

Mechanochemical activation influence of the ZnO/CeO₂ compositions on their structural characteristics and photocatalytic activity in safranin T degradation process

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Oxide zinc-cerium system ZnO-CeO₂ was modified by mechanochemical method. The change of dispersion, crystal and surface structure of the compositions is observed after mechanochemical modification. It is found mechanochemical treatment (MChT) accompanied by increasing of photocatalytic activity ZnO/CeO₂ in the photodegradation process of dye solution safranin T. It is shown composition with stoichiometric consist of zinc and cerium oxides has maximal photocatalytic activity. To use UV-spectroscopy it is noted in the mechanoactivation process hypsochromic bands displacement occurs.

1. Introduction

One of the main problems today is regular increase of organic pollutants quantity in air and wastewater that causes worsening of environment ecological state. There are many methods to removal and neutralization air, soil and waterborne pollutants such as settling, sorption, reduction, flotation, ionic exchange, distillation, magnetic method etc. [1, 2] but they are not provide of optimal parameters to clean environment from majority modern organic pollutants. So creation of new environmentally friendly utilization methods of synthetic organic materials is very actual. Now possibility to use materials based on zinc oxide is investigated intensively because ZnO is represented as a low cost alternative to the well-known and studied photocatalyst based on TiO₂ P-25. In this regard complex oxide zinc-cerium compositions are the most promising because the properties of ZnO as a photocatalyst and CeO₂ as a support or promoting to it are combined. It is found that traditional preparing methods of compositions contained a ZnO don't allow to prepare of effective photocatalytic systems. Mechanochemical treatment can be a perspective method to synthesis of complex zinc-cerium mixtures, which permits to obtain systems with nanosized particles.

The aim of the present work is the study of physicochemical properties and photocatalytic activity (the reaction of safranin T photodegradation in aqueous solution) of mechanochemical activated oxide compositions with anionic ratio Zn/Ce = 15 : 85, 25 : 75 and 50 : 50.

2. Experimental

2.1. Preparation of samples

Zinc-cerium compositions with anionic ratio Zn/Ce = 15 : 85, 25 : 75 and 50 : 50 were prepared by mixing ox-

ides of zinc ("pure") and cerium (IV) which was prepared by thermal treatment of ammonia solution Ce(NH₄)₂(NO₃)₆ at 120 °C. Mechanochemical treatment of the samples was conducted in the planetary ball milling Pulverisette-6 in air atmosphere during 4 hours with balls diameter 5 mm and balls to powder mass ratio (BPR) 10 : 1 at rotation frequency 550 rpm.

2.2. Characterization of samples

X-ray diffraction patterns were obtained with CuK α radiation (1.5418 Å) on diffractometer PW 1830 Philips, and the mean crystalline size (L) of the particles was determined from the full width at half maximum (FWHM) and Debye-Scherrer formula, according to equation (1):

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where, $K = 0.9$ is the shape factor, λ is the x-ray wavelength (Cu K α $\lambda \approx 0.154$ nm), β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

The FT-IR spectra were recorded on a spectrometer "Spectrum-One" (Perkin-Elmer Instruments) in air atmosphere at room temperature in transmittance mode (mass ratio sample/KBr = 1 : 20) in the range 4000–400 cm⁻¹.

Differential thermal analysis and thermogravimetry analysis (DTA-TG) were conducted on a DERIVATOGRAF-Q apparatus of F. Paulik, J. Paulik, L. Erdey (MOM, Hungary) system in air atmosphere in the temperature range 20–800 °C at a heating rate of 10 °C/min, sample weight was equal to 200 mg.

Nitrogen sorption was used to determine the specific surface areas of the powders at the temperature of liquid

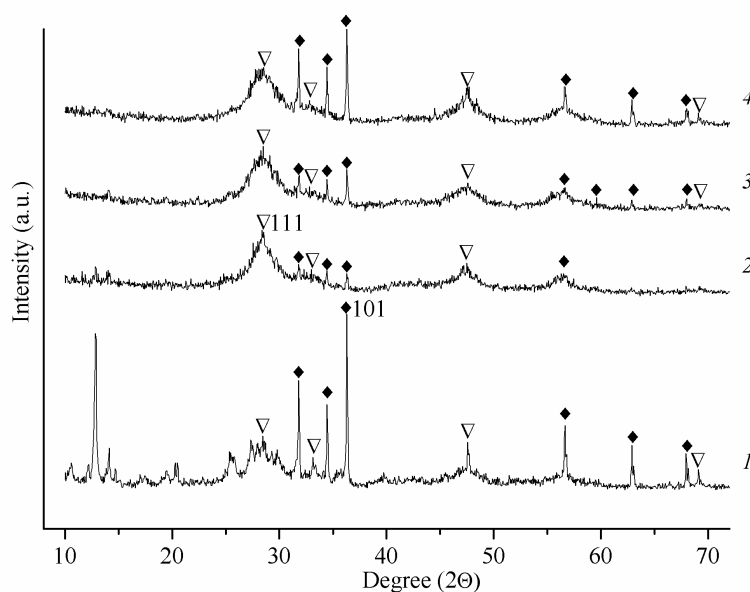


Fig. 1. XRD pattern of ZnO-CeO₂ system: 1 – initial, 2 – 15 : 85, 3 – 25 : 75, 4 – 50 : 50

nitrogen (–196 °C) in a Quantachrome instrument (NOVA-2200 Gas Sorption Analyzer). The distribution of pore volume by samples size was calculated to use of BJH method.

The samples were studied by transmission electron microscopy method after their previous ultrasound dispersing in ethanol to use device JEM 1230 (Jeol).

The photocatalytic activity was determined by measuring the degradation rate of aqueous solution safranin-T dye under visible light irradiation. Reaction was carried out at room temperature to use a Na-lamp (Philips, 70 W, 230 V, 50 Hz). Reaction suspensions were prepared to add the 150 mg photocatalyst into 300 ml of safranin-T solution taken with an initial concentration of 1.3×10^{-5} mol/liter. It was found the adsorption equilibrium achieved during 60 min. Suspension was irradiated under constant stirring. The analytical samples from the suspension were collected at regular intervals of time (30 min) during 5 hours, centrifuged and analyzed by spectrometer UV-2450 Shimadzu. The absorbance of the filtrates was then measured at maximum band ($\lambda = 520$ nm) to determine the safranin T concentration. The decolorization rate constant (Kd) was determined from the equation (2):

$$\ln(D/D_0) = -kt, \quad (2)$$

where D_0 and D are the optical density at times 0 and t , respectively and k is rate constant (time^{-1}). For research of optical properties the method of UV-visible spectroscopy was used. One of the main characteristic of semiconductor material is band gap which can be calculated by the absorp-

tion band edge to use the formula (3):

$$\Delta E = hc/\lambda_0 \quad (3)$$

where h – Planck's constant and is $4.135 \cdot 10^{-15}$ eV·s; c – light rate ($3 \cdot 10^8$ m/s); λ_0 – wavelength that correspond to absorption band edge.

3. Results and discussion

The X-ray diffraction pattern of the Zn-Ce-O system before and after MChT is represented in Fig. 1. According to XRD spectroscopy, initial samples independently on molar ratio ZnO-CeO₂ = 15 : 85, 25 : 75 and 50 : 50 demonstrate the reflexes of ZnO and CeO₂ phases with significant dominance reflex from the plane (101) which is indexed to wurtzite hexagonal phase ZnO with $d = 0.25$ nm and crystallite size $L = 74$ nm. It was established mechanochemical treatment leads to a decrease of intensity of basic reflexes with a simultaneous increase of their width what can indicate a particle size reduction of initial oxides. Also XRD pattern of the modified samples independently on Zn/Ce atomic ratio exhibits the peaks centered at $2\theta = 28.57, 33, 47.6, 69.51^\circ$ which correspond to the (111), (200), (220) and (400) of a cubic fluorite structure of CeO₂, that is in accordance with data [3]. It can be seen from the Fig.1 broad reflex of this phase from the plane of (111) is dominant to composition Zn/Ce = 15 : 85 and 25 : 75. The broadness of the ceria peak indicates crystallite sizes of the CeO₂ particles are of nanometer scale. The activation of composition with stoichiometric content of the oxides is accompanied by reduce of ZnO basic reflex intensity from

Some properties of ZnO-CeO₂ system after MChT

Molar ratio ZnO/CeO ₂	L (nm)	S _{BET} (m ² /g)	Kd (10 ⁻⁵ , s ⁻¹)	λ , nm	E, eV
15 : 85	4	7.4	0.46	371	3.34
25 : 75	5	1.8	0.33	390	3.18
50 : 50	4	2.6	1.50	385	3.22

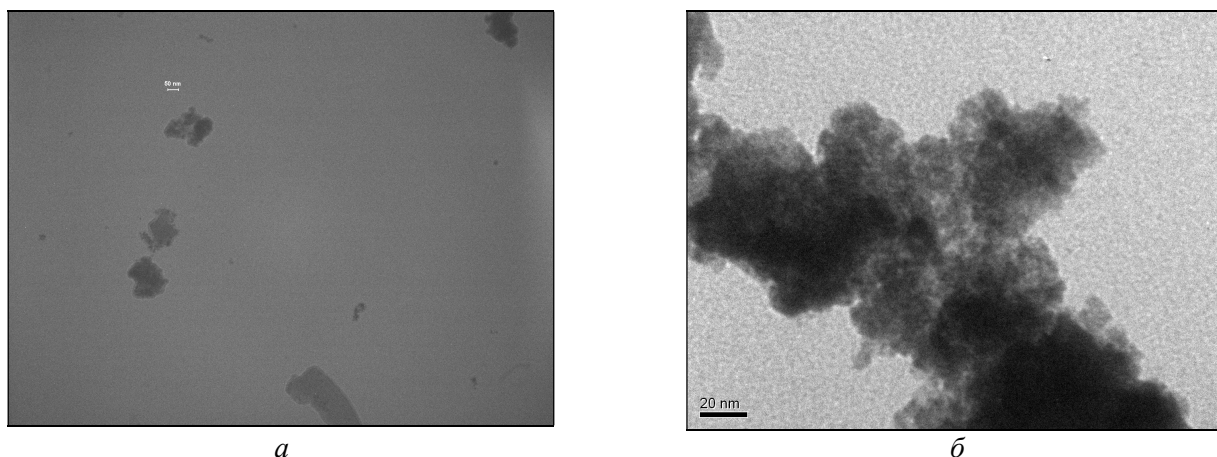


Fig. 2. TEM data for initial sample ZnO-CeO₂ (50 : 50) – *a* and after its treatment – *b*

the plane (101). The average crystallite size of the synthesized materials is presented in Table.

The decrease of particles sizes as result of treatment was confirmed by the TEM study (Fig. 2). The initial composition contains the particles with dimensions from 70 up to 100 nm which correspond to XRD calculation data. After mechanochemical treatment the size of particles essentially decreases and it is possible to observe partially agglomerated particles (which connected with low dimension of the particles and high surface energy) with primary size near to 4–5 nm.

The infrared spectrum (FTIR) of the synthesized Zn-Ce-O system identifies the chemical bonds, as well as functional groups in the compounds. Obtained results show that mechanochemical treatment leads to an increase of the intensity of large broad band in region 3240–3130 cm⁻¹ and bands centered at 1645 cm⁻¹ which are assigned to stretching and bending vibration of H₂O absorbed from the environment, respectively. All initial compositions of oxide zinc-cerium system are characterized by presence of absorption bands at 618, 949, 970, 1130 and 1405 cm⁻¹ which correspond to bending vibrations of Ce-O bond that crystallizes in cubic system and band centered at 484 cm⁻¹ which is responsible for Zn-O bond. It was found that mechanochemical treatment leads to appearance of additional peaks at 645 and 656 cm⁻¹ which assigned to Ce-O bond, to shift of absorption band of Zn-O bond up to 450 cm⁻¹ and very intense band Ce-O bond to high-frequency region (1150 cm⁻¹) that can indicate to change of bond lengths.

The all synthesized Zn/Ce = 15 : 85, 25 : 75 and 50 : 50 powders were subjected to DTA-TG analysis before and after modification. The obtained thermograms of initial samples show two endothermic peaks. The first major low temperature peak in the range 50–190 °C is primarily due to the loss of non-dissociative adsorbed water or water connected with the surface by hydrogen bonding and accompanied by weight loss 6 %. The second minor weight loss peak (2 %) could be due to loss water incorporated in the micropores of mixed oxides. An exothermic peak around

280–340 °C with maximum at 315 °C without a weight loss must be considered to the crystallization of the amorphous phase CeO₂ [4].

Thermal treatment of activated samples exhibits the series of endothermic effects between 50–500 °C that correspond to the water absorbed elimination and each of which is accompanied by loss of weight: around 110–190°C (10 %), 250–330°C (8 %) and in the region 405–480°C (8 %).

Adsorption studies show that all initial compositions were the powders with specific surface area around 13 m²/g and obtained for them nitrogen sorption isotherms are typical for the physical gas sorption by non-porous adsorbents with strong adsorbent/adsorbate interaction (type II classification IUPAC). This means that adsorption in this area is not in the pores, but in voids between loosely packed particles of powders [5]. Also curves of pore size distribution show that the main pores volume of compositions Zn/Ce = 15 : 85, 25 : 75 and 50 : 50 is in region macropores and has a maximum value at 75, 88 and 96 nm, respectively.

It is found mechanochemical activation during 4 hours of all samples leads to decrease of specific surface area about 2–6 times (table) and the change of isotherm types. Obtained isotherms have the hysteresis loop which belongs to H3 type according to classification IUPAC, i.e. pores have the shape of slits which consist from planar particles. For all compositions the curves of distribution of pore volume by size (DPVS) characterized by the presence of two maxima, one of which is in the region micropore (1.5–2 nm). The compositions Zn/Ce = 15 : 85 and 50 : 50 are characterized by the presence of the second peak which belongs to macropores – 90 and 68 nm, respectively. It should be noted for the composition Zn/Ce = 25 : 75 the second maximum is 30 nm, i.e. located in the mesopore region. So, the formation of double porous structure (meso- and microporous) is a result of mechanochemical treatment of non-porous system.

Figure 3 shows the change in absorption spectra for the photocatalytic degradation of safranin-T as a function of irradiation time. Shown, irradiation of aqueous suspension

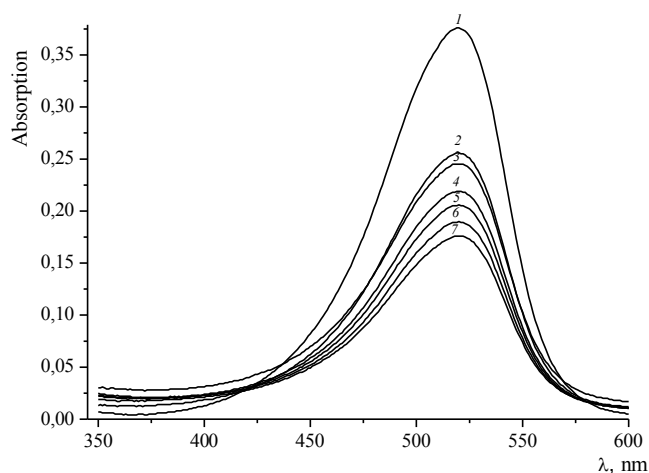
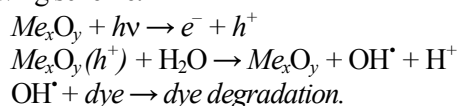


Fig. 3. Electron absorption spectra of aqueous dye solution of safranin T – 1, after dark sorption of Zn/Ce = 50 : 50 during 1 h – 2, after irradiation during 1h – 3, 2h – 4, 3h – 5, 4h – 6, 5h – 7

of safranin-T dye in the presence of ZnO-CeO₂ photocatalysts leads to intensity decrease in maximum absorbance at 520 nm with increase in irradiation time. The photocatalytic degradation/decolorization is initiated by excitation of the semiconductors, followed by the formation of electron-hole pair ($e^- + h^+$) on the surface of catalysts. The generated holes can directly react with dye and result in the direct oxidation of dye to reactive intermediates [6]. Highly reactive hydroxyl radicals formed either by the decomposition of water molecule or by the reaction of the hole with OH⁻ degrade the dye molecules present in the solution by the following scheme:



The hydroxyl radical is an extremely strong nonselective oxidant that leads to the partial or complete mineralization of several organic chemicals.

The degradation rate constants (table) were determined from the slopes of the plots of $\ln D/D_0$ vs time. Accordingly the color removal rate was increased significantly by increasing the amount of ZnO in the system. It is necessary to note that for all initial compositions the values of constant were less than $0.1 \times 10^{-5} \text{ s}^{-1}$. So, the mechanochemical treatment permits to increase of the dye decomposition rate.

Optical properties of nanocompositions in UV- and visible regions of spectrum were studied by UV-visible spectroscopy. The absorption bands edges of initial and modified samples presented on the fig. 4. Specter of initial pattern Zn/Ce = 50 : 50 shows absorption band edge is 393 nm (curve 1) that corresponds to band gap energy of 3.16 eV. For mechanochemical activated samples observed the clear absorption band edges and their hypsochromic shift (“blue shift”) to 371 nm ($E = 3.34 \text{ eV}$). Increase in value of hypsochromic shift of absorption band occurs due to band gap increase of semiconductor as a result of electron excess accumulation on the crystal surface [7, 8].

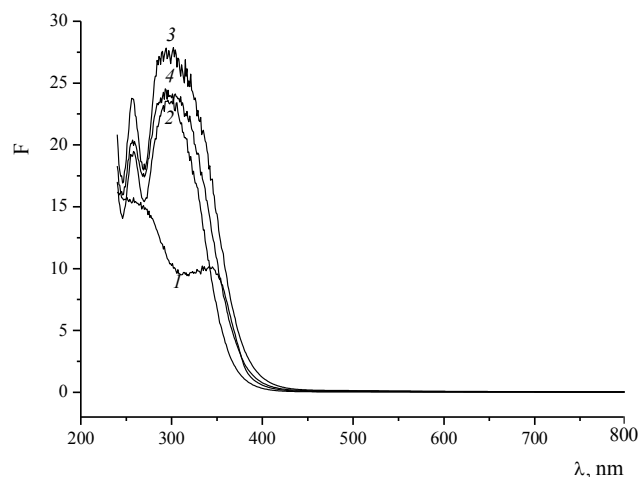


Fig. 4. Electron spectra of initial Zn/Ce = 50 : 50 – 1, modified Zn/Ce = 15 : 85 – 2, Zn/Ce = 25 : 75 – 3 and Zn/Ce = 50 : 50 – 4

From the data of photocatalytic degradation of dye solution and calculations of band gap energy can conclude samples with their lower band gap energy have the better photoactivity under visible light. This enhancement was found due to the presence of CeO₂ nanoparticles which inhibit the charge carrier recombination by electron capture resulting in more holes formation to produce hydroxyl radicals leading to increase in the rate of photodegradation reaction [9–11]. The key factor for the enhancement of photocatalytic activity of the composite oxides is the dispersion of ceria as nanosized crystallites over the ZnO surface.

Thus the above results clearly indicate oxide system ZnO-CeO₂ modified by mechanochemical method shows high photocatalytic activity and efficiency in the degradation of safranin T under visible light that are of great importance for the application of ZnO-CeO₂ as a photocatalyst.

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Вплив механохімічної активації композицій ZnO-CeO₂ на їх структурні характеристики та фотокаталітичну активність в процесі деградації сафраніну Т

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Оксидна цинк-церієва система ZnO-CeO₂ була модифікована методом механохімічної обробки. В процесі механохімічного модифікування спостерігається зміна дисперсності, кристалічної структури та будови поверхні. Встановлено, що механохімічна обробка супроводжується збільшенням фотокаталітичної активності ZnO/CeO₂ в процесі фотодеградації розчину барвника сафраніну Т. Показано, що максимальну фотокаталітичну активність проявляє композиція зі стехіометричним вмістом оксидів цинку та церію. За допомогою УФ-спектроскопії відмічено, що в процесі механоактивації відбувається гіпсохромне зміщення смуг.

Влияние механохимической активации композиций ZnO-CeO₂ на их структурные характеристики и фотокаталитическую активность в процессе деградации сафранина Т

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Оксидная цинк-цериевая система ZnO-CeO₂ была модифицирована методом механохимической обработки. В процессе механоактивации наблюдается изменение дисперсности, кристаллической структуры и строения поверхности. Установлено, что механохимическая обработка сопровождается увеличением фотокаталитической активности ZnO/CeO₂ в процессе фотодеградации раствора красителя сафранина Т. Показано, что максимальную фотокаталитическую активность проявляет композиция со стехиометрическим составом оксидов цинка и церия. С помощью УФ-спектроскопии отмечено, что в процессе механоактивации происходит гипсохромное смещение полос.