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# Investigation of properties of the sonomodified ZnO-CeO<sub>2</sub> system

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#### ABSTRACT

The ultrasonic treatment (UST) influence on properties of the ZnO-CeO<sub>2</sub> system (atomic ratios Zn/Ce = 25:75, 50:50, and 75:25) is studied. A decrease of the size of particles of the oxides, the formation of Zn-Ce-O nanocompositions, and an increase in the specific surface area of the samples are established. It is shown that the sonochemical treatment of oxide zinc-cerium mixtures allows one to increase their photocatalytic activity in the safranin T degradation process. A blue shift of the edge absorption in powder-like samples and an increase in the band gap energy (Eg) are fixed by the UV-vis spectroscopy. The catalytic test of the sonochemically treated ZnO-CeO<sub>2</sub> = 50:50 catalyst in the reaction of ethanol selective oxidation shows a possibility of its use in two processes: i) production of acetaldehyde with high selectivity in a low-temperature reaction (235 °C) with the recycle of the raw material, ethanol, and ii) hydrogen production without CO formation at temperatures more than 300 °C.

#### **KEYWORDS**

Sonochemical treatment; zinc-cerium oxide composites; nanoparticles; photocatalyst; ethanol

# **1. Introduction**

The oxides ZnO and CeO<sub>2</sub> are well-known as two key semiconductors and promising materials which attracted much attention in recent years for their potential application for the environment protection, in catalysis with the use of renewable raw materials, and in the technology of chemical materials [1, 2]. The properties of these individual oxides can be improved by the addition of a second oxide and the creation of a composition of complexes. The various kinds of Zn-Ce-O nanostructures have been synthesized by the use of various traditional methods such as the sputtering, reactive thermal evaporation, chemical spray technique, pulsed laser deposition, metal-organic vapor deposition, electrochemical impregnation, and sol-gel method [3–9]. But these techniques are characterized by the some disadvantages, namely, by the use of metal salts as raw materials, organic solvents, polymers, and surfactants which are potential harmful pollutants. The next step of the preparation of complex oxide compositions is connected with a high-temperature treatment accompanied by the aggregation of particles and an increase of their sizes, and a decrease of the specific surface area. As a result, a decrease of the catalytic activity is observed. So, the creation of new alternative methods of

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preparation of Zn-Ce-O nanoparticles is an actual problem. In [10, 11], the successful use of a mechanochemical treatment for the preparation of Zn-Ce-O nanocompositions was reported, and the obtained mesoporous samples had photocatalytic activity in the dye degradation process.

In this study, the possibility to apply the sonochemistry as a next alternative method to prepare nanocomposites of the  $ZnO-CeO_2$  system (Zn/Ce = 25:75, 50:50, and 75:25) from oxides is examined. The physical-chemical properties of prepared samples and their photocatalytic and catalytic activities toward the decomposition of Safranin T and a partial ethanol oxidation, correspondingly, are studied.

#### 2. Experimental

#### 2.1. Materials and Synthesis

The samples of the zinc-cerium oxide system with molar ratios  $ZnO/CeO_2 = 25:75$ , 50:50, and 75:25 were prepared by the mixing of powders of the oxides ZnO and CeO<sub>2</sub> (all reagents marked "pure"). The sonochemical treatment of the samples (total mass was 10 g) was conducted in an aqueous medium (80 ml) during 1 h in an ultrasonic disperser UZDN operating in the acoustic cavitation mode at a frequency of 22 kHz and an energy load of 3 W/cm<sup>2</sup>. The temperature was stabilized at 80 °C by the circulation of cold water around a reactor. The obtained suspensions were dried at 120 °C in air.

#### 2.2. Methods of analysis

The as-prepared ZnO-CeO<sub>2</sub> powders were examined by the X-ray diffraction analysis on a diffractometer D8 Advance (Bruker), by using the Cu K $\alpha$  radiation with 0.05° step size over the 2 $\Theta$  interval from 10° to 80°. The average size (L) of crystallites in the powders for the most intense reflections was estimated from the Scherrer relation

$$L = \frac{K\lambda}{\beta\cos\Theta},\tag{2.1}$$

where L is the size of crystallites (nm), K = 0.9 is the shape factor, the CuK $\alpha$  wavelength  $\lambda \approx 0.154$  nm,  $\beta$  is the full peak width at half maximum intensity (radians), and  $\Theta$  is the Bragg (diffraction) angle.

The specific surface area ( $S_{BET}$ ) was determined from nitrogen adsorption isotherms measured at 77 K using a Quantachrome NOVA-2200e instrument. Before the measurements, each sample was degassed under a vacuum of  $10^{-5}$  Torr at 453 K during 20 h.

The FT-IR spectra were recorded on a Spectrum-One spectrometer (Perkin-Elmer) in a region 400-4000 cm<sup>-1</sup> (mass ratio sample/KBr = 1:20). Thermogravimetric analysis (TG-DTA) was carried out in the interval 20-900 °C in air with a rate of temperature increase of 10°/min on a Derivatorgaph – Q equipment. The band gap was calculated, by basing on the absorbance spectrum of the samples according to the relation

$$E_{\rm g} = \frac{1240}{\lambda},\tag{2.2}$$

where  $E_g$  is the band gap (eV), and the  $\lambda$  is the wavelength (nm) of the absorption edges in the spectrum. The photocatalytic activity was evaluated by measuring the

degree of safranin T degradation, by using a high-intensity Na-lamp (70 W). The rate constants ( $K_d$ ) were calculated according to the first-order equation for the dye decolorization. UV-vis spectra were recorded from 240 to 800 nm, by using a UV-2450 Shimadzu instrument. The catalytic activity of samples in the ethanol oxidation was tested in a flow fixed-bed stainless microreactor at the atmospheric pressure in the temperature interval 25-350 °C. The initial components and reaction products have been analyzed on-line by the gas chromatography, with flame ionization (FID) and thermal conductivity detectors (TCD). The reaction of ethanol partial oxidation proceeds with main products  $H_2$  and acetic aldehyde and can be presented by the following equations:

$$C_2H_5OH + 1/2O_2 \rightarrow CH_3CHO + H_2O, \qquad (2.3)$$

$$2C_2H_5OH + 3O_2 \rightarrow 4CO + 6H_2,$$
 (2.4)

$$C_2H_5OH + 1.5O_2 \rightarrow 3H_2 + 2CO_2.$$
 (2.5)

The ethanol conversion, acetaldehyde selectivity, and its yield were calculated according to the formulas

$$X_{EtOH} = \frac{\left(C_{EtOH}(in) - C_{EtOH}(out)\right)}{C_{EtOH}(in)} \times 100\%,$$
(2.6)

$$S_{Ac} = \frac{C_{Ac}}{\left(C_{EtOH}(in) - C_{EtOH}(out)\right)} \times 100\%, \qquad (2.7)$$

$$Y_{Ac} = \frac{X_{EtOH}S_{Ac}}{100}.$$
(2.8)

Here,  $X_{EtOH}$  – ethanol conversion %,  $S_{Ac}$  – selectivity of acetaldehyde %,  $Y_{Ac}$  – acetaldehyde yield %,  $C_{EtOH(in)}$  – initial ethanol molar concentration,  $C_{EtOH}$  (out) – ethanol molar concentration after a reactor, and  $C_{Ac}$  – acetaldehyde molar concentration after a reactor.

# 3. Results and Discussion

The XRD patterns of ZnO-CeO<sub>2</sub> composites treated by ultrasound are shown in Fig. 1. It can be seen that the diffractograms of the initial and modified samples show ZnO peaks, which are indexed to the hexagonal wurtzite phase (PDF card No. 74-534), and reflections of CeO<sub>2</sub>, which correspond to the cubic fluorite structure of ceria (JCPDS No. 34-0394) with maximum reflex from plane (111). It is found that the ultrasonic treatment leads to an insignificant decrease of the intensity of basic reflexes without change of the dominant reflex, which can be connected with the isotropic deformation of CeO<sub>2</sub> and indicate a size reduction of particles of the initial oxides.

The calculations of the size (L) of particles demonstrate their decrease by 2-3 times after the treatment in comparison with initial mixture samples and individual oxides (Table 1). These results well agree with adsorption data, which show an increase of the specific surface area ( $S_{BeT}$ ). The change of porous structure parameters and total pore volume ( $V_{\Sigma}$ ) (Table 1) after the treatment were observed as well.

The FTIR spectra of ZnO-CeO<sub>2</sub> compositions after the ultrasonic treatment are shown in Fig. 2. It is established that, after UST the intensities of stretching and bending vibrations of the adsorbed water molecules (at 3200 and  $1692 \text{ cm}^{-1}$ , respectively)



Figure 1. XRD pattern of ZnO-CeO2 compositions: initial 50:50 – a, after UST 25:75 – b, 50:50 – c, 75:25 – d

| Sample           | L, nm | S <sub>Ber</sub> , m <sup>2</sup> /g | $V_{\Sigma} \times 10^{-2}$ , cm <sup>3</sup> /g |
|------------------|-------|--------------------------------------|--|
| ZnO              | 80    | 4                                    | 8  |
| CeO <sub>2</sub> | 57    | 3                                    | 5  |
| 50:50 initial    | 60    | 2                                    | 1  |
| 25:75            | 32    | 3                                    | 4  |
| 50:50            | 29    | 4                                    | 5  |
| 75:25            | 21    | 8                                    | 6  |

Table 1. Size of crystallites and the porous structure of samples after UST

L – average crystallite size; S<sub>Ber</sub> – specific surface area, and V<sub> $\Sigma$ </sub> – total pore volume of powders, respectively.

decrease, which is caused by a decrease of the content of surface groups  $OH^-$  as absorption centers. The initial sample Zn/Ce = 50:50 (Fig. 2, a) demonstrates a peak at  $613 \text{ cm}^{-1}$ , which is attributed to the characteristic absorption band of the ZnO bond, and a broad peak at  $1195 \text{ cm}^{-1}$ , which corresponds to the Ce-O-Ce bond. It is found that the sonochemical modification accompanied by a shift of these absorption bands in the short-wave region up to 609 and  $1177 \text{ cm}^{-1}$ , respectively, and the appearance of the absorption band of Ce-o bonds at  $970 \text{ cm}^{-1}$ , which is caused by the Ce-o bond redistribution as result of the treatment (Fig. 2, b-d).

The study of the thermal stability of oxide Zn/Ce composites show that the DTAcurve of the initial sample Zn/Ce = 25:75 has two endothermic effects, which correspond to the water elimination process - at 70-180 °C and 190-240 °C with a total weight loss of 8-10%. It is found that the sonochemical treatment leads to changes in DTA-TG curves. So, for the sample Zn/Mo = 25:75, the presence of two thermal effects on the DTA-curve is observed. The first endothermic peak, which corresponds to the water desorption, is observed at 95-210 °C and its accompanied by an insignificant weight loss (0.2%). The second exothermic effect at  $252-340^{\circ}$ C, which can be attributed to the crystallization process of  $CeO_2$ , and some loss of weight (0.5%) are observed. The thermal treatment of the sample Zn/Ce = 50:50 after the ultrasound modification shows that the dehydration process proceeds by one step before 163°C in contrast to the initial composition, where this process proceeds in two stages in the interval 70-240 °C. These changes can be related to the formation of a homogeneous porous structure of the sample after the treatment. In addition, two exothermic effects at 460 and 660°C, whose presence is associated with the Zno crystallization process and polymorphous transformations, respectively (without weight loss) are observed on the DTA-curve. Similar changes are characteristic of the sample Zn/Ce = 75:25.

In order to evaluate the oxide Zn/Ce system photocatalytic activities before and after UST, the degradation of dye Safranin T in an aqueous solution are studied. The results obtained at the visible light irradiation of a dye solution in the presence of sonochemically treated Zn-Ce-O photocatalysts demonstrate a decrease of the absorption maximum intensity at 520 nm, which indicates an increase of the photocatalytic activity of treated samples in comparison with the initial composition. The results of calculations of the degradation rate constants presented in Table 2 confirm this fact.

The optical properties of compositions, which were studied by the UV-vis spectroscopy, show that the absorption edge of the initial sample Zn/Ce = 50:50 is at 396 nm corresponding to the band gap energy equal to 3.13 eV. After the sonochemical treatment of samples, a blue shift of the absorption edge is observed, and the calculated band gap energies for treated samples have the values slightly lower in comparison with



Figure 2. FTIR spectra of the initial sample Zn/Ce = 50:50 - a, and compositions Zn/Ce = 25:75 - b, 50:50 - c, 75:25 - d after UST

Table 2. Results of optical and photocatalytic researches of the sonomodified ZnO-CeO<sub>2</sub> system

| Atomic ratio Zn/Ce | λ, nm | E <sub>g</sub> , eV | K <sub>d</sub> ×10 <sup>4</sup> , c <sup>-1</sup> |
|--------------------|-------|---------------------|---|
| ZnO                | 382   | 3.24                | 2.2   |
| CeO <sub>2</sub>   | 392   | 3.16                | 0.1   |
| initial (50:50)    | 396   | 3.13                | 0.2   |
| 25:75              | 393   | 3.15                | 1.4   |
| 50:50              | 392   | 3.16                | 3.3   |
| 75:25              | 391   | 3.17                | 3.7   |

 $\lambda$  - absorption edge, E<sub>q</sub> – band gap energy, K<sub>d</sub> - degradation rate constant of a safranin T water solution

the band gap value of pure zinc oxide (Table 2). These values are close to  $E_g$  of CeO<sub>2</sub>. The data presented in Table 2 show that, in the series Zn/Ce = 25:75, 50:50, 75:25 of treated samples, an insignificant increase of the band gap energy from 3.13 up to 3.17 is observed, which can indicate the quantum-dimensional effect of ZnO. We observe that a shift of the absorption band in the short-wave region and an increase of the band-gap of composites proceed with an increase of the zinc oxide content in a mixture. Such changes can be connected with the oxide dispersion, accumulation of an electronic density excess on the crystal surface, and formation of hydrogen bonds with solvent molecules as a result of the treatment in a water solution.

The sample ZnO-CeO<sub>2</sub> = 50:50 after the ultrasonic treatment was tested in the partial oxidation of ethanol (POE). It is well known that hydrogen may be generated from ethanol by different ways, namely, by the steam reforming (SRE), partial oxidation (POE), and oxidative steam reforming (OSRE). Generally, Ce- and Ni-containing catalysts are used for the H<sub>2</sub> production from ethanol [12–14]. SRE is a highly endothermic reaction. Therefore, the high operation temperatures are used, and an inert medium should be introduced, which leads to high capital and operation costs, as well as to problems with the environmental protection. An alternative approach is the partial oxidation of ethanol (POE), where the reaction can be realized at relatively lower temperatures. But it is worth to note that, before the POE reaction, the catalysts must be



Figure 3. Temperature dependence of the ethanol conversion and selectivity of the formation of reaction products on the sonomodified ZnO-CeO2 = 50:50 catalyst

previously reduced, and the in situ treatment by  $H_2$  should be used [14]. In our case for the ZnO-CeO<sub>2</sub> catalyst prepared by the sonochemistry, any preliminary  $H_2$ -treatment was used before the catalytic POE reaction.

The data presented in Fig. 3 show the ethanol conversion and the selectivity concerning the products in the temperature interval 235-300 °C on the  $\text{ZnO-CeO}_2 = 50:50$  sample after the ultrasonic treatment. The obtained results demonstrate that the main product of the POE reaction at 235 °C is acetic aldehyde, which is formed with a selectivity equal to 96%. Its amount is reduced, as the temperature increases, and its complete disappearance occurs at 300 °C. At the reaction temperature equal to 270 °C, the appearance of H<sub>2</sub> was observed, and its amount increases with the temperature.

So, the sample obtained by the sonochemical treatment demonstrates a possibility of its use in two processes on the base of a renewable raw material such as ethanol. The first process is the preparation of acetaldehyde with the high selectivity at a low ethanol conversion and with the possibility of the raw ethanol recycling, which proceeds at a low temperature of the reaction.

Second, the hydrogen production at a medium temperature with essential high selectivity and the possibility to use this hydrogen directly in fuel cells are related to the absence of CO in reaction products. The possibility of the stable operation of the catalyst during 18 h at 300 °C without changes in the distribution of reaction products is shown.

#### 4. Conclusion

A decrease of the size of particles of the initial oxides, increase of the specific surface area, and the formation of Zn-Ce-O nanocomposites are observed as a result of the ultrasonic treatment of ZnO-CeO<sub>2</sub> powder mixtures. The prepared nanostructured ZnO-CeO<sub>2</sub> compositions possess a higher photocatalytic activity than the initial sample in the reaction of degradation of Safranin T dye in a water solution. The new by-functional catalyst for the renewable raw material (ethanol) use is obtained by UST of this

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composition. At a low reaction temperature, this catalyst allows one to obtain acetaldehyde with high selectivity, and the process with a recycle of the raw material can be realized. Practically pure hydrogen (without CO traces) from ethanol (at its 100-% conversion) in air can be obtained at reaction temperatures more than 300 °C, which can be directly used in fuel cells. These catalytic results were obtained without any additional operation (catalyst pretreatment by H<sub>2</sub>), which is necessary, according to literature data, for the activation of the ZnO-CeO<sub>2</sub> system.

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