electrode (glass and a silver–silver chloride electrode). The obtained hydrous zirconia particles were examined by X-ray diffraction (XRD) (Siemens-D 500, CuK α) and thermal analysis (DuPont 2000 TA system with a thermobalance DuPont 951 TGA). In the thermogravimetric measurements, the samples (approx 10 mg) were heated in a platinum crucible (heating rate of 10 K min⁻¹) up to 1000 K and in air (10 l/h flow rate).

The zirconia sols were investigated by Scanning Electron Microscopy, SEM, (JEOL JSM - 6460L V), at a 4 nm nominal resolution. A drop of diluted sol dispersion was put onto a piece of aluminum foil and then allowed to dry under a lamp. The SEM measurements were carried out applying standard procedures for this technique.

RESULTS AND DISCUSSION

Six different hydrous zirconia sols were prepared by the previously described method. Table I shows the characteristics (solid phase content and pH) of the synthesized hydrous zirconia sols. The concentrations of the precursors (zirconium oxychloride or zirconium oxynitrate and nitric acid) are also given in Table I. According to the given data, the pH values of the sols decreased with increasing solid phase content which can be explained by Eq. (1):



In forced hydrolysis, easy deprotonation of the hydrated metal ions in the heated aqueous solution occurs and this process is followed by a pH decrease caused by the release of H⁺ ions. Therefore, the higher the zirconyl salt concentra-

tion in the solution, the greater is the number of H^+ ions released, *i.e.*, the pH decreases.

TABLE I. Characteristics of the synthesized zirconia sols. The concentration of the precursors, in parenthesis, are given in mol dm^{-3}

Zirconia sol	1	2	3	4	5	6
Precursors	ZrO(NO ₃) ₂ (0.065) HNO ₃ (0.05)	ZrO(NO ₃) ₂ (0.032) HNO ₃ (0.05)	ZrO(NO ₃) ₂ (0.012) HNO ₃ (0.05)	ZrO(NO ₃) ₂ (0.065) HNO ₃ (0.01)	ZrOCl ₂ (0.022) HCl (0.05)	ZrOCl ₂ (0.045) HCl (0.05)
Solid content/mass %	0.75	0.15	0.41	0.66	0.40	0.77
pH	1.11	1.41	1.21	1.14	1.25	1.14

For practical applications, it is advantageous that the final hydrous zirconia sol has a high solid content. However, it is impossible, to obtain directly a sol with a high solid content. This can be achieved by ultrafiltration.

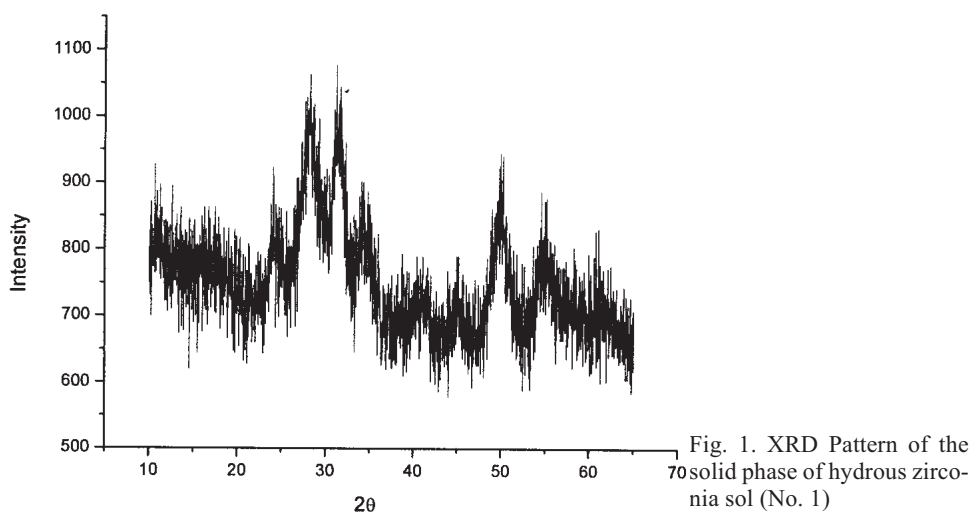


Fig. 1. XRD Pattern of the solid phase of hydrous zirconia sol (No. 1)

The final pH values of the hydrous zirconia sols show that the surface charge of zirconia particles is below the point of zero charge ($\text{pH}_{\text{pzc}} = 6.6$).²¹ This means that the surface charge of the colloidal hydrous zirconia particles is positive.

An XRD pattern of the solid phase of one of the obtained sols is shown in Fig. 1. The same pattern was obtained for the other sols. Several peaks at 2θ degrees of 24.1, 28.3, 31.6, 34.3, 50.2 and 55.4 can be seen. This pattern is characteristic for monoclinic zirconia. It proves that pure monoclinic zirconia can be prepared at low pH values a temperature of 102 °C and an aging time of 24 h. Similar results for hydrous-zirconia particles produced by hydrolysis of ZrOCl₂ solutions at boiling temperature for 70 – 400 h were obtained by Matsui *et al.*^{10–12} The apparent crystallite size of the zirconia powders was calculated from the highest peak, according to Scherrer's equation:²²

$$D = 0.90 \lambda / (\beta_{1/2} \cos \theta)$$

where λ is the wavelength for CuK α (0.15405 nm) radiation and $\beta_{1/2}$ is the width at half-height of the diffraction profile originating only from the crystallite size. The calculated crystallite diameters are about 6 nm.

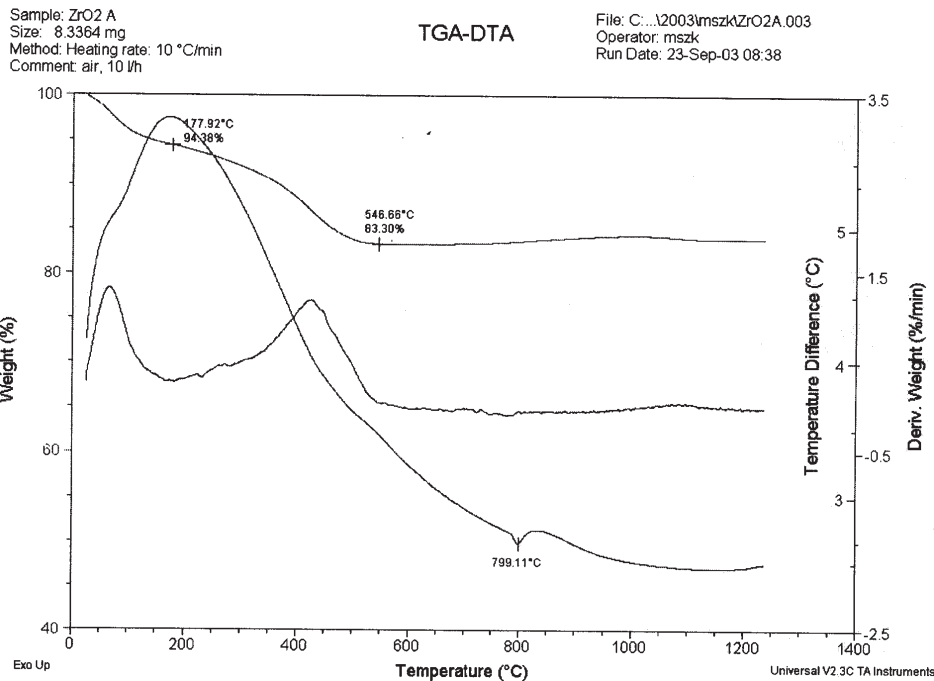


Fig. 2. Thermal analysis of the solid phase of a hydrous zirconia sol (No 1).

The thermogravimetric analysis (TG) curve Fig. 2 shows mass losses at 178 °C ($\approx 5.6\%$) and 547 °C ($\approx 16.7\%$), which are ascribed to dehydration of physically adsorbed water and desorption of chemically bound (as OH⁻ groups) water, respectively. It can be seen from the TGA curve that the mass loss ceased at ≈ 550 °C. At this temperature, the total mass was reduced by 22.5 %. In other words, the zirconia content in the solid phase of the prepared sol is 77.5 %, *i.e.*, the amount of zirconium is equal to 57.4 %. The DTA curve, Fig. 2, shows an endothermic peak at ≈ 178 °C, which corresponds to the above-mentioned mass loss (water) and an exothermic peak at ≈ 800 °C, which originates from a monoclinic to tetragonal crystal transformation.²³

SEM Measurements (Fig. 3) show that the particles of all the synthesized zirconia sols were almost spherical and similar in size (7–10 nm). Agglomeration of the spheres is an after-effect of the sol drying procedure, which preceded the SEM measurements.

CONCLUSION

All the synthesized hydrous zirconia sols were stable, with positively charged and spherical monoclinic particles. They were prepared from acidic solutions of

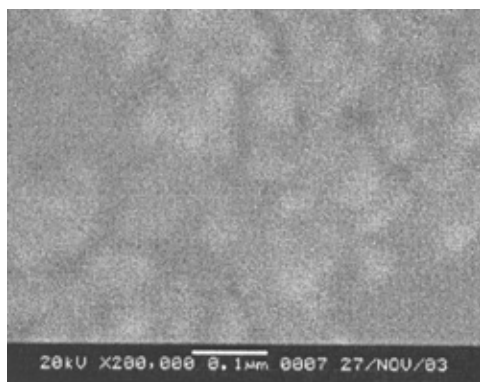


Fig. 3. SEM Micrograph of zirconia sol (No. 4) particles.

different concentrations of zirconyl oxychloride or zirconyl oxynitrate under reflux at 102 °C in a relatively short period of time (24 h). The pH values of sols decreased with increasing content of the solid phase. TGA Measurements revealed a hydrated structure of the dried sols, while the DTA curve shows a monoclinic to tetragonal phase transformation. The prepared particles were spherical, about 7–10 nm in diameter, as confirmed by SEM measurements.

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ИЗВОД

СИНТЕЗА КОЛОИДНИХ ДИСПЕРЗИЈА ЦИРКОНИЈУМДИОКСИДА МЕТОДОМ ФОРСИРАНЕ ХИДРОЛИЗЕ

ЈЕЛЕНА МАРКОВИЋ и СЛОБОДАН МИЛОЊИЋ

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Различите колоидне дисперзије (солони) цирконијумдиоксида припремљене су методом форсиране хидролизе раствора цирконилнитрата и цирконилхлорида. Хидролиза киселих раствора наведених електролита извршена је при 102 °C, уз интензивно мешање раствора, у трајању од 24 h. Извршена је карактеризација синтетизованих солова мерењем: рН, садржаја чврсте фазе, кристалне структуре, губитка масе (TGA/DTA) и облика и величине честица (SEM) чврсте фазе. Припремљени солони садрже сферне честице хидратисаног цирконијумдиоксида пречника 7–10 nm.

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