RADIATION STIMULATION OF THE CATALYTIC ACTIVITY OF ZIRCONIUM DIOXIDE NANOPARTICLES DURING THE CONVERSION OF HYDROCARBONS

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The comparison of the catalytic activity of the initial and activated by bremsstrahlung γ-radiation on a high-current electron accelerator of zirconium dioxide nanoparticles on the nature of the conversion of ethanol. The used γ-activation parameters contributed to the formation of a more perfect crystal structure of ZrO_2 nanoparticles. It was shown that when using γ-activated ZrO_2 nanoparticles as a catalyst, the yield of hydrocarbon products during the conversion of ethanol was several times higher than the yield of the same products in the case of using the initial ZrO_2 nanoparticles. The mechanism of such a conversion of ethanol can be associated with the synergism of large ionization losses of Auger electrons and the effect of highly reactive products involved in heterogeneous catalysis.
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1. INTRODUCTION

The processing of organic raw materials into low molecular weight hydrocarbons is becoming one of the promising areas in the production of valuable chemical products. The implementation of this direction is associated with the creation of active, selective, and stable heterogeneous catalytic systems that do not contain expensive metals and harmful substances. The main reactions that take place during the conversion of hydrocarbons are dehydrogenation reactions, intermolecular dehydration, and intramolecular dehydration. The ethanol, ethers, ethylene, and acetaldehyde in the catalytic conversion are formed. Non-toxic zirconium dioxide can be used as a catalyst and carrier, and the use of zirconium dioxide nanoparticles is even more effective and promising [1-4].

Zirconium dioxide (ZrO_2) nanoparticles are a widely studied and demanded compound [5]. The main characteristics of ZrO_2 are: high hardness, refractoriness, low thermal conductivity and wear resistance, high refractive index and high radiation resistance [6].

The catalytic activity of ZrO_2 is provided due to its high acidity and due to the nature of the electronegative surface of this compound. The activity of a catalyst largely depends not only on the electronegative surface but also on the distribution of basic and acidic centers necessary for the directed development of the process. It is these uncoordinated metal cations and oxide anions that can act as acids and bases. These are the so-called centers of Lewis acids - the proton theory of acids and bases, according to which acids (A) are able to donate protons, and bases (B) are capable of attaching them. “A” is the acceptor of this bond, and “B” is the donor of this bond (electronic theory of “A” and “B”). Coordination unsaturated cations that are present on the oxide surface can interact with the main molecules and create a new coordination bond while completing the complete coordination of the surface cations.

Accordingly, the high catalytic activity, for example, for ZrO_2 in the conversion of hydrocarbons, can be associated with differences in acid-base characteristics, taking into account the highly electronegative cations of "Lewis acids" such as Zr^{4+}, Ti^{4+} Cr^{3+}. The high Lewis acidity of the surface increases the approach of the main reagents to the active sites and promotes strong interaction with metal cations. Apparently, the ZrO_2 oxide catalyst will exhibit high conversion. On the other hand, the degree of polarization (the ratio of charge to ionic radius) can also affect the completeness of conversion. The stronger the polarization of the Lewis acid cation and the main strength of the adsorbent, the greater the power of the surface Lewis centers. Thus, compounds with Zr^{4+}, Ti^{4+} Cr^{3+}, for which the degree of polarization is 6.2, 6.6, and 4.9, respectively, should increase the interaction of Lewis centers with hydrocarbon molecules. The use of mixed oxide catalysts of the ZrO_2/Fe_2O_3 type in comparison with monocatalysts can significantly increase the reaction yield due to the additional acidity of Lewis acids, as a result of the presence of Fe^{3+} ions on the oxide surface.

Recently, in the field of heterogeneous catalysis, much attention has been paid to the effects of mutual amplification of various factors, for example, the treatment of catalysts with ultrasound, microwave radiation, the use of accelerator technology, and nuclear technologies. Until now, no studies have been carried out related to the gamma activation of metal oxide nanoparticles by bremsstrahlung gamma radiation from an electron accelerator. Preliminary studies carried out by us [7-10] showed that Auger electrons appear in metal oxide nanoparticles after gamma activation, as well as various radiation defects (interstitial atoms and vacancies, highly reactive oxygen forms, etc.) which can lead to an increase in the concentration of active centers on the surface of the oxide and, as a consequence, to an increase in its catalytic activity [11-13]. The effectiveness of a catalyst is determined by its ability to create active oxygen centers for breaking the CH bond in hydrocarbon molecules. The activity of catalysts also largely depends on the size of the nanoparticles used as catalysts.

The basic principles of the catalysts, their activity, and their selection for the oxidation reaction of hydrocarbons are still unresolved.

The aim of this work was to study the effect of gamma activation on the properties of nanoparticles of zirconium dioxide and on their catalytic activity during the conversion of ethanol.

2. MATERIALS AND METHODS

In the experiments, we used zirconium dioxide nanoparticles (40 nm) manufactured by Alta Aesar Sigma. Zirconium dioxide ZrO_2 nanoparticles were activated by gamma bremsstrahlung from the NSC KIPT linear accelerator with E = 22 MeV, I = 500 μA according to the reaction $^{90}Zr(\gamma,n)^{89}Zr$, $^{96}Zr(\gamma,n)^{95}Zr$. The maximum absorbed dose was 22 MGy. The gamma-ray spectrum was recorded with a Ge(Li)-detector.

Auger electrons with energies of 1.91 (78.6%) and 12.7 (19.2%) keV accompany the decay of ^{89}Zr.

Registration of IR spectra of zirconium dioxide nanoparticles was carried out on a Specord-75 IR in the frequency range 4000-400 cm^{-1} on samples in the form of tablets prepared by pressing with KBr [14].

The catalytic activity of the initial and gamma-activated nanoparticles of zirconium dioxide was compared by the optical density of hydrocarbon products that were formed in the process of ethanol conversion, as well as by the dynamics of the formation of highly reactive products by recording it is on a quantum installation with photomultiplier-39 [15].

3. RESULTS AND DISCUSSION

In fig. 1 shows the gamma spectrum of zirconium dioxide nanoparticles.

In the gamma spectrum of zirconium dioxide from the reaction ^{90}Zr, the presence of impurity elements is not recorded. The presence of isotopes ^{95}Zr (511 keV), ^{95}Zr (757 keV), ^{89}Zr (909, 1654, 1712, 1744 keV) is noted.

In fig. 2 shows the dynamics of the accumulation of free radicals during ethanol oxidation using the initial and γ-activated ZrO_2 nanoparticles.

The spectra exhibit absorption bands with a maximum at 745 and a doublet at 490 and 410 cm^{-1}, which refer to asymmetric Zr-O_2-Zr and stretching Zr–O vibrations, respectively.

It was shown by IR spectroscopy that there are no significant differences in the IR spectra of the initial and activated nanoparticles of zirconium dioxide. The nature of the location of the maxima in the absorption region, their width, and intensity indicate high crystallinity. There is a fundamental spectral similarity of the samples before and after activation: the spectral profiles are practically identical in shape. This indicates that in the activated nanoparticles of zirconium dioxide, the monophase, and crystal structure characteristic of the initial sample are retained. Such oxide samples with a cubic structure are characterized by pronounced stability. The retention of the absorption bands of the lattice vibrations of ZrO_2 and the constancy of their intensities indicate the identity of the research conditions.

In fig. 3 shows the IR spectra of ZrO_2 nanoparticles. When comparing these samples, neither shifts of the maxima, nor distortions of their shape were found. Minor differences were associated with changes in the intensity and integral area of the main peaks. In gamma-activated samples, the intensity of some lines increased and their broadening was observed. This indicated that the parameters of gamma activation of ZrO_2 nanoparticles contributed to the formation of a more perfect crystal structure of ZrO_2, which facilitated its dispersion. The table shows the crystallite sizes of the initial and γ-activated ZrO_2 nanoparticles.

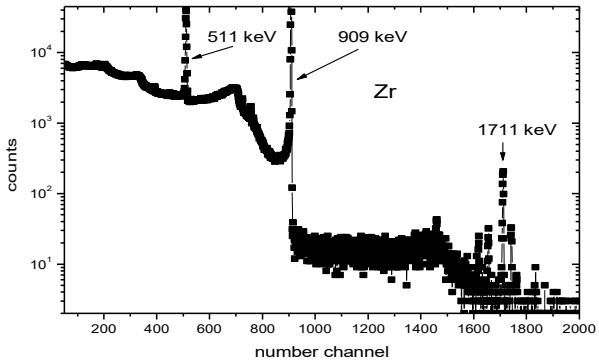

Fig.1. *The gamma spectrum of ZrO_2 nanoparticles*

Table
Crystallite sizes of the initial and γ-activated ZrO_2 nanoparticles

Peak position, 2θ°	CSR sizes in ZrO_2 powders, μm	
	In its original state	After γ–activation
28.2	3.89	3.41
31.5	2.63	2.32
40.7	0.58	0.49

Diffraction patterns of zirconium dioxide nanoparticles in the initial state and after irradiation to an absorbed dose of 22 MGy represent a polycrystalline monophase sample containing a monoclinic and cubic phase.

Under the microscope, ZrO_2 crystals are dense crystals with a glassy sheen and iridescent rings on the surface. Individual crystals had the shape of polyhedrons, which were separated by an accumulation of pores [7-13].

The structure of zirconium dioxide has a significant effect on its activity in various catalytic processes; therefore, ethanol conversions on the initial and activated ZrO_2 samples were studied.

The catalytic activity of ZrO_2 in the conversion of ethanol was estimated from the values of the optical density of the released products on spectrophotometer SF-46, as well as the intensity of free radical products on a quantum installation with a photoelectric multiplier (PEM-39). Measurements were carried out in dynamics after 1, 3 and 5 hours (fig. 3**)**.

All reactions showed a significant increase in the catalytic activity of ZrO_2 nanoparticles after their gamma activation. When using gamma-activated ZrO_2 nanoparticles, products such as dimethyl ether

(λ = 245 nm), diene ions (λ = 335 nm), aromatic products (λ = 395 nm) were also determined.

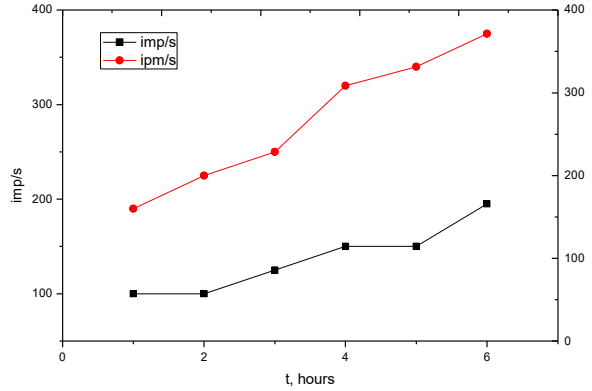

Fig.2. *The dynamics of the accumulation of free radicals during the oxidation of ethanol using the initial (■) and activated nanoparticles (●), error 20%*

The intensity of the bands in the absorption spectra of the reaction products of the catalytic oxidation of ethanol with the participation of the initial and activated ZrO_2 nanoparticles had the following ranges: after 1 hour for the initial ZrO_2 nanoparticles 0.073 rel. units and for activated ZrO_2 nanoparticles 0.241 rel. units; after 3 hours - 0.048 rel. units and 0.225 rel. units, respectively; after 5 hours - 0.0021 rel. units and 0.347 rel. units., respectively. From the data presented, one can see the advantage in catalytic processes of γ–activated ZrO_2 nanoparticles in comparison with the initial samples. The observed effect can be explained, firstly, by the large ionization losses of Auger electrons from the ^{89}Zr isotope and, secondly, by the gamma-induced chemisorption of oxygen O_2^- on the catalyst surface due to the lattice oxygen released as a result of ZrO_2 radiolysis. An increase in the catalytic activity of gamma-activated zirconium dioxide nanoparticles, apparently, can be associated with an increase in the activity of the oxide surface as a result of the action of bremsstrahlung gamma radiation and Auger electrons from ^{95}Zr and ^{89}Zr (fig. 3).

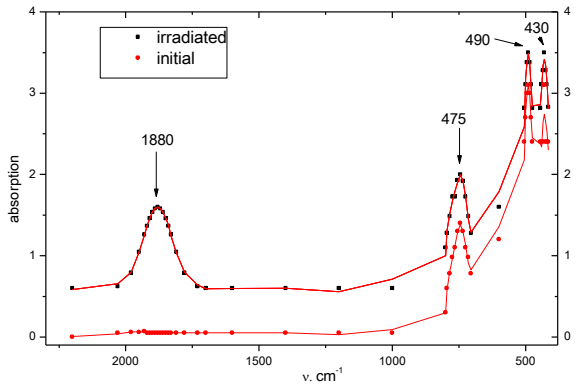

Fig.3. *IR spectra of pure nano-ZrO_2 (initial) and after exposure to γ-radiation on the nano-ZrO_2 + H_2O system at 673K (irradiated)*

The process of gamma activation of samples of zirconium dioxide nanoparticles can lead to the appearance on the surface of nanoparticles of possible radiation defects, such as vacancies of oxygen ions, interstitial metal ions, and conduction electrons. And this, in turn, effectively affects the adsorption properties of a given sample. Part of the electrons in surface anion vacancies can be captured by atmospheric oxygen molecules, since the irradiation was carried out in the air, resulting in the formation of adsorbed oxygen O_2^- ads. It is the adsorbed oxygen O_2^-ads that play an essential role in the initiation of the oxidation of hydrocarbons [16].

The initial samples of zirconium dioxide nanoparticles showed significantly lower activity in the values of the absorption spectra of the products of the catalytic oxidation of ethanol.

The intensity of free radical formation was more pronounced when using gamma-activated ZrO_2 nanoparticles. The direct effect of Auger electrons on zirconium dioxide nanoparticles creates a reaction medium in which the formation of highly reactive oxygen forms such as hydroxyl radicals (OH•), peroxides (H_2O_2), which actively participate in the accelerated conversion reaction, is possible. Therefore, the registration time of the formation of free radical products during the conversion of ethanol in the presence of an activated catalyst, nanoparticles of zirconium dioxide, is accelerated by almost an order of magnitude.

$$ZrO_2 + h\nu \rightarrow ZrO_2 + e^- + h$$

$$e^- + O_2^- \rightarrow {}^{\bullet}O_2^-$$

3. CONCLUSION

1. The possibility of using high-power electron beams at a high-current accelerator for the activation of zirconium dioxide nanoparticles is shown.

2. Comparative analysis of the phase composition and state of the crystal structure of the initial and gamma-activated nanoparticles of zirconium dioxide showed that the parameters activations contributed to the formation of a more perfect crystal structure of ZrO_2.

3. The catalytic ability of ZrO_2 nanoparticles after γ–activation is several times higher than the conversion of ethanol due to the synergism of radiation-induced Auger electrons and active centers on the ZrO_2 surface.

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РАДИАЦИОННАЯ СТИМУЛЯЦИЯ КАТАЛИТИЧЕСКОЙ АКТИВНОСТИ НАНОЧАСТИЦ ДИОКСИДА ЦИРКОНИЯ В ПРОЦЕССАХ КОНВЕРСИИ УГЛЕВОДОРОДОВ

Н.П. Дикий, Ю.В. Ляшко, Е.П. Медведева, Д.В. Медведев

Проведено сравнение каталитической активности исходных и активированных тормозным γ–излучением на сильноточном электронном ускорителе наночастиц диоксида циркония на характер конверсии этанола. Используемые параметры γ-активации способствовали формированию более совершенной кристаллической структуры наночастиц ZrO_2. Показано, что при использовании в качестве катализатора γ–активированных наночастиц ZrO_2, выход углеводородных продуктов при конверсии этанола, превышал в несколько раз выход таких же продуктов в случае использования исходных наночастиц ZrO_2. Механизм подобной конверсии этанола может быть связан с синергизмом больших ионизационных потерь Оже электронов и воздействием высокореакционных продуктов, участвующих в гетерогенном катализе.

РАДІАЦІЙНА СТИМУЛЯЦІЯ КАТАЛІТИЧНОЇ АКТИВНОСТІ НАНОЧАСТИНОК ДІОКСИДУ ЦИРКОНІЮ У ПРОЦЕСАХ КОНВЕРСІЇ ВУГЛЕВОДНІВ

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Проведено порівняння каталітичної активності вихідних та активованих гальмівним γ–випромінюванням на потужному прискорювачі електронів наночастинок діоксиду цирконію на характер конверсії етанолу. Параметри γ–випромінювання, які використовували, сприяли формуванню більш досконалої кристалічної структури наночастинок ZrO_2. Показано, що у випадку використання у якості каталізатора γ-активованих наночастинки ZrO_2 вихід вуглеводних продуктів при конверсії етанолу підвищується у декілька разів відносно таких же продуктів у разі використання вихідних наночастинок ZrO_2. Механізм подібної конверсії етанолу може бути пов’язаним з синергізмом великих іонізаційних втрат Оже електронів та впливом високо реакційних продуктів, які приймають участь у гетерогенному каталізі.