MODIFICATION OF NANOMATERIAL BY RADIATION

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The radiation technology of influence of high-energy radiation for modification of properties of inorganic nanoparticles of (Fe_2O_3, ZnO, ZrO_2) is presented. The sorption activity of radiation-induced nanoparticles of γ-hematite and clinoptilolite against ^{235,238}U radionuclides, ^{241}Am, ^{234}Th and ^{132}Cs was revealed. For the first time the radiation-stimulated catalytic activity of ZnO, ZrO_2 nanoparticles in the processes of conversion of hydrocarbon compounds was detected.

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1. INTRODUCTION

The first experiments of the influence of high-energy radiation on nanoparticles of oxides, aluminum silicates, etc. have shown a wide variety of radioactive effects [1,2].

Previously, the effect of irradiation of properties of nanomaterials almost has been not studied, but lately the radiation-induced changes in the nanoparticles is of considerable interest. It is assumed that the radiation effects on various dimensions of nanoparticles have been accompanied by a change of their properties. For example, the appearance of radiation point defects such as interstitial atoms and vacancies were possible. Radiation defects may contribute to the annihilation of the nanostructure and their transformation into an amorphous state. Irradiation can also lead to processes of recrystallization (abnormal grain growth). The nanoparticles size is comparable with the diffusion of the defects to the surface. Therefore, radiation resistance nanoparticles are higher than their micron analogues.

Considerable interest for radiation chemistry is the purposeful change in the properties of nanoparticles. For example, activation of the nanoparticles by bremsstrahlung leads to the formation of radioactive isotopes that decay is accompanied by a significant yield of Auger electrons. Deceleration of low-energy electrons at the surface of the nanoparticles leads to synergistic influence the effect of radiolysis products and properties of the nanomaterial surface. This phenomenon causes a significant increase in catalytic activity, the implementation of the processes of formation of necessary products at a lower temperature, etc.

Passage of Auger electrons in water accompanied by the formation of free radicals such as hydrated electrons (e^-_{aq}) and of hydrogen atoms ($H^\bullet$), which are strong reducing agents with a corresponding redox potentials E° (H_2O/e^-_{aq}) = – 2.87 V_{NHE} and E° ($H^+/H^\bullet$) = – 2.3 V_{NHE}. In water, hydroxyl radical ($HO^\bullet$), which are strong oxidative species E° ($HO^\bullet/H_2O$) = + 2.8 V_{NHE}, are formed also. The 2.6 hydrated electrons (e^-_{aq}), 2.6 hydroxyl radicals ($HO^\bullet$), 0.4 atoms of hydrogen ($H^\bullet$) and small amount H_2 and H_2O_2 are being produced by the 100 eV of ionization losses of particles in pure water.

The aim of this work was to study the influence of γ-activation on the properties of metal oxides (Fe_2O_3, ZnO, ZrO_2), which used in the sorption processes of actinides, radionuclides, as well as the conversion of hydrocarbons.

2. MATERIALS AND METHODS

In this work the nanoparticles of metal oxides (Fe_2O_3, ZnO, ZrO_2) were used, producer: firm Alta Aesar Sigma. The size of nanoparticles was ∼50 nm for Fe_2O_3, ∼40 nm for ZnO, and ∼40 nm for ZrO_2.

Samples of nanoparticles (1 g) were placed in aluminum foil and were irradiated by brake γ-rays on linac KIPT with E = 22 MeV and I = 500 μA. The nuclear reactions ^{54}Fe(γ,n)^{53}Fe, ^{66}Zn(γ,n)^{65}Zn, ^{90}Zr(γ,n)^{89}Zr, ^{96}Zr(γ,n)^{95}Zr were used. The maximum absorbed dose during γ-irradiation accounted for Fe_2O_3 – 0.8 MGy, ZnO – 20 MGy, ZrO_2 – 20 MGy.

3. RESULS AND DISCUSSION

According to our previous articles [3-6], the nanoparticles have kept a basic similarity about structural and morphological properties, and also the polycrystallinity and the monophasic after

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γ-activation. It has been shown that Fe_2O_3 nanoparticles after activation has high crystallinity, without essential modifications in the initial structure of Fe_2O_3. The character of a locating of the interference maximums, their breadth and intensity of nanoparticles ZnO after activations is attributed of a high crystallinity and cleanliness. Any peaks concerning to any other phase ZnO or impurities, and also peak of metal zinc it was not discovered.

γ-activation of the monoclinic structure of ZrO_2 leads to the formation of a perfect structure of ZrO_2, the appearance of crystals of the cubic system. It was noted a decrease in crystallite size.

Fig. 1 shows the γ-spectrum of Fe_2O_3 nanoparticles.

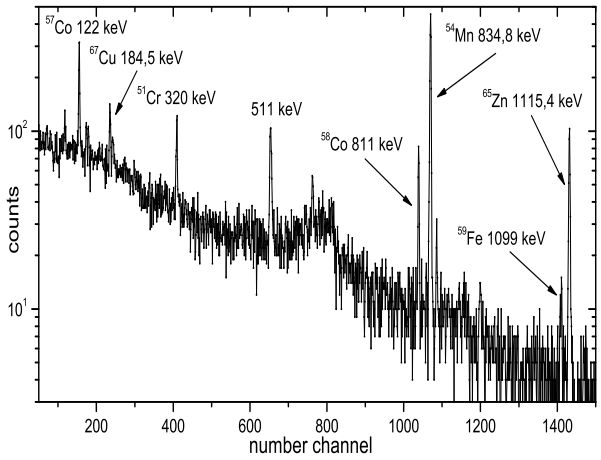

Fig.1. *The γ-spectrum of nanoparticles Fe_2O_3*

Various elements were detected in nanoparticles of Fe_2O_3 in the capacity of impurities: Ca, Na, Mn, Ni, Mg, and others. The detection limit of the elements was 10^{-5}wt.%.

Fig. 2 shows the γ-spectrum of ZnO nanoparticles.

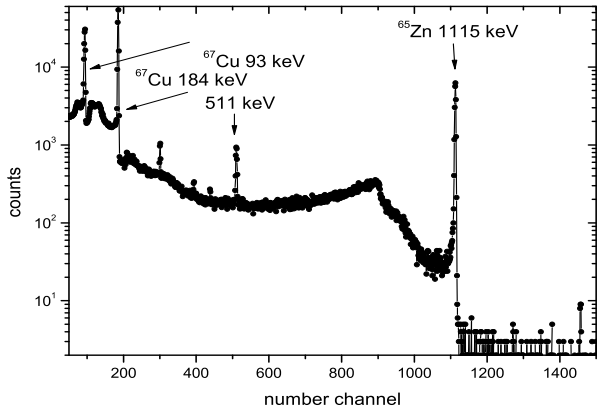

Fig.2. *The γ-spectrum of ZnO nanoparticles*

In the γ-spectrum of ZnO nanoparticles observed lines of ^{67}Cu from the reaction ^{68}Zn(γ,p)^{67}Cu.

Fig. 3 shows the γ-spectrum of ZrO_2 nanoparticles.

In the γ-spectrum of ZrO_2 nanoparticles were not observed the presence of any impurity elements.

The problem of immobilisation spent fuel and radioactive waste is extremely actual. In latest years the use of inorganic sorbents is increased for processing radioactive waste, which possess high chemical resistance, radiation stability and show selectivity to some radionuclides.

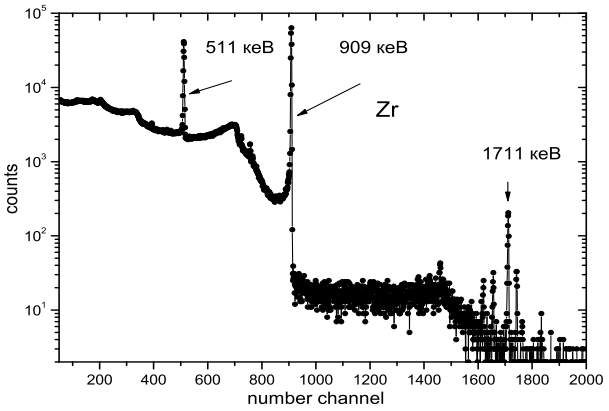

Fig.3. *The γ-spectrum of ZrO_2 nanoparticles*

The minerals of iron oxide which widespread in nature, such as hematite (γ-Fe_2O_3) and a magnetite (Fe_3O_4) are effective sorbents of actinoids. The γ-Fe_2O_3) shows extremely high getter ability to such actinoids, as uranium, plutonium, neptunium, americium, etc.

Even more high selectivity to uranium and transuranium elements is shown in relation to sorbents on a basis of nanostructure materials which possess such advantages as dimensionality at the level of tens and hundreds of nanometers, high reactionary ability at high temperatures and pressure, etc. [7].

Sorbent on a basis of iron oxide can be effectively used for water purification of atomic reactors from uranium and transuranium elements. At designing of the radioactive waste storage of spent fuel and the radioactive waste, these sorbents can be used as the intermediate barriers at a motion of actinoids in the colloid state. Thus, it is possible to study the mechanism of sorption of these elements by the natural minerals.

As a rule, in natural water mediums, the actinoids are in hydrated ionic and colloid forms. Extraction of uranium from water mediums represents the considerable difficulty since uranium possesses the high complex-formative ability, but at low pH, it is capable of being transformed to soluble complexes.

The oxide and hydroxide of iron in environment easily are exposed to oxidation-reduction processes. Therefore, they can change of oxidation-reduction state uranium, neptunium, plutonium. Ions Fe, in this case, plays a role structural site "cation-templane", which enlarges sorbent capacity in relation to an actinoid.

The sorption research of $^{235,238}U$ and of concomitant isotopes of ^{241}Am, ^{232}Th in water realized by use of γ-activated nanoparticles of Fe_2O_3 and nanoparticles of ZrO_2 concerning a traditional method of sedimentation of uranium by salts of iron chloride ($FeCl_3 \cdot 6H_2O$), with adding hydrate ammonium (NH_4OH). The sample of sorbents was 1 g, pH=5.5.

The content (C) of actinides in water

N	Sorbent	C for ^{238}U, μg/l	C for ^{241}Am, r.u.	C for ^{232}Th, r.u.
1	Coprecipitation $FeCl_3 \cdot 6H_2O$	17.0	124	231
2	γ-activated nanoparticles of Fe_2O_3	20.8	174	266
3	γ-activated nanoparticles of ZrO_2	15.8	50	191

In the article [8] the possibility of use natural clinoptilolite as a sorbent for extraction of uranium from aqueous solutions is shown. Soluble complexes of an uranyl-ion are high mobile and consequently represent the considerable danger to a surrounding medium. Under certain hydrothermal conditions, a natural mineral clinoptilolite absorbs about 83...85% of uranium. Also, it is known that use of special microporous membranous filters for refinement of water-salt solutions from radionuclides of ^{137}Cs and ^{90}Sr based on the use of natural minerals in the form of fine nanopowders. The fixation by clinoptilolite of these radionuclides represents their uptake which does not cause usual ion-exchange character and leads to the transition of ions into a strong bound state. The fixation means the introduction of these radionuclides in space of a lattice or migration along interstitials, or fastening in a lattice cavity. Anyway, a process of transition of ions of radionuclides in the fixed state is carried out due to of diffusion processes in a crystalline lattice natural aluminum silicate.

The active getter centres of clinoptilolite are coordinate unsaturated ions Al^{3+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, etc. and hydroxyl groups.

For raise of selectivity of clinoptilolite to caesium, it is possible by modification of its surface γ-activated nanoparticles of Fe_2O_3.

The two-component system on a base of γ-activated nanoparticles of Fe_2O_3 with adding nanopowder (<80 nanometers) a natural mineral (clinoptilolite) has been used for a selective sorption of ^{132}Cs.

On a surface of this system there are Fenton-reactions ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^-$) which initiate occurrence of active centres $OH^\bullet$, OH^-. Downsizing of clinoptilolite compositions promotes intensifying of redox reactions an ion-exchange of forms of iron with the generation of the active hydroxyl radicals $OH^\bullet$.

The increase of sorption efficiency of ^{132}Cs for clinoptilolite increases with growth pH from 6 to 8. The sorption of ^{132}Cs was carried out (activity of solution $CsNO_3$ – $6.5 \cdot 10^6$Bq/l from reaction $^{133}Cs(\gamma,n)^{132}Cs$) with use as sorbents of clinoptilolite nanoparticles, γ-activated nanoparticles of Fe_2O_3 and two-component system on the basis of γ-activated nanoparticles of Fe_2O_3 with adding nanopowder of clinoptilolite which was deposited on various surfaces at pH=8.5 and at room temperature. Residual ^{132}Cs activity on surfaces and flushing waters has been measured Ge(Li)-detector. The obtained results have shown that residual activity of $1^{132}Cs$ on a surface equal (0.45±0.04), (0.63±0.005), and (0.99±0.06) %, accordingly.

After centrifugation, the ^{132}Cs specific activity was of the precipitate of γ-activated hematite + clinoptilolite nanoparticles – ∼60% and in the supernatant – ∼1.1%.

Thus, the use of γ-activated nanoparticles of Fe_2O_3 and nanopowder of clinoptilolite can achieve effective immobilisation from the liquid medium of actinides ($^{235,238}U$, ^{241}Am, ^{232}Th) and of radionuclides, for example ^{132}Cs.

The perspective direction in addressing the modification of the catalytic properties of metal oxides of nanoparticles is the conversion of hydrocarbon compounds, based on the use of modern nuclear technology. On the one hand, this is the effect of ionizing radiation on the properties of nanoparticles and on the other hand, this is heterogeneous catalysis. In this area previously, such studies have not been conducted.

There are numerous processes for the processing of the hydrocarbon feedstock: cracking (processing of oil to produce gasoline), pyrolysis (the breakdown of complex organic compounds into simple), Fischer-Tropsch synthesis - the hydrogenation of CO under pressure to form a CO-H_2 (biogas) to produce formaldehyde, ethylene, olefin and etc.

These chemical processes are used in the presence of expensive catalysts (Pd, Ti) and at high temperature.

Oxide catalysts on the basis of zinc oxide nanoparticles (ZnO) and zirconium dioxide (ZrO_2) exhibit high catalytic activity in hydrocarbon conversion. It can be expected that the presence of a variety of radiation defects (conduction electrons, interstitial atoms, and vacancies, etc.), which caused by bremsstrahlung and Auger electrons, in the case the decay of ZnO and ZrO_2 would increase the concentration of active centers on the surface of nanoparticles oxides and as consequently, to increase its catalytic activity.

The catalytic activity of ZnO and ZrO_2 nanoparticles after activation by the use of bremsstrahlung in the case of conversion of methanol at room temperature estimated on the optical density of obtained products were measured with use of the SF-46 in visible and UV range (λ from 200 to 600 nm).

The absorption spectra (Figs. 4, 5) of methanol

conversion products for use as catalysts γ-activated nanoparticles ZnO and ZrO_2 are shown.

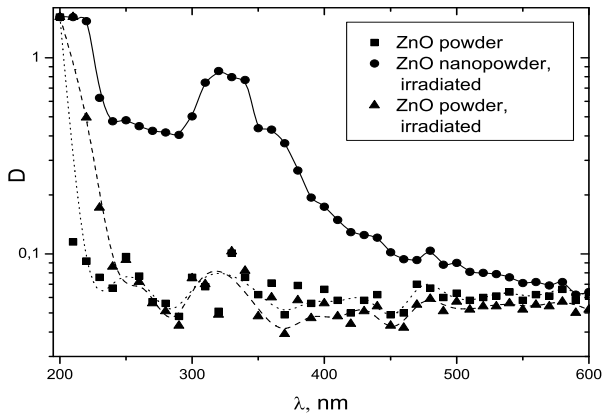

Fig.4. *The absorption spectrum of the methane conversion with using as catalysts γ-activated ZnO nanoparticles*

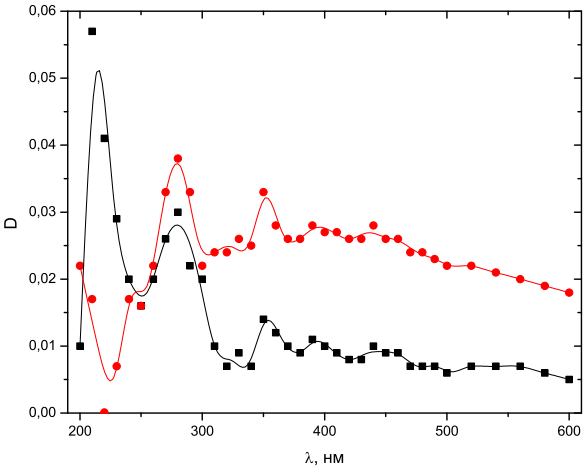

Fig.5. *The absorption spectrum of the methane conversion with using as catalysts γ-activated ZrO_2 nanoparticles*

From the results seen that the yield of secondary products when used as catalysts γ-activated nanoparticles of ZrO_2/Fe_2O_3 as compared to γ-activated nanoparticles ZrO_2 and ZnO 10 times more (Figs. 4, 5 6).

Presumably, this result is achieved by the synergistic effect of radiation-induced active sites on the surface of oxides and conversion medium formed of highly reactive compounds. A combination of factors such as:

1. The Auger electrons having high specific braking capability (for ^{65}Zn – 10...27 keV/micron and ^{89}Zr – 25 keV/micron);

2. Comparable with the size of oxide particles the range of electrons;

3. The formation of high concentrations of active energy hydrated electron (e^-_{aq}), hydroxyl radicals ($OH^\bullet$), peroxide (H_2O_2) and other highly reactive groups – all these contribute to the direction and accelerated development of the hydrocarbon conversion reaction.

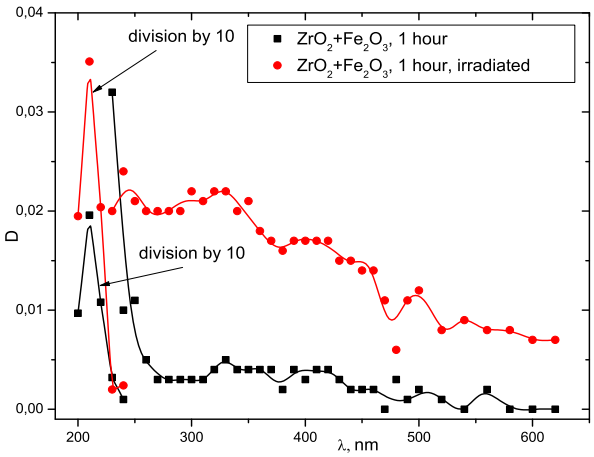

Fig.6. *The absorption spectrum of methane conversion products with using as catalysts γ-activated nanoparticles of ZrO_2/Fe_2O_3*

4. CONCLUSIONS

1. The main advantage of the use of sorbents with respect to actinides (^{235,238}U, ^{241}Am, ^{232}Th) and to radionuclides of ^{132}Cs is determined by size. Nanoparticles of sorbents possess a highly active surface and a chemical reactivity of the surface, due to activation by bremsstrahlung.

2. A high adsorption capacity of selective sorbents is being carried out even for the trace amounts of materials used.

3. The synergism confirmation of the combination of radiation excitation and advantage of reactionary nanostructured sorbents that enhance their functionality in the processes of immobilization of actinides and radionuclides - of analogues of radioactive waste of liquid media was obtained.

4. The mechanism of increasing the activity of a catalyst of organic material at room temperature due to the synergistic interaction of radiation-induced Auger electrons of the active centers and of highly reactive hydrocarbon compounds for nanoparticles of ZrO_2/Fe_2O_3, ZrO_2 and ZnO after irradiation by bremsstrahlung was detected.

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РАДИАЦИОННОЕ МОДИФИЦИРОВАНИЕ НАНОМАТЕРИАЛОВ

Н. П. Дикий, А. Н. Довбня, Ю. В. Ляшко, Е. П. Медведева, Д. В. Медведев, И. Д. Федорец

Представлены радиационные технологии воздействия высокоэнергетического облучения на свойства неорганических наночастиц (Fe_2O_3, ZnO, ZrO_2) для их направленного модифицирования с целью расширения их функциональности. Показана сорбционная активность радиационно-индуцированных наночастиц γ-гематита и клиноптилолита в отношении радионуклидов ^{235,238}U, ^{241}Am, ^{232}Th и ^{132}Cs. Впервые обнаружено радиационно-стимулированное повышение каталитической активности наночастиц ZnO, ZrO_2 в процессах конверсии углеводородных соединений.

РАДІАЦІЙНЕ МОДИФІКУВАННЯ НАНОМАТЕРІАЛІВ

М. П. Дикий, А. М. Довбня, Ю. В. Ляшко, О. П. Медведєва, Д. В. Медведєв, І. Д. Федорецъ

Представлено радіаційні технології впливу високоенергетичного опромінення на властивості неорганічних наночастинок (Fe_2O_3, ZnO, ZrO_2) для їхнього спрямованого модифікування з метою розширення їхньої функціональності. Показана сорбційна активність радіаційно-індукованих наночастинок γ-гематиту і кліноптилоліту у відношенні радіонуклідів ^{235,238}U, ^{241}Am, ^{232}Th і ^{132}Cs. Уперше виявлене радіаційно-стимульоване підвищення каталітичної активності наночастинок ZnO, ZrO_2 у процесах конверсії вуглеводневих з'єднань.