RADIOACTIVE ENHANCEMENT OF METHANOL CONVERSION BY ZINC OXIDE NANOPARTICLES

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(Received August 21, 2011)

On the example of a model system the methanol conversion on activated ZnO nanoparticles is investigated at room temperature. Activation of ZnO nanoparticles is carried out by bremsstrahlung at $E_{\gamma max}$=22 MeV and I=500 μA. The analysis of component-phase structure and state of crystal structure of activated and of original nanoparticles ZnO was carried out by X-ray diffractometry. The transformation have been analyzed and it was shown that there were no essential changes in structure of ZnO: activated nanoparticles of zinc oxide keep monophase state and crystallinity of original state. Measurement of photoluminescence allow to suppose, that the observable increase in intensity of a luminescence in a case γ-activated of ZnO nanoparticles is reached as a result of mutual amplification of action of the highly active oxygen superficial centers and Auger electrons from ^{65}Zn. The analysis of absorption spectra from identified of products of conversion CH_3OH at use of activated and not activated micro- and nano- ZnO as catalysts has shown, that more than 10 times the yield of these products more at use of activated nano- ZnO. In our opinion, explanation of such high activity ZnO nanopowder in methanol conversion are big ionization losses of Auger electrons near a surface ZnO nanoparticles from ^{65}Zn.

PACS: 32.80.Hd; 61.46.+w; 82.30.-b

1. INTRODUCTION

Growth of energy needs in the world, increase in the prices of natural gas causes steadfast attention to potential sources of methane which at present are not used. For example, the amount of methane, which trow out in an atmosphere at a coal mining in the USA (2007) has 9,7% from total of the methane connected to activity of the person [1]. However, according to the published data of U.S. Environment Protection Agency, in last years this situation has improved considerably. Many coal enterprises have found an opportunity for extraction of methane and a delivery of natural gas into pipeline systems. Due to this the annual income has about $97 million. Unfortunately, significant opportunities for use of this resource all over the world including in our country, till now still remaining not realized. For example, at ventilation Donbass mines is annually eject 2.2 b m^3 methane in an atmosphere.

The similar situation is at processing natural fuel (oil, coal, gas). The main opportunities of optimum conditions of full and complex use of hydrocarbonic raw material are processes like cracking, pyrolysis, reactions of oxidation, dehydrogenation, replacements, etc. For example, methane can be transformed by synthesis into gas, acetylene, methanol, formaldehyde, etc. These processes can be carried out under such condition as high and very high temperatures by means of use of complex and expensive catalysts. Therefore economic characteristic of processing of gas are connected with development of new processes at use of moderate temperatures and accessible and inexpensive catalysts. These requirements can be executed at use of hydrocarbonic raw material and improvement of selectivity of conversion transformations.

Now considerable progress already has been achieved at the utilization of methane of mines and significant resource for this process has been spent. New opportunities have opened with development of new types of catalysts on a basis nanomaterials. It is nanostructured ordinary and complex oxides. Now the huge number of works is published (see the review [2]). They are devoted to studying of synthesis and properties of these materials. The highdispersed aluminosilicate [3], metals [4], metal oxides and nanocomposites [2,5-7] can be used as catalysts. ZnO nanoparticles cause special interest because of properties nano- ZnO, they have very various morphology and functionality [8-10].

ZnO is one of the major semiconductor materials which is widely applied in acoustic-, micro-, optoelectronics, by manufacture luminophores, photo cells, gas sensor controls, etc. [8]. Also ZnO is widely used as the effective photocatalyst for recycling and mineralization of ecological contaminant [11]. ZnO is high

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PROBLEMS OF ATOMIC SCIENCE AND TECHNOLOGY, 2011, N5.
Series: Nuclear Physics Investigations (56), p.48-57.

important as it inserts such properties as anisotropy of crystal structure, nonstochiometric composition (a deviation aside of zinc excess) and amphoteric chemical properties [12]. The center of symmetry is absent in crystal ZnO, that is characteristic for display piezo- and pyrogenic properties. ZnO is amphoteric oxide, it is dissolved in alkaline and in the acid medium, water solutions NH_4OH. These properties allow to receive various zinc compounds, including ZnO (at decomposition hydrates or salts of zinc). Methods of synthesis which are based on solutions, allow to make huge amount of matter of zinc compounds [8,12-14]. Also owing to nonstoichiometric composition in ZnO structure the achievement of high concentration of active defects are possible: oxygen vacancies (V_o), interstitial atoms of zinc and vacancies of zinc (V_{Zn}) which allow to receive predicted change of its properties. The deviation from stoichiometry and, hence, concentration of active centres, (own and extrinsic defects) can be changed by variation of conditions of synthesis or termo- a photo- and by radiation treatment.

ZnO nanoparticles have not only the mentioned properties, but also show new properties in area nanoelectronics and piezoelectric nano generators [15,16], etc. They also are used for manufacturing photo-electric converters [17], for chemical sensors, for luminescent materials [18] and for photocatalysts [19-22]. Functional properties ZnO nanoparticles are defined, mainly, by superficial activity of particles and effects quantum confinement. These two factors considerably influence chemical reactivity, electronic and optical properties of zinc oxide and of characteristic of electric transport. The significant part of last researches concentrate on studying of interrelation of the sizes of particles and the active centres on their surface (V_o, V_{Zn}, etc.) with photoluminescent, photocatalytic and other characteristics of ZnO nanoparticles [8,9,23]. On the other hand, many works are devoted to the analysis of the reasons of initiation of electronic, of absorptivity and other new properties into ZnO nanocrystals which are caused by dimensional quantization of spectra electron states, holes and excitons in low-dimensional semi-conductor systems, so-called quantum points. The detailed analysis of effects of spatial restriction (confinement) of elementary excitations in quasi zero-dimensional semiconductor systems and their influence functional characteristics nanomaterial is recently presented in [24].

Recently there are messages about development of various ways of increase of functional efficiency ZnO nanoparticles by methods of physical modification. Annealing at various temperature can influence density of defects in ZnO nanostructure and can change thus its electric and optical properties [25]. In [26] the method of ionic doping ZnO was used for creation of the "diluted" magnetic semiconductors - perspective materials for spintronics. Influence of electronic irradiation on the size of synthesised ZnO nanoparticles and on their absorptive properties were investigated in [23]. Catalytic activity of three-dimensional structures of zinc oxide was studied in [27] by influence of radiation.

Use of accelerating technics and of high-sensitivity nuclear-physical methods of the analysis for ZnO modification practically is not reflected in the published works. The activation ZnO nanoparticles by brake radiation on the electronic accelerator causes increase of their functional efficiency. Apparently this effect can be reached by means of synergistic influence of reactionary oxygen compounds and Auger electron from ^{65}Zn. Surface of ZnO considerably influence radiation-chemical synthesis. Thus participation of ZnO as chemical reagent predetermines absolutely other mechanisms of reactions which distinguish their from similar reactions in the homogeneous medium.

The purpose of the present work consisted in studying of nuclear-chemical processes of conversion transformation of hydrocarbonic compounds due to synergistic actions of Auger electrons and of photochemical reactions on surface of activated ZnO nanoparticles.

2. EXPERIMENT

Micro- and nanopowder of ZnO (Sigma-Aldrich, Product of USA) have been used as original materials. ZnO nanoparticles are stable and have no expressed tendency to agglomeration and formation of clusters, as against others known nanomaterials. Activation of samples was carried out by brake γ-radiation on linear accelerator NSC KIPT with E=22 MeV, I=500 μA. The spectrum of γ-radiation was registered by the Ge(Li)-detector with the energy resolution 3.25 keV (1333 keV). Activation of samples was carried out on air, the temperature of samples was not higher 35°C. The maximal doze of absorption of γ-irradiation (E$_\gamma$=5.2 MeV) in ZnO was equal 20 MGy.

X-Ray Diffraction

X-ray diffractometry has been used for determination of phase structure and the crystallite size of powders ZnO. For these purposes diffractometer DRON-2.0 with monochromatic Cu_{K_α}-source of radiation in a range of angles from 20 up to 120° at speed of scanning of 1°/min, at the voltage 30 kV and the current 10 mA has been used. The standard data (card JCPDS number 36-1451) have been used for comparison with the received results of determination of phase structure, cleanliness of samples according to position of peaks and their relative intensity.

The crystallite size (D) of ZnO powders was calculated according to broadening lines with use of a X-ray method and the software (Fityk). The crystallinity estimation of ZnO powders has been carried out according to the of the area under chosen peaks.

Photoluminescence spectra

Spectra of photoluminescence (PL) activated and non activated micro- and nano- ZnO powders was registered by Hitachi F-4010 spectrofluorophotometer in

the range of wavelengths 350-700 nm. For registration of spectra PL of ZnO powders the Xe lamp with wavelengths of excitation 300 and 350 nm has been used at room temperature. ZnO powder by smooth layer was placed in cylindrical copper flask (d=12 mm) with a mobile bottom wall. The flask has been placed in the cylindrical box and has been pressed by a mobile wall to a quartz window.

Catalytic activity

Activated and nonactivated of ZnO micro- and nanopowders have been used in model system with methanol for analysis of conversion of the last. The weight of ZnO samples amounted 100 mg. Samples have been placed in a solution of methyl alcohol CH_3OH (3 ml) and left at room temperature

(22°C). After 2, 5 and 20 hours of interaction of 0.5 ml from each researched solution has been added to 4 ml CH_3OH and were inserted in quartz flask (1 cm). The centrifugation has been carried out for micropowders zinc oxide within 40 minutes with 18 thousand rpm. The optical density of samples has been measured using CF-46 UV-Visible Spectrophotometer at 200-600 nm.

3. RESULTS AND DISCUSSION

The γ-spectrum nano- ZnO is submitted on Fig.1. γ-spectrum ZnO have γ-lines Zn from reaction $^{66}Zn(\gamma,n)^{65}Zn$ (the most intensive line 1115.5 keV) and also lines of isotope ^{67}Cu ($^{68}Zn(\gamma,p)^{67}Cu$, lines with energy 93, 184.5, 300 keV, accordingly).
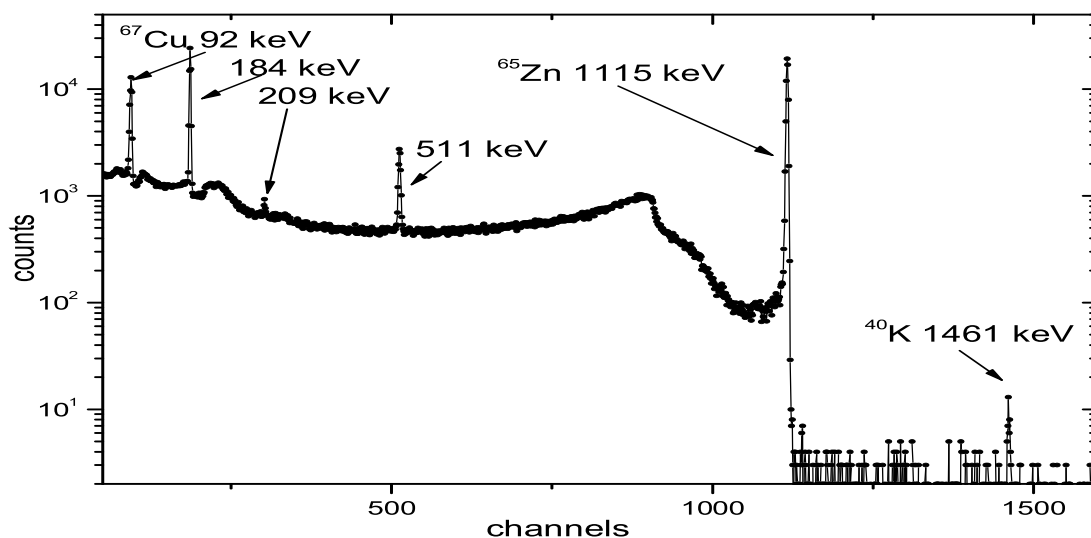
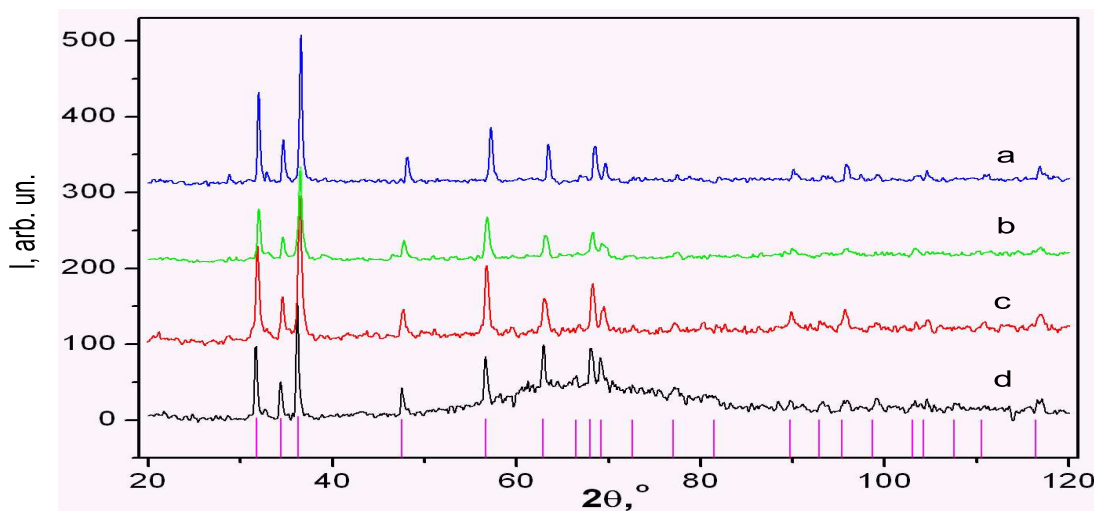

Fig.1. *Gamma spectrum of ZnO nanoparticles*

Fig.2. *Diffractogram of ZnO in an initial condition and after an irradiation up to the absorbed doze 20 MGy, a, b - nonirradiated and irradiated ZnO microparticles, c, d - nonirradiated and irradiated ZnO nanoparticles*

X-ray diffraction patterns of ZnO powders are submitted on Fig.2. The kind of these diffraction patterns is similar for activated and nonactivated samples. The location of interference maxima, their width and intensity show high crystallinity of samples.

All spectra have diffraction maxima that are typical for ZnO monophase (three peaks with Bragg angles). The shape and location of diffraction maxima is characteristic for crystal planes of ZnO with the periods of lattice a=0.325, c=0.521 nm. On axis X we can see the linear diagram of data for ZnO phase (JCPDS, 36-1451) which is completely indexed with experimental data. Any other peaks or extrinsic peaks are not determined, i.e., researched of ZnO powders have high cleanliness. The Zn metal peak at $2\theta=44.5°$ in samples is not detected. The X-ray analysis has determined, that the contents of crystal phase in ZnO powder equals 99%.

X-ray diffraction paterns of activated and nonactivated ZnO samples are similar. Shifts of maxima and distortion of the shape of spectra (see Fig.2, curves a,b,c and d) are not found out. Variation of intensity of lines of some basic reflections have been registered out. These variations are observed more clearly in spectra nano ZnO. Fragments of X-ray diffraction paterns of these samples are registered in a range of angles from 20 up to 80° (Fig.3).
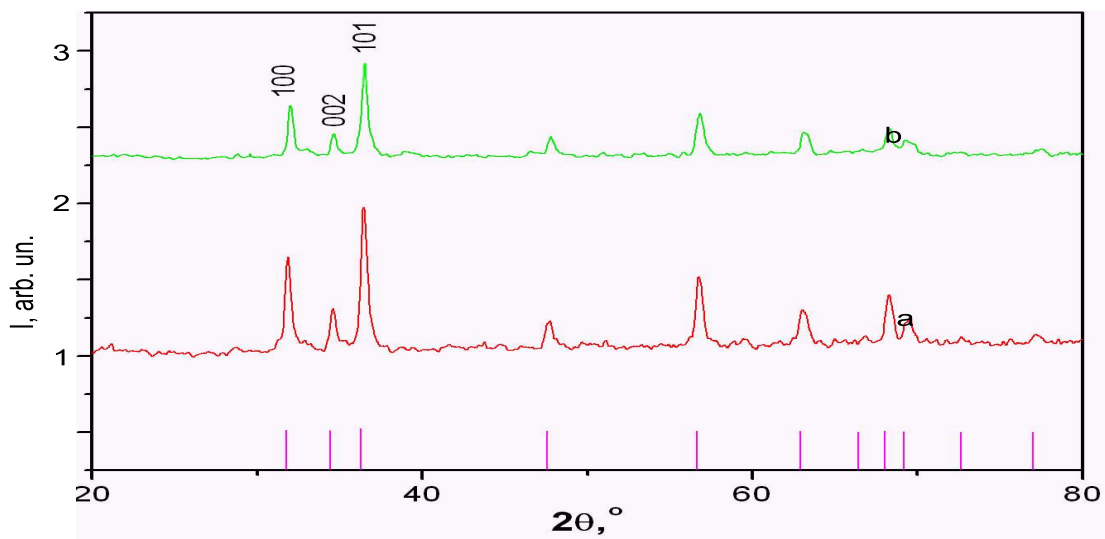

Fig.3. *Diffractogram of ZnO nanoparticles in an initial condition and after an irradiation up to the absorbed doze 20 MGy, a, b, - nonirradiated and irradiated ZnO nanoparticles*

Decrease intensity of all three peaks ($2\theta=31.7°$, $34.4°$, $36.2°$) and peak ($\theta=47.6°$) was detected after γ-activation of ZnO (at $2\theta=34,4°$ in 1.3 times) (see Fig.3). Decrease of intensity of interference lines is as a result of distortion of crystal lattice of ZnO: atoms are displaced from ideal sites. Evaluation of the general widening in spectrum of nano ZnO was carried out under the description of diffraction maxima 100, 002 and 102. Calculation of the sizes of areas of coherent dispersion was carried out under formula Scherrer:

$$L = 0.9\lambda/\beta\cos\theta,$$

where λ - length of a wave of X-ray radiation (0,154056 nm), β - physical widening of diffraction maximum (in terms of a radian), θ - location of diffraction peak. The average size of area of coherent dispersion nano- ZnO equals to 57 nm. The sizes nano- ZnO after γ-activation are determined also. According to ratio Scherrer, the width of peaks is in inverse proportion to the crystallites sizes. The form of the spectra allowed to estimate changes in dispersiveness nano ZnO (see Fig.3). Comparison of peaks at $\theta=31.7°$, $34.4°$ and $36.2°$ of activated and nonactivated samples point out the narrowing and reduction of activated nano- ZnO dispersiveness. Change of area of coherent dispersion has not exceeded 10%. Thus, γ-activation ZnO nanopowder causes some structure defects. In addition, phase composition and crystal structure of a material do not change.

Spectra PL activated and nonactivated micro- and ZnO nanoparticles (350 ... 700 nm) at various modes of photoexcitation (300 and 350 nm) are submitted in Fig.4 (a,b,c,d,e).

ZnO samples show strong and wide signal of PL in a range from 385 up to 600 nm. Two peaks PL (465 and 485 nm) correspond to band edge of free and connected excitons, accordingly [12].
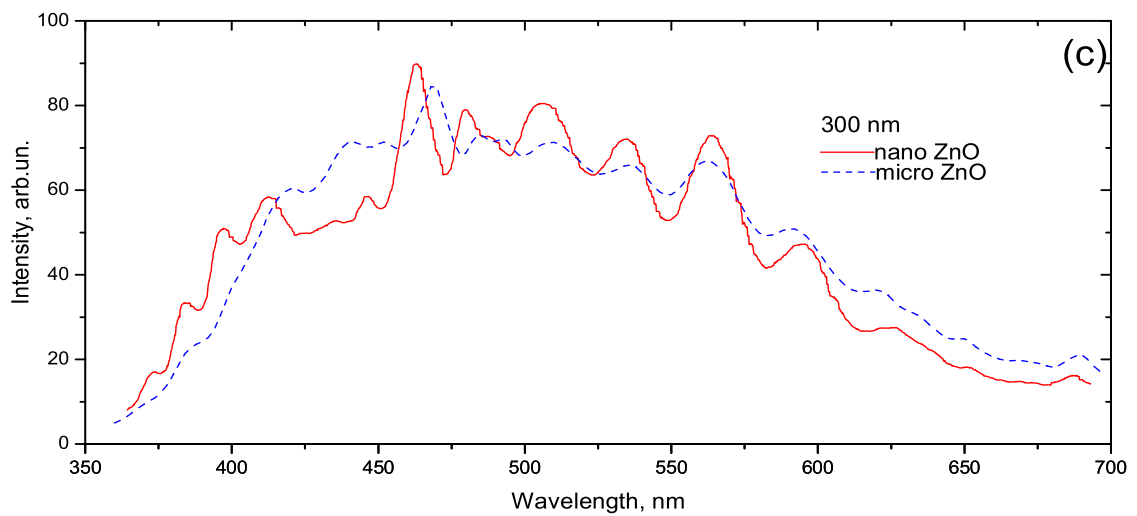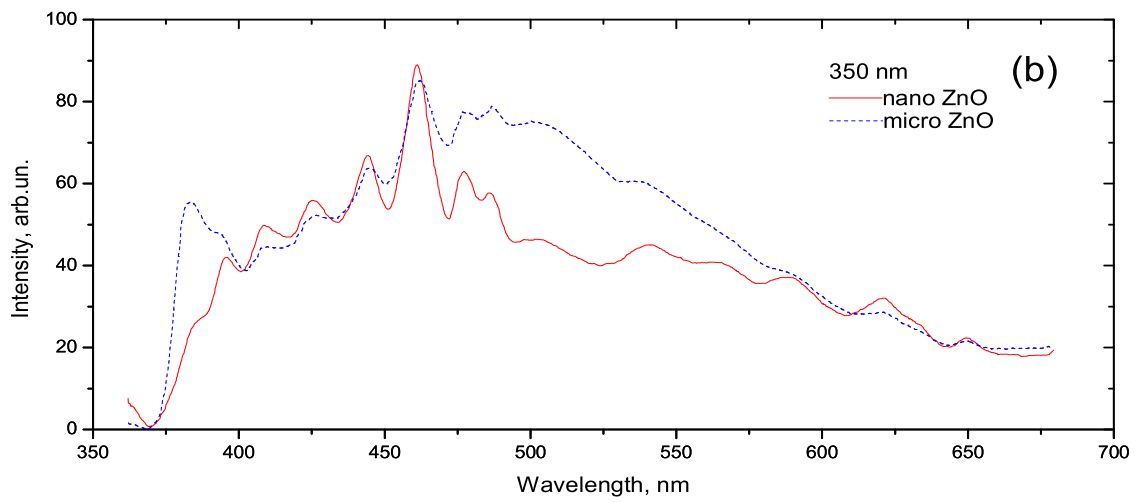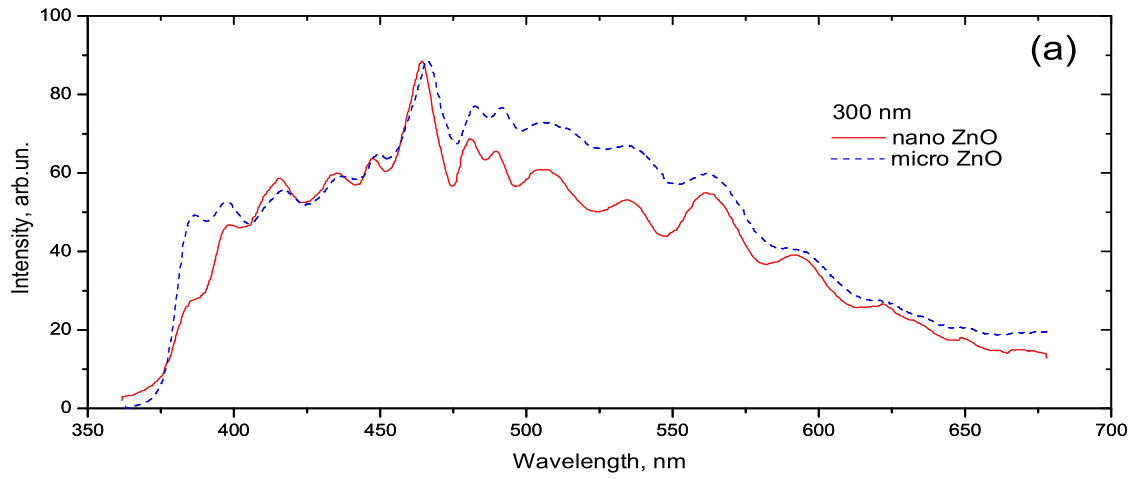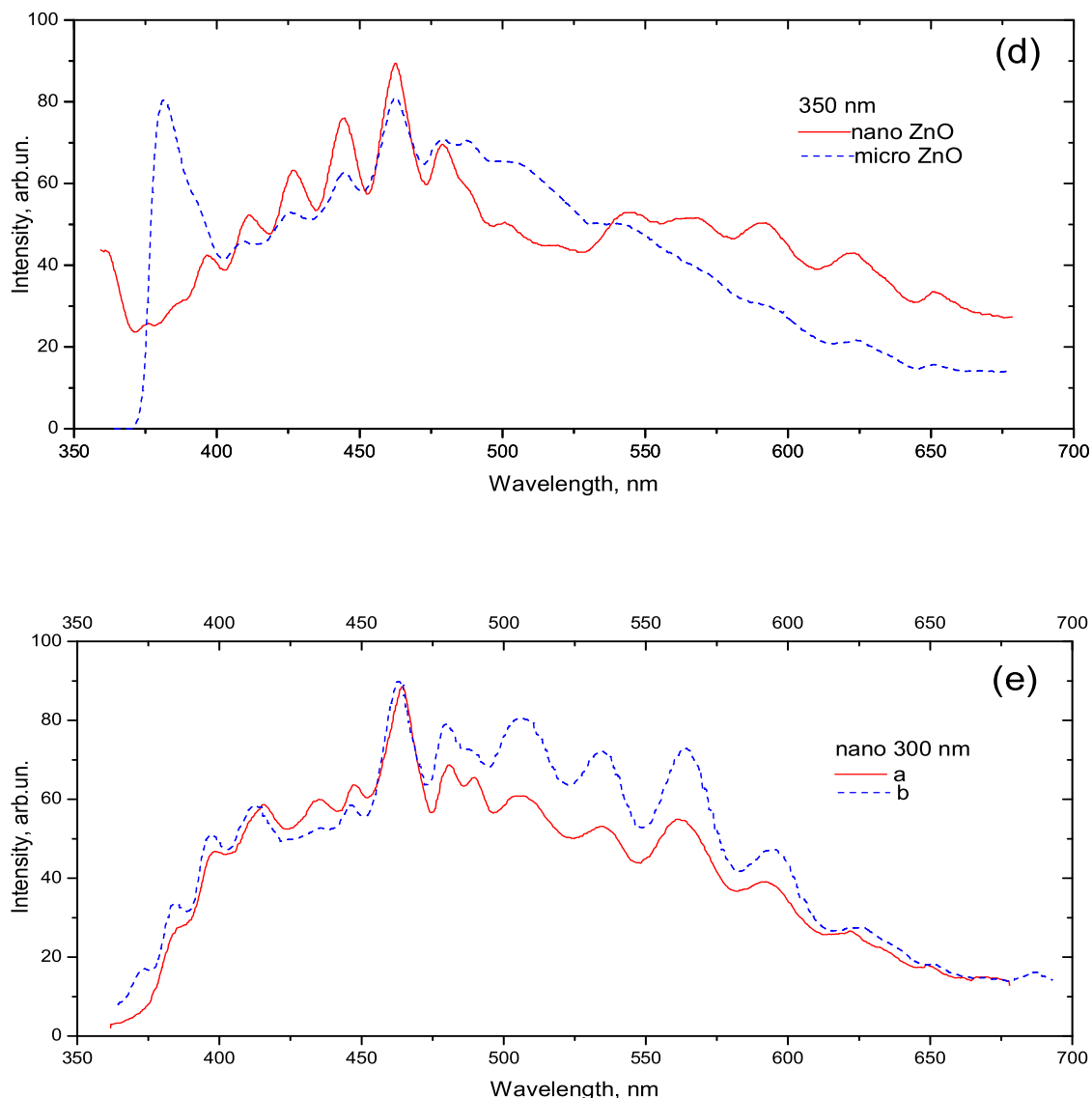
Fig.4. *Photoluminescence spectra of the ZnO micro- and nanoparticles before and after γ-activation in the range 350 - 700 nm with different exciting wavelengths (300 and 350 nm): (a) and (b)- micro- and nanoparticles before γ-activation with exciting λ = 300 and 350 nm, (c) and (d) - micro- and nanoparticles after γ-activation with exciting λ = 300 and 350 nm, (e) nanoparticles before and after γ-activation with exciting λ = 300 nm*

The series of equidistant emission bands in the blue-UV region of spectrum with several weak peaks at 388, 390, 410, 425, 485 nm and a strong band at around 465 nm have been registered. The weak green band (510 ... 550 nm) and very small yellow-orange band (560 ... 620 nm) in visible region of a spectrum have been registered also. Energy of excitation was higher, than energy of ZnO forbidden zone, thus spectra PL were different. Appreciable distinction of the shape and intensity of peaks PL has been noted. Peak of PL of ZnO nanoparticles at ≈465 nm, in comparison with similar peak of microdimensional particles, is more abrupt and more intensive. In ad-

dition, peaks of PL ZnO microparticles in the field of a spectrum 475 ... 550 nm are wide and asymmetric (see Fig.4a, b), apparently, at the expense of two kinds of the emissive centres. For example, two kinds of oxygen states are: oxygen in a crystal lattice and the adsorbed oxygen [12].

Besides, all small peaks in spectrum PL of ZnO nanoparticles, in comparison with microparticles, are more obviously expressed. In PL spectrum of ZnO nanoparticles there are small peaks which confirm surplus of the superficial centres in these samples. Change of wavelength of excitation does not influence location of PL peaks of ZnO particles. Apparently,

on a surface of ZnO particles there are some levels of energy excitons which depend on the superficial centres [9]. These centres appear from oxygen vacancies and the adsorbed oxygen. Essential changes in PL spectra of ZnO powders are marked after γ-activation (see Fig.4c, d, e). These variations are especially appreciable in PL spectra ZnO nanoparticles for wavelength of excitation of 300 nm (see Fig.4e). Intensity of small peaks of green and yellow-orange band in visible region of a spectrum (510 ... 595 nm) has been increased by $\approx$20%.

As is known, that the green emission band corresponds to the singly ionised oxygen vacancy in ZnO, that is F^{+}-centre [12]. Therefore, than the stronger the intensity of the green luminescence, the more singly ionised oxygen vacancies there are. Thus the intensive green band in Fig.4 shows that there is a high concentration of oxygen vacancies in the γ-activated ZnO nanopowders. In general the oxygen vacancies are very active species, easily combined with other groups to become stable, which is responsible for the existence of a certain amount of adsorbed oxygen on the nanoparticle surfaces [28].

For example, under the publication data [12], the local increase of oxygen connected with high adsorption by ability of nanoparticles corresponds to the centre which is responsible for the complex yellow-orange band of a spectrum. The increase in maxima in UV and blue region of a spectrum is marked for γ-activated macro ZnO unlike nanoparticles. Intensity of UV peak (388 nm) increases especially, apparently, at the expense of increase in concentration free electrons from ionisation of small donors [12].

Measurement of PL allow to suppose, that the observable increase in intensity of a luminescence in a case γ-activated of ZnO nanoparticles is reached as a result of mutual amplification of action of the highly active oxygen superficial centers and Auger electrons from ^{65}Zn.

Really, there are lots of oxygen vacancies on the nanoparticle surface, and the particle size is extremely small so that the average distance the over which Auger electrons can move freely is very short. This allow to the oxygen vacancies to easily capture electrons to form excitons.

Catalytic activity of activated and nonactivated micro- and ZnO nanoparticles in model with methanol was evaluated by realization of some reactions with formation of intermediate products. As a rule, these reactions have cyclic character. Determination of composition of products of methanol conversion was carried out by means of measurement of optical density in spectral area of regional absorption, and also in the region of a transparency of nominally pure ZnO. The spectra of absorption (range of 200 ... 600 nm) are characterized by presence of an intensive band in short-wave region of spectrum (Fig.5) of 200 ... 245 nm, which are attributed to absorption dienes [29]. Some wide bands are observed in the field of 300 ... 450 nm. The band with a maximum at 323 nm is connected to absorption dimerized

alkenyl carbenium ions, the band of 360 ... 370 nm is associated with absorption monodienylic carbocations, and the band of 430 nm is associated with absorption small aromatic cations. Such attribution of bands is in the consent with [29].

As shown in Fig.5, activated nano- ZnO have significant influence on catalic activity of the created model. Concentration of all identified components of reaction which was determined by means of optical density has higher of yield of these products concerning other samples.
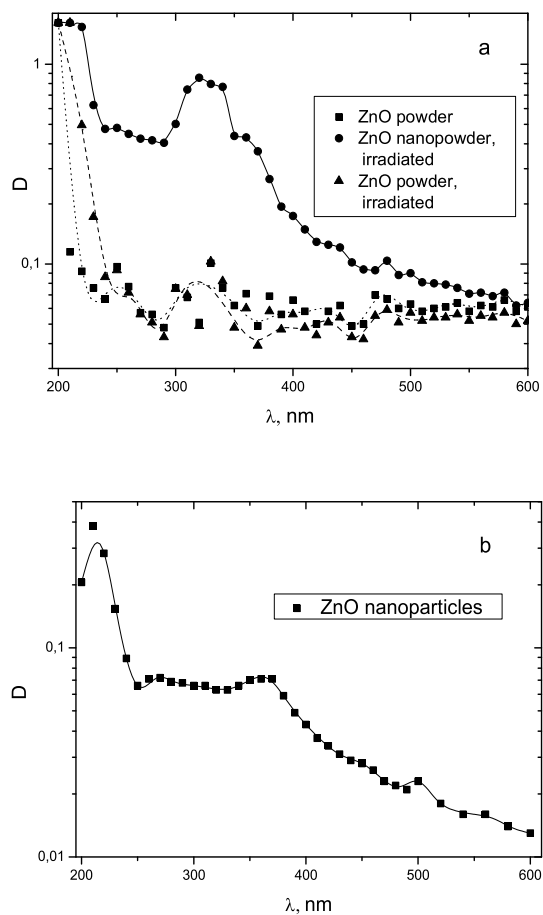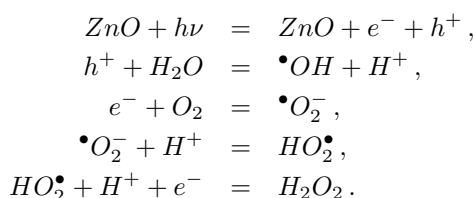

Fig.5. *Transmission UV-VIS spectra of products of conversion transformation of methanol with use as catalysts ZnO micro- and nanopowder: a - ZnO micropowder (nonirradiated and irradiated) and ZnO nanopowder after γ-activation, b - ZnO nanopowder in an original state (conditions of registration of the spectrum are similar Fig.5,a)*

Such high activity nano- ZnO in methanol conversion can be explained by two principal causes. On the one hand, the ability of smaller-size nano- ZnO promote greater levels of reactive oxygen species.

This may occur because for nano-ZnO size decreases the nanocrystal quality is modified as a result of increased Zn ions and oxygen vacancies [30]. These crystal defects lead to a large number of electron-hole pairs (e^{-}, h^{+}), which are typically activated by both UV and visible light. However, for nanoscale ZnO

the holes can split water molecules derived from ZnO into H^+ and OH^-. The resulting electrons react with dissolved oxygen molecules to generate superoxide radical anion ($^\bullet O_2^-$), which together with H^+ to generate $HO_2^\bullet$ radicals. These $HO_2^\bullet$ molecules following encounter with electron produce (HO_2^-), which can react with hydrogen ions to produce hydrogen peroxide (H_2O_2).

$$
\begin{aligned}
ZnO + h\nu &= ZnO + e^- + h^+\,, \\
h^+ + H_2O &= {}^\bullet OH + H^+\,, \\
e^- + O_2 &= {}^\bullet O_2^-\,, \\
{}^\bullet O_2^- + H^+ &= HO_2^\bullet\,, \\
HO_2^\bullet + H^+ + e^- &= H_2O_2\,.
\end{aligned}
$$

On the other hand, it can be big ionization losses of Auger electrons at a surface ZnO nanoparticles from ^{65}Zn isotope.

It is known, that disintegration ^{65}Zn is accompanied by start Auger electrons with E=0.92 keV (I=126,7%) and 7.03 keV (I=47.5%) which have high specific brake ability (10-27 keV/μm). For the given values ionization losses Auger electrons on a surface nanoparticles ZnO high concentration hydrated electrons (e_{aq}^-), hydroxide radicals ($OH^\bullet$) and some H_2O_2 and owing to the photochemical reactions resulting in formation of radicals $HO_2^\bullet$ is realized and, accordingly, H_2O_2 essential strengthening formation of hydrocarbonates from methnol is observed. Obviously, effect of superficial nano- ZnO electronegativity and presence of reactive oxygen species ($OH^\bullet$, H_2O_2, $HO_2^\bullet$) are two important factors which provide the directed development of intensive methanol dehydration and formation of various hydrocarbonic products (diethyl ether, olefin, propane, etc.).

4. CONCLUSIONS

1. The opportunity of use of powerful electron beams for activation nanoparticles zinc oxide by bremsstrahlung on powerfull electronic accelerator NSC KIPT with electron energy 22 MeV and a current 500 μA is shown.

2. The X-ray diffractometry was realized for the comparative analysis of phase structure and a state of crystal structure of ZnO samples before γ-activation. It is shown, that samples initial and after bremsstrahlung influence zinc oxide consist from polycrystalline monophase of zinc oxide and contain diffractional peaks are characteristic for crystal planes of zinc oxide of hexagonal structures with the periods of a lattice a = 0.325 nm, c = 0.521 nm.

3. Spectra of a photoluminescence of activated and not activated micro- and nano- ZnO show the highest concentration of oxygen vacancies of adsorbed oxygen is on a surface of activated nano- ZnO. These variations are most manifestly appeared for wavelength of excitation 300 nm, and also in intensity of all small peaks in visible spectrum (510 ... 595 nm).

4. The analysis of absorption spectra from identified of products of conversion CH_3OH at use of activated and not activated micro- and nano- ZnO as catalysts has shown, that more than 10 times the yield of these products more at use of activated nano- ZnO. The received results confirm effect of mutual amplification of action of highly active oxygenous superficial centers and Auger electrons from ^{65}Zn.

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РАДИОАКТИВНОЕ УСИЛЕНИЕ КОНВЕРСИИ МЕТАНОЛА ПРИ ПОМОЩИ НАНОЧАСТИЦ ОКСИДА ЦИНКА

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На примере модельной системы исследована конверсия метанола на активированных наночастицах ZnO при комнатной температуре. Проведена активация наночастиц оксида цинка тормозным γ-излучением на ускорителе при энергии электронов 22 МэВ и токе 500 мкА. Методом рентгеновской дифрактометрии проведен анализ компонентно-фазового состава и состояния кристаллической структуры активированных и исходных наночастиц ZnO. Проанализированы особенности структурных превращений в γ-активированном ZnO и показано, что в структуре ZnO не произошло существенных изменений: активированные наночастицы оксида цинка сохраняют монофазность и кристалличность исходного

состояния. По проведенным измерениям фотолюминесценции можно предположить, что наблюдаемое увеличение интенсивности свечения в случае γ-активированных наночастиц ZnO достигается в результате взаимного усиления действия высокоактивных кислородных поверхностных центров и Оже-электронов от ^{65}Zn. По результатам изучения конверсионного превращения метанола в присутствии в качестве катализатора наночастиц ZnO показано, что концентрация всех идентифицированных продуктов реакции, судя по их оптической плотности, при использовании нанопорошков ZnO, более чем на порядок превышала выход этих же продуктов в случае неактивированного оксида цинка. Объяснением такой высокой активности нанопорошков ZnO в конверсии метанола являются, на наш взгляд, большие ионизационные потери Оже-электронов у поверхности наночастиц ZnO от ^{65}Zn.

РАДІОАКТИВНЕ ПІДСИЛЕННЯ КОНВЕРСІЇ МЕТАНОЛУ ЗА ДОПОМОГОЮ НАНОЧАСТИНОК ОКСИДУ ЦИНКУ

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На прикладі модельної системи досліджена конверсія метанолу на активованих наночастинках ZnO при кімнатній температурі. Проведена активація наночастинок оксиду цинку гальмівним γ-випромінюванням на прискорювачі при енергії електронів 22 MeB і струмі 500 мкА. Методом рентгенівської дифрактометрії проведено аналіз компонентно-фазового складу і стану кристалічної структури активованих і початкових наночастинок ZnO. Проаналізовано особливості структурних перетворень в γ-активованому ZnO і показано, що в структурі ZnO не сталося істотних змін: активовані наночастинки оксиду цинку зберігають монофазність і кристалічність вихідного стану. По проведеним вимірам фотолюмінесценції можна припустити, що спостережуване збільшення інтенсивності світіння у випадку γ-активованих наночастинок ZnO досягається в результаті взаємного посилення дії високоактивних кисневих поверхневих центрів і Оже-електронів від ^{65}Zn. За результатами вивчення конверсійного перетворення метанолу в присутності в якості каталізатора наночастинок ZnO показано, що концентрація всіх ідентифікованих продуктів реакції, судячи з їхньої оптичної щільності, при використанні нанопорошку ZnO, більш ніж на порядок перевищувала вихід цих продуктів у випадку неактивованого оксиду цинку. Поясненням такої високої активності нанопорошку ZnO у конверсії метанолу є, на наш погляд, більші іонізаційні втрати Оже-електронів біля поверхні наночастинок ZnO від ^{65}Zn.