

TASK-ORIENTED TECHNOLOGY FOR PRODUCTION OF PHOTOCATALYTIC ACTIVITY OF ZIRCONIA NANOPARTICLES

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Abstract: The catalytic activity of material was tested by ESR spectroscopy and investigation of the formation of the super-anion radicals of oxygen on surface zirconia particles in dependence on dopant amount, pressure. UV-visible spectroscopy was used for estimation of optical properties of these materials. It was found the introduction of Y₂O₃ allows to creation of structure defects in partially stabilized zirconia, and its influence for tetragonal crystals is not monotonic in range 2-4 mol. %. It is connected with boundary of stable tetragonal phase at Y₂O₃ adding. The pressure is active factor of changing of surface state due to tetragonal – monoclinic transformation and may be used for improvements of catalytic properties of zirconia NPs.

Keywords: ZIRCONIA NANOPARTICLES, SUPEROXIDE ANION RADICAL, HIGH PRESSURE, PHOTOSENSITIVE

1. Introduction

The modern world industry the moves to side of application of hightechnological or another words “high-tech” products which are oriented on properties of finished products. For zirconia materials this is a wide spectrum of applications, fig. 1.

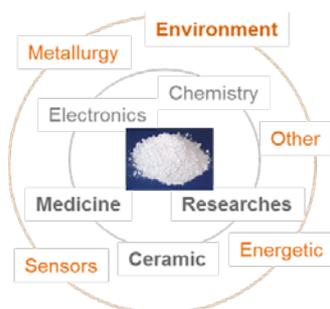


Fig.1 - The world market of zirconia applications.

Distribution of oxide nanopowders using in same industry on main industry world regions, fig. 2.

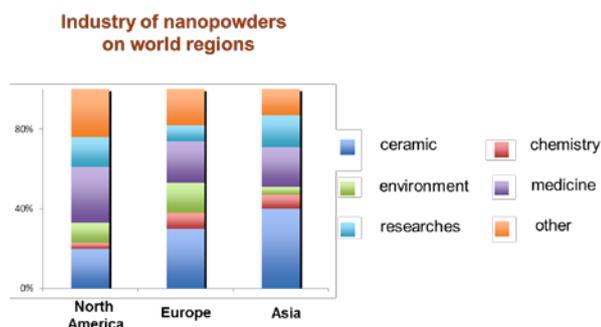


Fig. 2 Distribution of oxide nanopowders using in same industry on main industry world regions

In this case the questions about developing of technologies which are directed on creation of nanopowders and other production based on nanopowders are significantly in materials science [1].

The creation of these productions is inseparably connected with the developing of a new direction of modern materials science – nanodimensional materials [2]. It is the base for creation of principal new technologies which have methods and methodologies for controlling of properties and structures of nanomaterials.

However, in present time the technologies of obtaining nanopowders which are oriented direct on finished productions, in particular, ceramic, functional nanopowders or composite, is not much. Perspective technologies of obtaining of oxide nanopowders are technologies which are based on methods of “wet chemistry”, in particular, hydrothermal, hydrolysis and chemical precipitations methods. The method of chemical precipitation is a simple method in hardware [3]. This method can easy adapt to syntheses of surface and bulk modified systems [4]. Another feature of this method in contrast of other methods is carried out of syntheses of oxide nanoparticles (NPs) as sequential separate stages: zirconia hydrogel obtaining - zirconia amorphous xerogel – crystalline zirconia NPs [5]. It is obtained as amorphous product of zirconia which is used as sorbent of water cleaning and as crystalline zirconia NPs as product for using in ceramic technologies. Also the presence of several stages of this process of NPs obtaining allows introducing the separate stage of modifications for changing of cationic and anionic sublattice or surface state. The modifications methods may be as physical and chemical nature or their complex [6].

The knowledges about mechanisms of processes which take place at syntheses of zirconia nanopowders and under physical and chemical modifications of these systems allow creation effective methods of task-oriented controlling of properties and structures of finished product. Thus the complex technology which is based on chemical precipitation methods with introducing of different methods of physical and chemical modifications allows creating high-tech oxide nanopowders with properties aims on finished operation tasks.

In this work the complex technology of complex oxide obtaining is developed and the questions of modification of oxide nanoparticles for photocatalytic tasks are studied.

2. Preconditions and means for resolving problems

2.1 Technology of zirconia NPs obtaining

Fig.3 shows the schemes of technology of Y-doped zirconia NPs obtaining. As we can see the technology of obtaining of complex oxides contains several stages and can be divided on two technological cycles in which two independence products are made. These products are amorphous xerogel and crystalline zirconia.

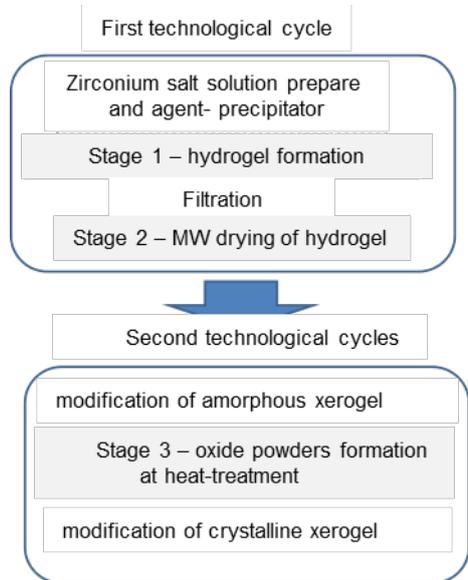


Fig.3 The schemes of technology of Y-doped zirconia NPs obtaining

The realization of this scheme is based on chemical precipitation method. It allows obtaining a complex oxide when the different salts co-precipitate simultaneously, for our case yttrium and zirconium salts are base. The physical actions may be used on any stage of process. Thus for decreasing of drying time of hydrogel microwave irradiation is used and heat treatment of amorphous xerogel with variation of rate of non-isothermal and time of isothermal stages is used for variation of structure, size and surface state of NPs. The detail scheme of first stage of technology is shown on Fig.4.

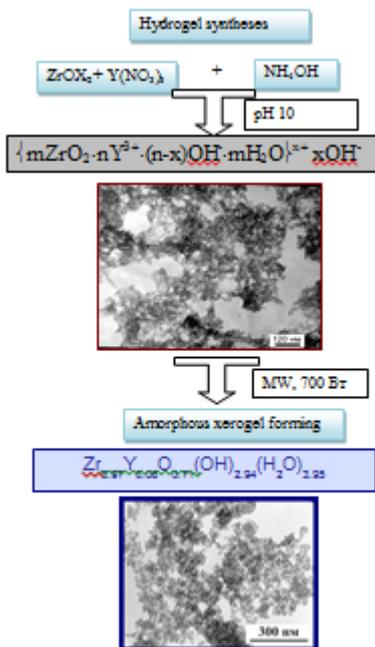


Fig. 4 –Detail scheme of first technology stage

It is noted that amorphous xerogel is genetically inheritance of feature of hydrogel structures which depend from many parameters of syntheses, in particular, salt concentrations, salt and agent-precipitated type, dopant nature and amount et al.

It is determined the dehydration rate, hydrate shell state, porous of xerogel, specific surface area, morphology and surface state. It may influence on distribution of dopant between phases and led to synthesized inhomogeneity product. The increasing of

concentration of initial salts (considering of complex structure of colloid solutions of zirconium salts [7]) may significantly influence on amount of unwanted additions and as results led to change of dehydration and crystallization of sediment and aggregation of amorphous xerogel NPs. The last fact influences on zirconia NPs morphology and dispersity. Thus the residual amount of ammonium chlorine in amorphous xerogel may significantly influence on behavior of crystalline zirconia NPs at their sintering [8], because the properties of zirconia NPs are formed due to water and additions removing, dehydration, dehydroxylation, dehydrogenization, destruction and crystallization of amorphous xerogel. Realization of these processes takes place under heat treatment of amorphous NPs in temperature diapason of 400-1000°C, fig. 4.

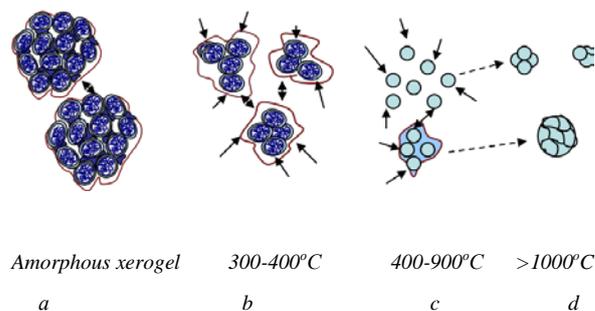


Fig 4 Scheme of oxide NPs forming a) amorphouse xerogel structure, b) partially dehydrated and broken solution domens, c) NPs forming, d) oriental sintering of NPs.

2.2 NPs surface state and their activity to producing of O₂⁻

Photocatalytic activity of materials connected with ability to produce of super-oxide radical O₂⁻ and OH radicals under UV-visible irradiations. The forming of these oxidative particles on zirconia surface may be investigated by ESR spectroscopy [9, 10]. Thus the paramagnetic sites correspond to the pseudoaxial (non-bridging) oxygen O⁻. This center has isotropic line in ESR spectrum with g-value is 2,05 for dispersed material or anisotropic line with c g_⊥= 2,045-2,055 or g_∥=2,040-2,047 for bulk material. The adsorbed O₂⁻ on oxide surface has anisotropic signal with three peaks with g₁=2,033, g₂=2,008 и g₃=2,003 according to data [10] or g₁=2,027, g₂=2,0085 и g₃=2,0042 according to data [11]. The g₁ value of this signal is sensitive to change of environment of adsorbed oxygen molecule [12] and the g₁ factor value may be using for estimation of connectivity extent of oxygen with metal ions of oxide surface [13]. For Y-doped zirconia with different Y₂O₃ amount and calcination temperature the possibility of generation of O₂⁻ under UV irradiation was studied [14]. It was shown that the increasing of calcination temperature above 700°C led to decreasing of intensity of O₂⁻ generation [15].

The Y-doped zirconia is a wide band oxide. Fig. 5 shows the UV-visible spectrum of Y-doped zirconia NPs (Y₂O₃ amount of 2, 3, 4 mol. %) with calcination temperature 700°C. It was shown investigated systems absorbed irradiation with photon energy above 5 eV. The values of the fundamental absorption edge are 5.3, 5.3 and 5.48 for systems with Y₂O₃ amount of 2, 3, 4 mol. %, accordingly. The change of values of the fundamental absorption edge has non-monotonic behavior which possible corresponded to presence a very small amount of monoclinic phase for ZrO₂-2 mol. % Y₂O₃ and of cubic phases for ZrO₂-4 mol. % Y₂O₃. Spectrum of each system demonstrates the presence of tail bellow the fundamental absorption edge. It is determined by defects of crystalline structure which give the additional levels in forbidden band. It makes the zirconia photosensitive materials, especially for systems with Y₂O₃ amount of 2 or 4 mol. % in zirconia.

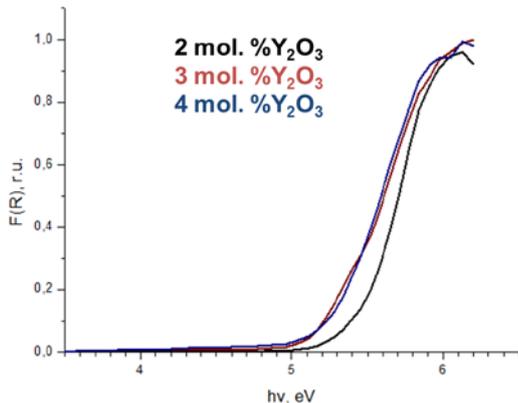


Fig. 5 UV-visible spectrum of Y-doped zirconia NPs (Y_2O_3 amount of 2, 3, 4 mol. %) with calcination temperature $700^\circ C$

According [14] the anion radical superoxide is a very good formed on surface of investigated Y-doped zirconia with calcination temperature up to $600^\circ C$. At calcination of zirconia above these temperatures the forming of O_2^- is very weakly. It may be connected with change of surface state of NPs at heat treatment, in particular with disappearance of the places of specific absorption of oxygen molecules.

According [15] the pressure is active factor for controlling of NPs phase composition, surface state etc, but influence of pressure action on NPs structural characteristics can depend on dopant amount. Fig. 6 shows the change of NPs dispersity at pressure action on NPs with different amount of dopant.

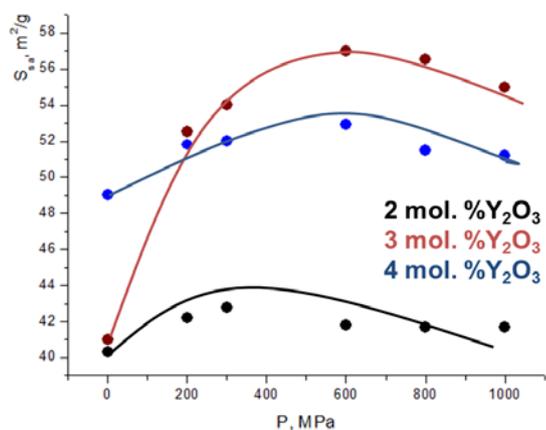


Fig. 6 Dependence of specific surface of NPs dispersity on pressure action on NPs with different amount of dopant (calcination temperature is $700^\circ C$)

The dispersity of NPs after pressure action and milling are increased, and dependence of dispersity from pressure values has non-monotonic characters. The position of extremum on these dependences is determined by amount of Y_2O_3 in zirconia. It may be connections with tetragonal-monoclinic transformation which takes place in Y-doped zirconia under pressure [15]

In table 1 the structure parameters (size, phase composition) are given for initial systems with calcination temperature of $700^\circ C$. As we can see size and phase composition are changed from dopant amount and values of pressure. The increasing of dopant amount led to stabilization of NPs to tetragonal-monoclinic transformation which is initialized by pressure.

Table 1. Phase composition and size of Y-doped zirconia NPs ($T_{cal}=700^\circ C$)

Y_2O_3 , %	% Monoclinic phase					
	Pressure, MPa					
	100	300	400	600	700	1000
2	8	10	13	15	18	19
3	17	28	28	31	41	50
4	45	68	83	83	88	90

As we can see the accumulation of amount of monoclinic phase in systems under pressure takes place at increasing of pressure and for Y-doped zirconia (2 and 4 mol. %) it is practically constant. Comparison the phase composition data and response of systems on UV-visible irradiation allows marking systems which will be perspective for investigations. Two systems (dopant amount of 2 and 4 mol. %) which were modified by pressure at 600 MPa was choose for testing of O_2^- forming.

Fig. 7 shows the ESR spectra of initial and modified systems (dopant amount of 2 or 4 mol %, calcination temperature is $700^\circ C$).

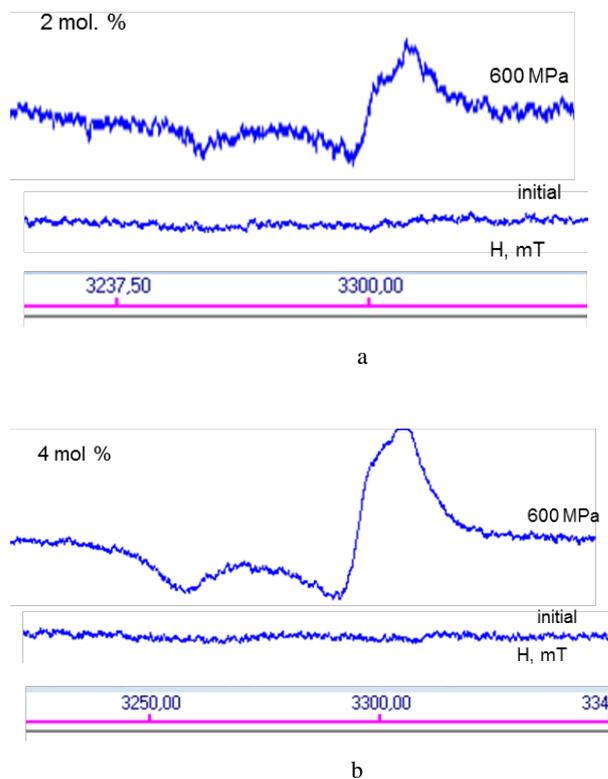


Fig. 7 ESR spectra of initial (without pressure action) and modified systems (600 MPa pressure action) for systems with calcination temperature is $700^\circ C$ and Y_2O_3 amount a) 2 mol. %, b) 4 mol. %.

According to presented data the ESR spectrum of investigated pressure modified powders has anisotropic signal with three peaks and g-tensors of which have the values close on $g_1=2,03$, $g_2=2,01$, $g_3=2,009$. This signal corresponds to the triplet state of the adsorbed O_2^- on oxide surface. Isotropic signal with the g-value close on 2.003 appears in the ESR spectrum also. This signal evidences about generation F^+ -centers on zirconia surface under UV irradiation.

Conclusion

It was shown that the technology of co-precipitation is a perspective technology for creation of complex oxide. The developing of this technology by including of physical and chemical actions in their process, in particular pressure or concentration actions, allows the varied of characteristics of NPs and their properties. It was found the introduction of Y_2O_3 allows to creation of structure defects in partially stabilized zirconia, and its influence for tetragonal crystals is not monotonic in range 2-4 mol. %. It is connected with boundary of stable tetragonal phase at Y_2O_3 adding. The pressure is active factor of changing of surface state due to tetragonal – monoclinic transformation and may be used for improvements of catalytic properties of zirconia NPs.

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