COMPARATIVE ANALYSIS OF THE PHASE COMPOSITION AND MORPHOLOGICAL STRUCTURE OF ZrO_2 AND A MIXTURE OF ZrO_2/Fe_2O_3 NANOPARTICLES BEFORE AND AFTER GAMMA ACTIVATION

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A comparative analysis of the phase composition and morphological structure of ZrO_2 and a mixture of ZrO_2/Fe_2O_3 nanoparticles before and after gamma irradiation using a linear electron accelerator with E = 22 MeV and a current of 500 μA was conducted. It was shown that gamma irradiation of ZrO_2 and a mixture of ZrO_2/Fe_2O_3 nanoparticles does not lead to changes in the phase composition or to the destruction of the crystalline structure of the studied objects.

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INTRODUCTION

Zirconium dioxide, due to its characteristics, is among the most widely studied and used materials. The combination of mechanical and electrical properties permits its use in many technical sections of electronic equipment. Among the successful applications of zirconium dioxide is its use as an effective pigment for reflective surfaces, as catalyst supports [1–3]. Zirconium dioxide has high radiation resistance and, due to its high acidity, is preferable for using oxides of other transition metals in applied areas. Therefore, considerable attention is paid to the general state of metal oxides – the possible effects of morphology, the size of oxide nanoparticles, mixtures of oxide nanoparticles with various additives, etc. are studied. The effects of pre-treatment (vacuum, annealing, radiation, etc.) and its influence on the structural and functional characteristics of zirconium dioxide nanoparticles are comprehensively studied [4].

A promising approach in this area is the *synergy* among various factors – the addition of other metal oxide nanoparticles, various types of ionizing radiation, and other physical effects – that enhances their interactions. A series of experiments was conducted to test this hypothesis.

This study aimed to investigate the phase composition, crystal structure, and morphology of ZrO_2 and ZrO_2/Fe_2O_3 nanoparticles before and after gamma irradiation.

MATERIALS AND METHODS

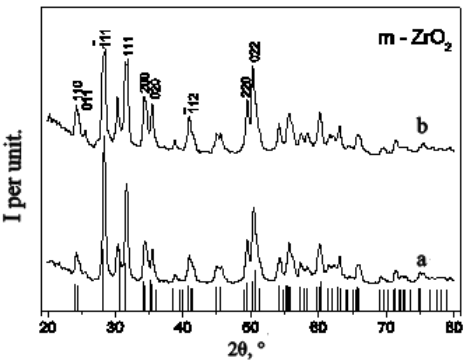
Crystalline monoclinic zirconia nanopowder with a maximum particle size of ~50 nm was used as the starting material. Data on the phase composition and crystal structure of the zirconia nanoparticles were obtained using X-ray diffraction. The structural and phase composition of the zirconia nanoparticles was recorded by X-ray diffraction using a DRON-2 diffractometer with copper radiation at a voltage of 30 kV and a current of 10 mA. Spectra were recorded in the range from 20 to 80° at a scanning rate of 1°/min. Diffraction reflection from the (200) plane of a NaCl single crystal was used as the standard for recording X-ray diffraction patterns. The resulting X-ray diffraction patterns were analyzed using the ICDD PDF-2 database. Crystal sizes were calculated from the broadening of the X-ray diffraction peaks, and crystallinity was calculated from the sum of the areas of the selected peaks.

Zirconium dioxide nanoparticles were activated using bremsstrahlung gamma radiation from a linear electron accelerator with an energy of 22 MeV and a current of 500 μA. The absorption dose was $4 \cdot 10^7$ Gy. Irradiation of the samples resulted in the activation of Zr via the reactions $^{90}Zr(\gamma,n)^{89}Zr$ and $^{96}Zr(\gamma,n)^{95}Zr$. Auger electrons with energies of 1.91 (78.6%) and 12.7 (19.2%) kV accompany the decay of ^{89}Zr.

Crystal-optical studies were performed using a POLAM-L211 microscope with immersion liquids (set IJ, OVIJ).

RESEARCH RESULTS

The figure shows diffraction patterns of zirconia before and after gamma activation.



Diffraction pattern of zirconia before(a) and after(b) gamma activation

Both patterns exhibit steep, highly intense diffraction lines for monoclinic zirconia. The X-ray histogram, taken from the reference data (PDF No. 37 1484) for the monoclinic phase of crystalline zirconia, agrees well with the experimental data. No peaks attributable to any other zirconia phase or impurity were observed in the spectra.

The comparison of the spectra of zirconium dioxide before and after gamma activation (curve a and curve b), no shifts in the maxima or distortions in their shape were detected in the diffraction pattern of the gamma-activated samples. The relative intensity and width of the diffraction peaks for the gamma-activated samples were generally similar to their initial state.

The observed differences were associated with changes in the intensity and integrated area of the main peaks. For gamma activated zirconium dioxide, the intensity of some lines increased slightly, and, in addition, their narrowing was observed. This indicated that the conditions of gamma activation of zirconium dioxide nanoparticles, on the one hand, contributed to the formation of a more perfect crystalline structure of the oxide, as indicated by the strengthening of the peaks, and on the other hand, judging by the narrowing of the main lines, led to a decrease in its dispersion.

The studied samples were found to be polycrystalline and single-phase (>97%): all reflection peaks in the diffraction patterns were in good agreement with the tabulated JCPDS data for monoclinic zirconia (JCPDS 13-0307).

The diffraction pattern of the gamma-activated ZrO_2/Fe_2O_3 sample showed low-intensity reflections with values of 26.00, 33.16, and 55.00, corresponding, according to ASTM Powder Diffraction Card No. 76-1821, to the iron oxide phase γ-hematite (γ-Fe_2O_3).

The diffraction pattern of ZrO_2/Fe_2O_3 indicates the presence of Fe_2O_3 (JCPDS 84-0311) and monoclinic ZrO_2. The radiogram of the samples before and after gamma activation was virtually identical; the crystallinity and original phase composition were retained in the samples.

The nanoparticles Fe_2O_3 in ZrO_2 are an active compound and can be considered an effective dispersing agent. With the combination of gamma irradiation, a reaction medium is created the formation of high concentrations of energetic hydrated electrons (e^-_{aq}), hydroxyl radicals ($OH^\bullet$), H_2O_2 (peroxides), and other highly reactive groups for the targeted and accelerated development of reactions necessary for hydrocarbon conversion.

The crystallite size in the samples before and after gamma activation, as well as the lattice deformation, were calculated from line broadening (X-ray diffraction). The initial nanoparticle sizes ranged from 50 to 70 nm, and after gamma activation, from 75 to 95 nm. Apparently, the radiation energy used promoted coalescence (sticking together) of small nanoparticles.

Under a microscope, ZrO_2 and ZrO_2/Fe_2O_3 crystals appeared as dense crystals with a glassy luster and iridescent rings on the surface. Individual crystals had the shape of large polyhedrons (7 to 3 μm), separated by clusters of pores and small particles (<1 μm).

CONCLUSIONS

Qualitative X-ray analysis showed that gamma irradiation of nanoparticles of ZrO_2 and mixed ZrO_2/Fe_2O_3 does not lead to a change in the phase composition or to the destruction of the crystalline structure of the studied objects.

The high radiation stability of mixed nanosystems makes them suitable for use in areas with high ionizing radiation fields. Mixed nanosystems can also be used as catalysts in hydrocarbon conversion due to the formation of highly reactive oxygen species during the oxidation of Fe_2O_3 nanoparticles, as well as “lattice” oxygen released during the radiolysis of ZrO_2.

REFERENCES

1. Q. Gao, X. Fang, X Wu, et al. Mesoporous zirconia nanobelt: Preparation, Characterization and Application in Catalytical Methane Combustion // *Micropor. Mesop. Mat.* 2011, v. 143, p. 333-340.

2. J.E. Medvedeva, A.J. Freeman. Screened-exchange determination of the electronic properties of monoclinic, tetragonal and cubic zirconia // *Phys. Rev.* 2007, v. 76B, p. 115-123.

3. Y. Murase, E. Kato. Role Water Werop in Crystalline Growth and Transformation of ZrO_2 // *J. Amer. Chem. Soc.* 2020, v. 66, p. 196-200.

4. R.A. Andievski. Behavior of radiation defects in nanomaterials // *Rev. Adv. Mater. Sci.* 2011, v. 29, p. 59-67.

ПОРІВНЯЛЬНИЙ АНАЛІЗ ФАЗОВОГО СКЛАДУ, МОРФОЛОГІЧНОЇ СТРУКТУРИ ZrO_2 ТА СУМІШІ НАНОЧАСТИНОК ZrO_2/Fe_2O_3 ДО ТА ПІСЛЯ ГАММА-АКТИВАЦІЇ

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Проведено порівняльний аналіз фазового складу, морфологічної структури ZrO_2 та суміші наночастинок ZrO_2/Fe_2O_3 до та після гамма-опромінення за допомогою лінійного прискорювача електронів з E = 22 МеВ та струмом 500 мкА. Показано, що гамма-опромінення ZrO_2 та суміші наночастинок ZrO_2/Fe_2O_3 не призводять до змін фазового складу або руйнування кристалічної структури досліджуваних об'єктів.