Influence of Synthesis Conditions on the Structure and the Surface State of Zirconia Nanoparticles

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The paper studies the influence the nature of the salt anion and the base of precipitant, used in the synthesis of zirconia nanoparticles by chemical coprecipitation, on process parameters of the hydrogel drying, xerogel dehydration and crystallization, and the occurrence of polymorphic transitions in crystalline oxide systems are considered in this paper. The features of the structure, surface condition and properties of zirconia nanoparticles, which were obtained by using different precursors, are examined by FTIR and EPR spectroscopy, DSC and XRD methods.

1. INTRODUCTION

Nano-sized zirconia is a popular material for use in various industries, including catalysis, ceramic industry, creation a solid oxide fuel cells (SOFC), prostheses, etc. Such a wide range of nano-sized zirconia is due to the possibility of varying the phase composition, particle size and properties of zirconia. Note that the characteristics of zirconia are largely dependent on the conditions of synthesis of this material, since formed during its synthesis. The use of chemical coprecipitation for zirconia oxide, the most common in the industry, makes it necessary to focus not only on the mode of synthesis, namely, the modes of precipitation, drying and annealing of the material, but also on studies of the effects of nature of precursors used in synthesis.

The aim of this work was to study the effect of the nature of precursors in the synthesis of the basic processes of nano-sized zirconia, namely, the processes of drying, crystallization, and as a consequence, its structure, surface condition and properties.

2. SYNTHESIS AND CHARACTERIZATION OF NANOPARTICLES ZIRCONIA

Synthesis of zirconia nanoparticles has three stages — the synthesis of hydrogel, the formation of xerogel and obtaining of the crystalline oxide. The hydrogel system $ZrO_{2-x}HO_n$ (n = 1, 2) was synthesized by precipitation from solutions of oxychloride ($ZrOCl_2 \cdot 8H_2O$) or zirconium oxynitrate ($ZrO(NO_3)_2 \cdot 6H_2O$) salts. Bases with different basicity (pK_b) are used as precipitants: hydrazine hydrate $N_2H_4 \cdot H_2O$ ($rK_1 = 6.07$; $rK_2 = 15.07$) and ammonium hydroxide $NH_3 \cdot H_2O$ ($pK = 4.75$). The synthesis performed in the range pH 9 – 10. Deposition carried out for 1 hour with a stirring at 200 rev/min. Drying of the hydrogel performed at the microwave radiation with a frequency of 2.45 GHz and a power of 700 W with a constant diversion of water vapor from the surface of the sediment and control of the mass of the sample. Formed under these conditions xerogel was subjected to annealing in the temperature range 500 – 1300 °C.

At each stage of the synthesis was carried out characterization of the material by appropriate methods. Thus, the kinetics of drying of the hydrogel was studied by gravimetry under conditions of the microwave radiation, characterization of the structure of the xerogels performed by measuring the specific surface area by BET, by differential scanning calorimetry (DSC) and thermogravimetry (TG), as well as by FTIR spectroscopy and electron paramagnetic resonance (EPR). For the characterization of oxide nanoparticles, also used the method of X-ray diffraction (XRD).

3. RESULTS AND DISCUSSION

Note, that the structure and condition of the surface of zirconia is formed as a result of sequential processes — precipitation of the hydrogel, drying of the hydrogel, the processes of dehydration and crystallization of the material.

We have previously shown that the nature of the anion salts of zirconium determines its structure [1], which may affect the amount of structured water in the sediment and the amount of occluded impurities on its surface. The second factor affecting the properties of the precipitating hydrogel is a pH of precipitation process, this quantity is regulated by the concentration and nature of the precipitant used.

According to the study of electrokinetic hydrogel resulting sedimentation can be represented in the form of micelles:

$$\{[mZrO_2] \cdot xOH^- \cdot pA^- \cdot (x + p - y)R^+ \cdot nH_2O\}^{y-} \cdot yR^+,$$
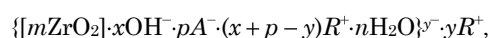
where A is the anion of salt: NO_3^- and Cl^-, which are

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included in potential forming layer, and R is the precipitating ions: NH_4^+ or $N_2H_5^+$, which form a diffuse region of the micelle. Note, that the members of the micelle ions differently structured around a water molecule, which may significantly affect the kinetics of drying of the hydrogel. Drying of the hydrogel is a complex process involving a series of transformations, namely, the phase transition of water-vapor diffusion of water molecules inside the pores and on the sediment surface, and desorption of water molecules from the surface sediment. To describe such a process commonly used formalism of the kinetics of Avrami–Erofeev [2].

As can be seen from the data in Table the deposition of the hydrogel in the presence of ammonia, two stepwise mechanism is implemented care of water, each of which is characterized by its kinetic parameters, whereas the dry hydrogel precipitated in the presence of hydrazine hydrate proceeds as a one-step process. Note, that the maximum drying rate is observed for the hydrogel prepared from nitrate salts and a basic precipitant for both stages. This leads to the formation of xerogels with large specific surface compared to other and lesser degree of aggregation. Comparison of data on the measurement of BET specific surface and the rate constants of water evaporation from the surface of the hydrogel reveals a correlation between these values $ZrO_2\_(NO_3)\_NH_3$ (342 m²/g) > $ZrO_2\_(Cl)\_NH_3$ (331 m²/g) > $ZrO_2\_(NO_3)\_N_2H_4$ (294 m²/g) $ZrO_2\_(Cl)\_N_2H_4$ (284 m²/g).

According to IR spectroscopy of the surface of the xerogels has a number of features depending on the nature of the precursors used for synthesis. So, for xerogels derived from at least the main precipitant in the area stretching vibrations have a significant contribution to the low-frequency component at 3200 cm⁻¹ band intensity in the $3000 - 3700$ cm⁻¹. This indicates a greater connection with the surface water components of the sediment. In the region of deformation vibrations in the transition to a lower basicity of the precipitant decreases the contribution of the band at $1500 - 1680$ cm⁻¹, which vibrations of terminal OH groups and observed its shift from 1570 cm⁻¹ to 1514 cm⁻¹ in the transition from xerogels formed from ammonia to the xerogel the formation of which took place in the hydrazine hydrate solution. Thus, the number of terminal OH groups and loosely coupled with the surface of the water increases with the speed of drying of the hydrogel, which leads to the formation of various defects for the xerogels formed from different precursors. Thus, for the xerogel formed from nitrate raw materials in the EPR spectrum shows an anisotropic paramagnetic signal with g-factors $g_\perp = 1.97$ and $g_{||} = 1.95$ appropriate Zr_3^+. In systems based on synthetic raw materials of chloride, the paramagnetic center does not occur. It is interesting to note that the surface of these systems have a different activity with respect to the generation of superoxide radical (O_2^-). So, on the surface of the xerogels synthesized from chloride raw material, a paramagnetic center O_2 generated more intensively, despite the lower specific surface area of these systems. This is consistent with the data of IR spectroscopy, which show for these systems the presence of the band at 1089 cm⁻¹, responsible for the variations of surface oxygen. This indicates a difference in the surface state, namely the difference in their hydration shells and surface defects, which manifests itself in the peculiarities of their subsequent dehydration and crystallization.

As can be seen from the DSC measurements at the position of the maximum temperature of the endothermic process of dehydration affects the nature of the anion of salt, and type of precipitating agent used for the synthesis of xerogel, see Fig. 1. This is consistent with the data of IR spectroscopy, the formation of xerogels with varying degrees of water connectivity and hydroxyls on the surface of various precursors. Further dehydration of such systems leads to different defects in the material, which is reflected in the shift of the maximum temperature of crystallization, see Fig. 1. At the same time, a greater influence on the crystallization process has a type of precipitating agent, used in the synthesis. Thus, the transition in the synthesis of zirconia from ammonia to the hydrazine hydrate the beginning of crystallization of this material is delayed by 10 ± 2.5 °C. Thus, the crystallization temperature in zirconia is controlled by the type of precipitant, whereas the degree of order with which the system approached the crystallization depends on the nature of the anion of salt, which is chosen for synthesis. And this is what determines the parameters of the flow of polymorphic transformations from monoclinic to tetragonal modification of zirconia in the temperature range $1160 - 1180$ °C, and the reverse transition tetragonal-monoclinic during cooling of the material. According to the DSC temperature of the monoclinic-tetragonal transformation depends on the nature of anion salts, selected for synthesis. Whereas, on the temperature of the reverse transition upon cooling of the material affects the nature of the anion and the salt and the type of precipitant. This fact may also be related to differences in the size of nanoparticles, obtained from different precursors, as confirmed by X-ray diffraction data of these materials.

Thus, the structure of the xerogel inherits the changes that occur in the hydrogels by varying the synthesis parameters, in particular the type of salt and base precipitant. It is shown that this causes the rate of dehydration, the state of hydration shell, the porosity, the value of specific surface area, morphology and size of nanoparticles of xerogel and oxide nanoparticles, obtained on its basis.

Table 1 – Parameters of the dehydration process of the hydrogel.

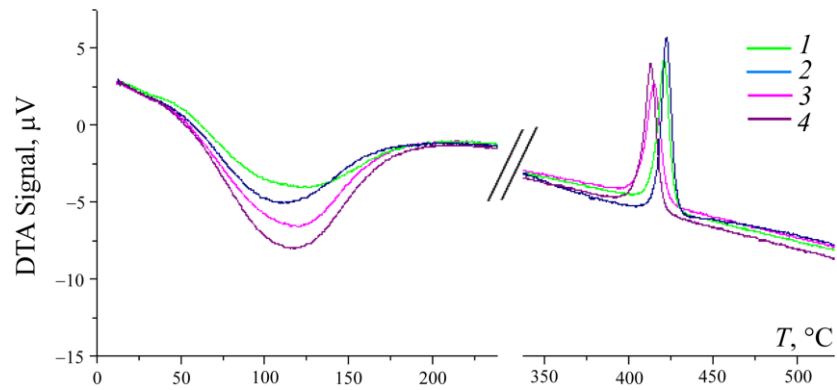| Precipitator	$NH_3 \cdot H_2O$		$N_2H_4 \cdot H_2O$	
Anion salts	Cl⁻	NO³⁻	Cl⁻	NO³⁻
n_1	1.60	1.67	1.68	1.62
lnk_1	−3.21	−2.54	−3.40	−3.18
n_2	0.75	0.72	—	—
lnk_2	−3.68	−2.39	—	—

Fig. 1 – DSC curves of xerogels ZrO_2 which were precipitated with different precursors: 1 – $ZrOCl_2(N_2H_4)$; 2 – $ZrO(NO_3)_2(N_2H_4)$; 3 – $ZrO(NO_3)_2(NH_3)$; 4 – $ZrOCl_2(NH_3)$

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