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NANOSIZED Cu/ ZnO CATALYTIC SYSTEMS – CHARACTERIZATION AND ACTIVITY TOWARD OZONE DECOMPOSITION

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Abstract

Nanosized doped with low concentrations of copper ZnO samples were synthesized using precipitation method. The samples were characterized by XRD, AAS, IR, XPS and EPR, the specific surface area was determined by BET. The X-ray diffraction analysis of the samples give evidence for the formation of wurtzite phase ZnO. The determined dopant contents in the investigated samples are 0.010 and 0.034 wt. %. The calculated mean size of the crystallites is in the range of 40 ÷ 43 nm. The presence of Cu^{2+} ions is confirmed by EPR analysis. XPS investigations show that probably the ZnO is in the oxygen deficient state. The catalytic activity of the samples with the time for ozone decomposition was investigated and moderate deactivation was observed. The increase of the Cu content in ZnO samples leads to enhancement of their catalytic activities.

Key words: *ZnO catalysts, copper doping, ozone decomposition.*

1.IINTRODUCTION

Ozone is widely used in different industrial and environmental processes such as semiconductor manufacturing, deodorization, disinfection and water treatment. Ozone is an environmentally friendly oxidant since it decomposes to O_2 without producing self-derived byproducts in the oxidation reactions, in contrast with organoperoxides. The reactivity of ozone toward organic compounds has been extensively studied both in the liquid phase and in the gaseous phase (Einaga, 2005 and Asgari, 2013). Heterogeneous catalytic ozonation has received increasing attention in recent years due to its potentially higher effectiveness in the degradation of different organic compounds (Stoyanova, 2006).

Nanomaterials have been widely applied as perspective materials for the elimination of pollutants in air and water purification. The preparation of nanoscale materials with specific structural features has received growing interests in the last years, due to their novel functional and size-dependent properties (Xu, 2013). ZnO is considered to be one of the most important oxide materials because of its unique features and wide range of technological applications, it is cheap and environmentally friendly. Due to these properties, it has found potential applications in ozone decomposition (Singhal, 2012). The catalytic activity of nanostructure ZnO sample for the ozone decomposition was investigated by (Xu, 2013). Dong, 2011 has synthesized ZnO powder with 200 nm crystallites sizes catalyst for degradation

of phenol in presence of ozone and that resulted in sizably higher (23.7%) efficiency compared to non catalytic ozonation. Nanosized ZnO catalysts were used effectively for degradation of dichloroacetic acid (Zhai, 2010) and para-Chlorobenzoic acid in the presence of ozone which enhanced their decomposition rate (Jung, 2006). Removal of 2,4,6-trichlorophenol (TCP) from water has been accomplished through zinc oxide (ZnO) catalytic ozonation (Huang, 2005). The combined use of O_3 and ZnO catalyst leads to 99.8% of TCP conversion. The author concluded that the nano-ZnO particles have unique catalytic activity different from micro-ZnO or submicro-ZnO particles.

The aim of the present paper is to investigate the texture and the structure of nanosized Cu doped ZnO synthesized from oxalate precursor and to study its catalytic activity towards ozone decomposition.

2. MATERIALS AND METHODS

2.1 Synthesis of the samples

The samples of copper-doped ZnC_2O_4 were obtained using precipitation synthesis method. The experimental conditions were: temperature T = 25.0 ± 0.5˚C; initial acidity of the system pH = 3.0. $ZnC_2O_4.2H_2O$ was carried out as equal volumes (0.150 cm^3) of the initial $ZnSO_4$, $K_2C_2O_4$ and 0.25 M $CuSO_4$ solutions were poured out simultaneously into the reaction vessel upon continuous stirring. The obtained white precipitate was filtered, washed twice and submitted to ultrasound. In order to prepare copper-doped ZnO the synthesised oxalate precursors were calcined for 1 h in air at 470˚C.

Designation of the obtained samples:

0.004%Cu/$ZnC_2O_4{\cdot}2H_2O$ – sample with 0.004 wt% content of copper;

0.015%Cu/$ZnC_2O_4{\cdot}2H_2O$ – sample with 0.015 wt% content of copper;

0.010%Cu/ZnO– sample with 0.010 wt% content of copper;

0.034%Cu/ZnO– sample with 0.034 wt% content of copper;

2.2 AAS analysis

hemical composition of the samples was determined using Atomic Absorption Analysis FAAS - SOLAAR M5 spectrometer. For preparation of standard solutions standards produced by “Titrisol” (Merck) – Germany were used, the concentration of reference metal content was 1000 ppm.

2.3 X-ray diffraction (XRD) analysis

The X-ray diffraction (XRD) analysis was carried out on a Siemens powder diffractometer model D500 using CuKα radiation within a 2θ angle of diffraction interval of 10-60 degrees. The identification of the phases was done by means of the JCPDS database of the International Center of Powder Diffraction Data.

2.4 X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) studies were performed in a VG Escalab II electron spectrometer using AlKα radiation with energy of 1486.6eV. The residual gas pressure in the analysis chamber was 10^{-7} Pa.

2.5 Infrared Spectroscopy (IR)

The IR spectra were recorded in the range of 4000 to 400 cm^{-1} on a IFS 25 spectrometer (Brűker) with resolution of less than 2 cm^{-1}. The samples were prepared as tablets from KBr, with content of investigated samples.

2.6 Adsorption – texture analysis

The determination of the specific surface area and the characterization of the porous texture of the samples was carried out by nitrogen adsorption at the boiling temperature of liquid nitrogen (77.4 K) using a conventional volume-measuring apparatus. Before the measurements, the samples were degassed at 423 K until the residual pressure became lower than $1.333x10^{-2}$ Pa. The nitrogen (N_2) adsorption-desorption isotherms were used to calculate the specific surface area (A_{BET}) based on the BET equation. The total pore volume (V_t) was estimated in accordance with the Gurvich rule at a relative pressure (P/P_o) 0.95.

2.7 Catalyst activity measurements.

The catalytic activity of the sample in the reaction of ozone decomposition was investigated in a plug flow reactor system permitting isothermal operation. The reactor was made of glass and had an inner diameter of 4.1 mm. The catalyst particle sizes were 0.25–0.6 mm. The volume rate was 120 000 h^{-1}. Ozone was synthesized in a flow of oxygen (99.7%) and dried with silica gel using an ozone generator with silent discharge and coaxial electrodes. The inlet concentration of ozone varied from 13 to 15 g/m^3 (0.25–0.3 mol/m^3). Ozone concentration was measured by an Ozomat GM (Anseros, Germany) ozone analyser with a resolution of ± 0.1 g/m^3.

3. RESULTS AND DISCUSSION

In Table 1 are presented the contents and specific surface areas for the investigated precursors and thermally decomposed samples. Two ZnO catalysts with copper content up to 0.03 wt. % have been prepared. The BET-determined surface area of the used precursors is not high and is between 1 ÷ 1.4 m^2/g while the specific surface areas of the obtained oxides increase significantly and reach 24 ÷ 25 m^2/g. The reasonable explanation for such high specific area is the decomposition process which proceeds by releasing of higher quantity gasses in comparison with the decomposition process taking place when other precursors as carbonates nitrates or hydroxides were used.

Table 1. Dopant content and specific surface area (A_{BET}) of Cu-doped $ZnC_2O_4{\cdot}2H_2O$ and ZnO

Samples	**Copper content wt, %**	**A_{BET}, m^2/g**
0.004%Cu/$ZnC_2O_4.2H_2O$	0.004	1.0
0.015%Cu/$ZnC_2O_4.2H_2O$	0.015	1.4
0.010%Cu/ZnO	0.010	23.7
0.034%Cu/ZnO	0.034	24.9

XRD patterns for the used precursors are shown in Figure 1. The results had confirmed the formation of monoclinic $ZnC_2O_4.2H_2O$ phase in accordance with (JCPDS 25-1029). XRD patterns for the

obtained 0.010%Cu/ZnO and 0.034%Cu/ZnO oxides (see Figure 2) show that hexagonal ZnO structure in accordance with (JCPDS 36-1451) was formed. The comparison of the parameters of the cell between precursors and oxides are given in Table 2. It is obvious that the Cu doping lead to decrease of the cell parameters b, c and β as well as the crystallites sizes. The obtained values of the cell parameters for the synthesized ZnO samples are close to the values for the standard ZnO. The investigated precursors and thermal decomposed oxides have nanocrystal structure.

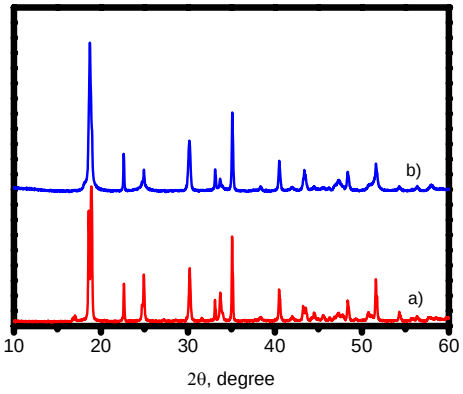


Figure 1. X-ray diffractograms of: a) 0.004%Cu/$ZnC_2O_4 \cdot 2H_2O$; b) 0.015%Cu/$ZnC_2O_4 \cdot 2H_2O$

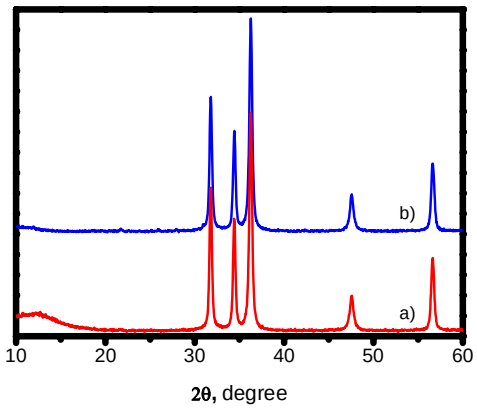


Figure 2. X-ray diffractograms of: a) 0.010%Cu/ZnO b) 0.034%Cu/ZnO

Table 2. Parameters of the crystal lattice and crystallites size of Cu-doped $ZnC_2O_4 \cdot 2H_2O$ and ZnO

Samples	Lattice constants a,b,c (Å) and β (degr)				Size, nm
	a ± 0.0002	**b ± 0.0002**	**c ± 0.0002**	**β ± 0.15**	
Ref. JCPDS 25-1029	11.8040	5.4030	9.9210	127.7	
0.004%Cu/$ZnC_2O_4 \cdot 2H_2O$	11.8373	5.4007	9.9019	127.6	57
0.015%Cu/$ZnC_2O_4 \cdot 2H_2O$	11.8168	5.3923	9.8506	127.1	35
Ref. JCPDS 36-1451	3.2490		5.2060		
0.010%Cu/ZnO	3.2501		5.2082		40
0.034%Cu/ZnO	3.2508		5.2096		43

The IR spectroscopic characterization has been performed for the Cu doped ZnO samples and the results are presented in Figure 3. The broad band has been observed at around 490cm^{-1} for the pure ZnO corresponding to the formation of Zn–O bond (Singhal, 2012) and wide band around 1404 cm^{-1} (Barick, 2010) and 1562cm^{-1} (Liu, 2008) indicates the formation of ZnO.

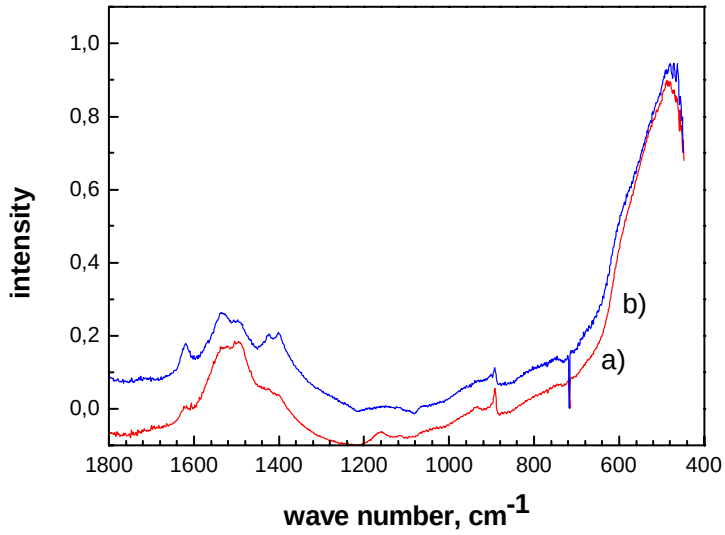


Figure 3. IR-spectroscopy of a) 0.034%Cu/ZnO; b) 0.010%Cu/ZnO

The copper ion distribution in the doped oxalate samples was studied by EPR spectroscopy and the result is shown in Figure 4. The presence of isolated copper ions has been observed, which is an indication for the uniform dispersion of Cu^{2+} in the used precursors.

The EPR results concerning Cu doped ZnO obtained by decomposition of oxalate precursors are shown in Figure 5. The weak signals belonging to Cu^{2+} ions (Elilarassi, 2010) were registered. The copper ions in 0.034%Cu/ZnO are isolated while in 0.010%Cu/ZnO they form clusters. It is worth to mention here that the intensity of EPR signals is independent from the dopant concentration (that statement is a result of investigation of more samples than the mentioned ones in the article). Most probably this is due to the fact that the large amounts of copper ions are not detected by EPR, because of the possible formation of magnetic system. Other explanation could be the substitution of Zn^{2+} by Cu^{+} ions (Bahsi, 2007 and Feng, 2004). Cu^{+} ions have diamagnetic properties and could not be detected by EPR. This model was proposed after investigation of electrical properties of pure and copper doped ZnO.

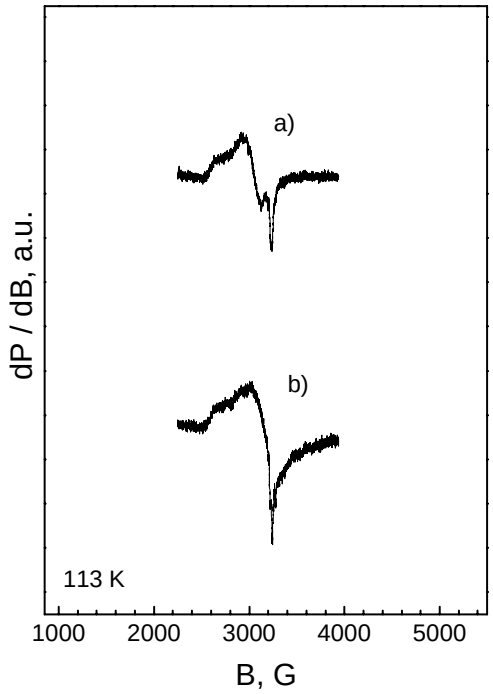


Figure 4. EPR spectra of: a) 0.004%Cu/$ZnC_2O_4 \cdot 2H_2O$; b) 0.015%Cu/$ZnC_2O_4 \cdot 2H_2O$

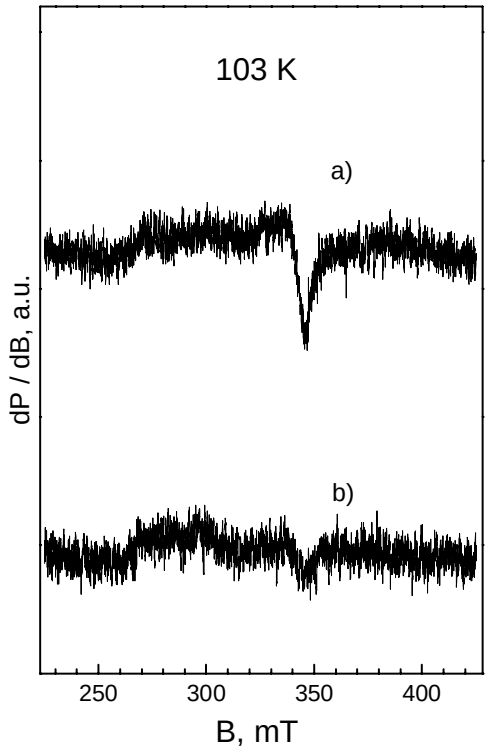


Figure 5. EPR spectra of: a) 0.034%Cu/ZnO b) 0.010%Cu/ZnO

X-ray Photoelectron Spectroscopy investigations for the Cu doped ZnO samples have been done and the results for O1s line are presented in figure 6. The well resolved doublet of $Zn2p_{3/2}$ and $_{1/2}$, respectively is observed (not shown here) and is typical for ZnO. The O1s photoelectron line of the investigated oxides is asymmetric and has a maximum at ~ 530.4 eV and this is the indication that the examined samples have very good crystal structure. The presence of high energy shoulder (second peak) in the spectra could be also indication that the ZnO is in the oxygen deficient state. (Chen, 2000). The peak at higher binding energy side at ~532,4 eV probably is due to the chemisorbed oxygen from the ZnO surface in form of hydroxyl or carbonyl groups (Dupin, 2000). So the O^{2-} ions mainly exist in intrinsic states as well as in oxygen deficient states, respectively. The copper on the surface was not detected.

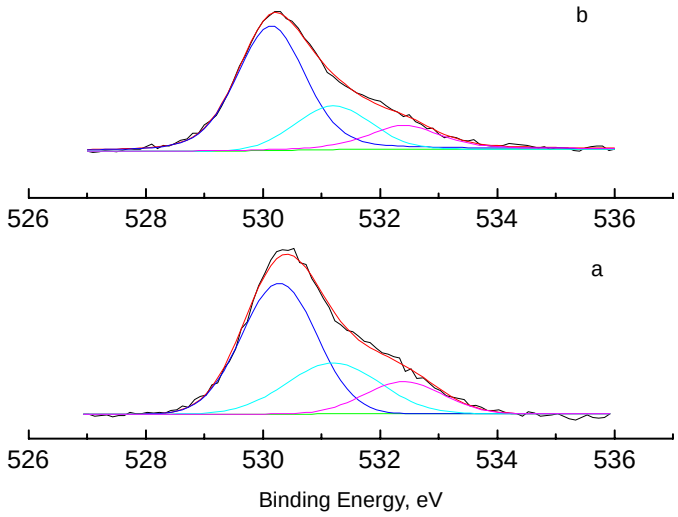


Figure 6. XPS spectra of O1s for samples: a) 0.010%Cu/ZnO b) 0.034%Cu/ZnO

On Figure 7 are shown the results concerning the ozone conversion over the studied materials. For the Cu doped ZnO samples limited deactivation is observed. The ozone conversion for the 0.010%Cu/ZnO decrease from 51.8 to 41.1 % after 260 min. The conversion of ozone for the 0.034%Cu/ZnO sample decrease from 63.4 to 56 % for the same time. The reached conversion for 0.034%Cu/ZnO sample is higher and the observed deactivation is lower compared to the 0.010%Cu/ZnO one, which probably is a result from the higher amount of copper in it. Accordingly the catalyst deactivation is a result of the accumulation of O_3^- ions over the active surface which leads to the mechanical blocking of part of active centers so the ions could not participate in the chemical reaction.

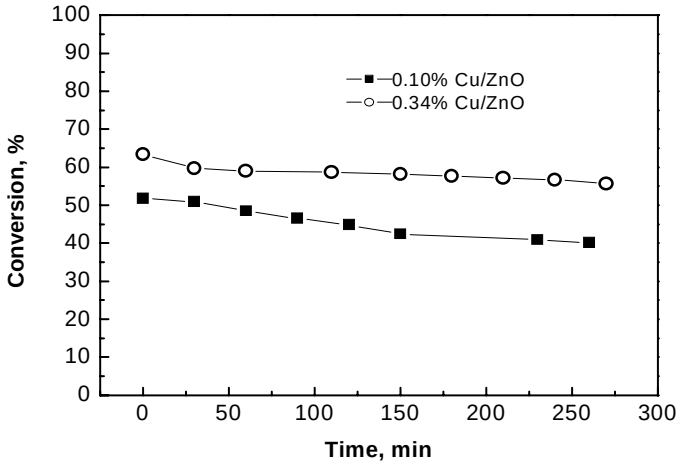


Figure 7. Decomposition of ozone at 75 ^oC - 0.010%Cu/ZnO; 0.034%Cu/ZnO

4. CONCLUSION

The ZnO samples doped by copper with 0.010 and 0.034 wt% were obtained. The investigated samples have nanocrystal structure with crystallites sizes of 40 and 43 nm. On the base of the results from EPR can be concluded, that Cu^{2+} ions are not evenly dispersed in ZnO structure. The obtained catalysts were investigated toward ozone conversion versus time and the limited deactivations have been observed. The ozone conversion for 0.034%Cu/ZnO sample was higher and its deactivation is lower compared to the 0.010%Cu/ZnO one, which is a result from the higher amount of copper in it. The catalyst deactivation most probably is a consequence of the accumulation of O_3^- ions on the active surface, which mechanically block part of the active centers and ions could not participate in the chemical reaction.

ACKNOWLEDGEMENTS

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