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ADSORPTION CHARACTERIZATION OF TRANSITION METALS DOPED NANOSIZED ZnO

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Abstract

ZnO samples, doped with transition metals (Mn and Cu) with content of the dopant less than 0.05 wt % were prepared. The samples were characterized applying the following methods - AAS, XRD, XPS, IR and BET. The calculated crystallite sizes of Mn and Cu doped ZnO nanoparticles were ~20 and ~50 nm, respectively. The porous structure of pure and doped with manganese or copper zinc oxide samples was studied by adsorption methods. The doping does not influence the specific surface areas of the oxides, but it modifies the porous structure of zinc carrier. There is trend to homogeneity in the structure of internal pore space after doping with Mn, while doping with Cu leads to absence of any homogeneity. The obtained materials are appropriate for catalytic application for ecological purposes.

Key words:*ZnO, manganese, copper, nanoparticles, adsorption.*

1. INTRODUCTION

Zinc oxide is a well-known mesoporous material with interesting structure and adsorption properties that is why it finds wide application in catalysis, photocatalysis, and optics and for preparation of photoluminescence materials. Qualities like well developed specific surface area, high porosity and low density take attention to many research works (Abdollahi 2011, Barick 2010). The entrance size of most of the pores is in the nanoscale, which allows deposition of different nanoparticles of other materials, making the ZnO excellent support of nanomaterials. The doping of ZnO with manganese or copper is often used to modify its electronic and surface properties. The transition metal ions can decrease the particle size down to the nanometric size (Chauhan 2010, Djaja 2012 and Sharma 2012) and can increase the density of the oxygen vacancies and surface defects. It is well known that in Cu doped ZnO, the Cu^{2+} ions (atomic radii 0,057nm) and Mn^{2+}(atomic radii 0,066 nm) could substitute the Zn^{2+} ions (atomic radii 0,060 nm). The diffusion process during the sintering may lead to defect formation, in which Cu^{2+} and Mn^{2+} ions substitute Zn^{2+} cations in the wurtzite unit cell of ZnO (Bahsi 2009, Rekha 2010). The aim of the present work is to investigate the influence of doping with small amount of Mn and Cu on the texture of wurzite ZnO by adsorption methods.

2. MATERIALS AND METHODS

2.1 Synthesis of the samples

The samples of copper-doped or manganese-doped ZnC_2O_4 were obtained using precipitation synthesis method. The experimental conditions were as follow: temperature T = 25.0 ± 0.5˚C; initial acidity of the system pH = 3.0 ± 0.1. $ZnC_2O_4.2H_2O$ was carried out as equal volumes (0.150 cm^3) of the initial $ZnSO_4$, $K_2C_2O_4$ and 0.25 M $CuSO_4$ or $MnSO_4$ 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 or manganese-doped ZnO the synthesised oxalate precursors were calcined for 1 h in air at 470˚C.

AAS analysis

Chemical 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.

2.2 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.

2.3 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.

3. RESULTS AND DISCUSSION

X-ray diffraction analysis of oxide samples show formation of hexagonal structure of ZnO (JCPDS 36-1451). There were not observed peaks of copper and manganese due to very low content of the dopants, which is in accordance with the work of Abdollahi (2011). The composition, specific surface area (A_{BET}), the crystallite sizes and pore volumes of ZnO are presented in Table 1. The manganese and copper content in oxide samples is less than 0.05 wt.% for manganese and less than 0.035 wt.% for the copper. The specific surface area of the oxides is approximately identical - 24÷25 m^2/g for all

of the samples. Doping does not have influence over the specific surface area of the obtained oxides. The sizes of crystallites (19÷50 nm) are calculated by Sherer's equation, using the results from XRD analysis. Similar results are obtained by Barick (2010) and by Rekha (2010) for Mn doped ZnO – about 17 nm size, Chauhan (2010) reported about 38 nm crystallites size of Cu doped ZnO sample. IR and XPS spectroscopy registered only existence of ZnO. The bands registered by IR at 1404 cm^{-1} and 1562cm^{-1} are related to Zn-O bond (Barick 2010 and Liu 2008). By XPS the Zn $2p_{3/2}$, typical of ZnO, similar for all samples with maximum at 1021.7 eV has been observed. The O1s peaks are located at 530.3 eV – they are attributed to O^{2-} ions in ZnO crystal lattice. Due to the low concentration of the transition metal dopants none of them is detected on the surface.

Table 1. Specific surface area, A_{BET}, sizes of crystallites and pore volume ($V_{0.95}$), of pure and doped with Mn and Cu ZnO.

Sample	**Mn and Cu concentration, wt %** ±0.001	**A_{BET}, m^2/g** ±3 %	**Crystallites sizes, nm**	**$V_{0.95}$, cm^3/g** ±0.001
0.011 Mn/ZnO	0.011	25.2	20	0.041
0.047 Mn/ZnO	0.047	25.3	19	0.038
0.015 Cu/ZnO	0.015	24.8	50	0.049
0.034 Cu/ZnO	0.034	24.9	43	0.039
ZnO	-	27.4	20	0.042

Adsorption-desorption isotherms of ZnO, Mn/ZnO and Cu/ZnO samples are presented in Figures 1, 2 and 3. As it can be seen, the type of the isotherms is similar. The isotherms are from IV type (Barick 2010) with hysteresis loops from type H1 according to IUPAC. This is an indication that pore space is filled with particles with similar sizes, which are collected in agglomerates. The pores volume is 0.038 ÷ 0.05 cm^3/g (see table 1).

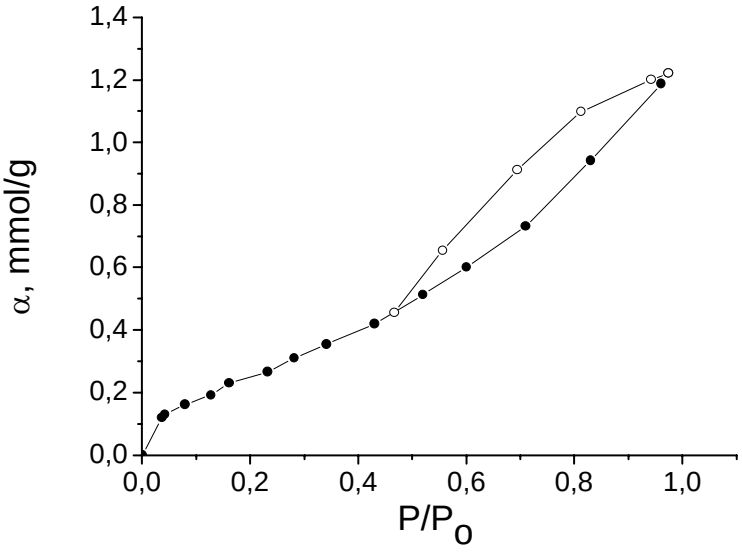

Figure 1. Adsorption-desorption isotherm of ZnO

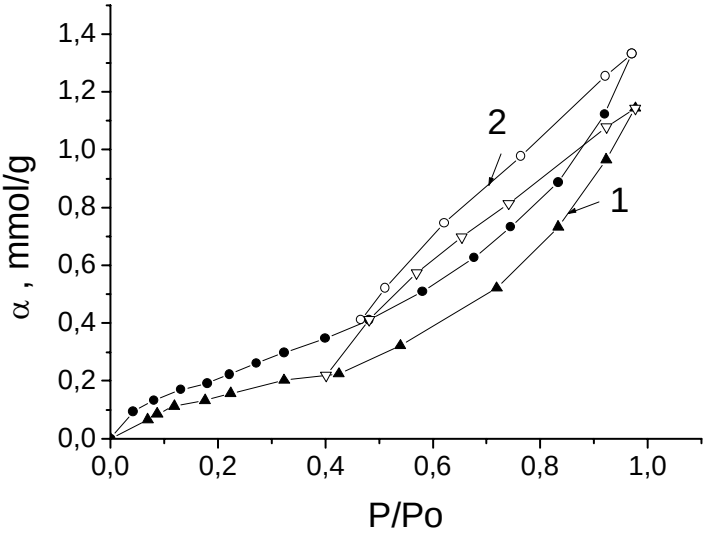

Figure 2. Adsorption-desorption isotherms of 0.047Mn/ZnO – (1); 0.011Mn/ZnO – (2) samples.

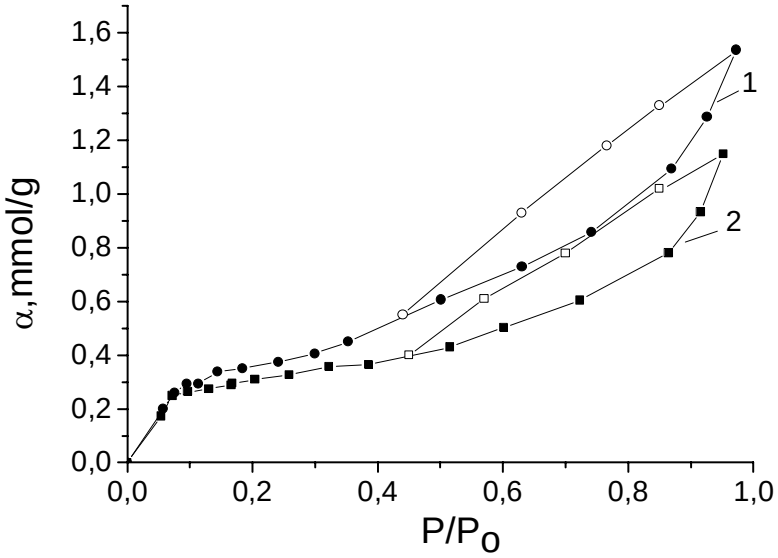

Figure 3. Adsorption-desorption isotherms of 0.034 Cu/ZnO – (1); 0.015 Cu/ZnO – (2) samples.

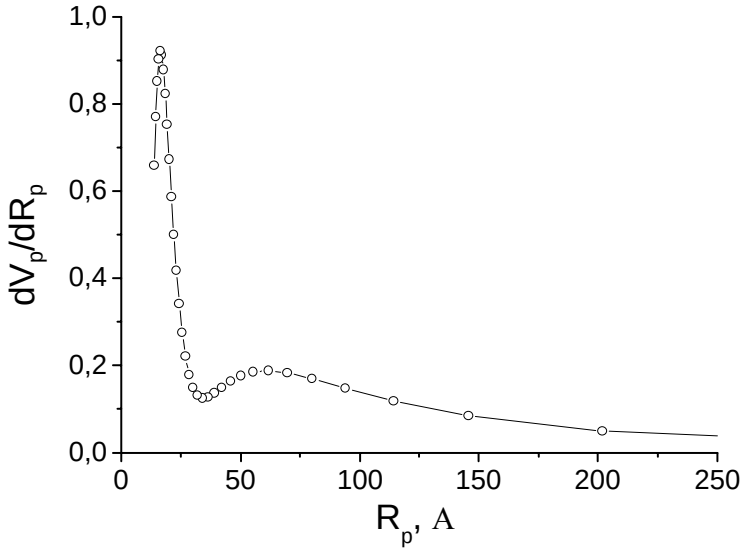

Figure 4. Distribution of pore sizes for sample ZnO

The results from the analysis of adsorption isotherms and pore size distribution curves (shown in Figures 1÷6) present the fact, that existence of dopant and its concentration affects the size of initial aggregates from ZnO particles. That has influence on their order, respectively on intra-aggregate pore space. The distribution curve of pure ZnO (Fig. 4) shows peak at Rp= 20-25 Å, which most probably is a result from intra crystallite pores. This peak is with low intensity which shows limited access to the pores. The intra aggregate pore sizes vary from 40 to 120Å, as indication that intra aggregate pore space is formed from chaotically connected particles, forming pores with different sizes.

Inclusion of manganese ions in the structure exert influence over porous texture of ZnO and depend on the exact content of manganese in it. In Fig. 5 it is observed redistribution in the volume of intra aggregate space for 0.047Mn/ZnO sample. The intra aggregate pores are observed at Rp = 40-80Å. For 0.011 Mn/ZnO sample pore distribution curve probably shows stronger and chaotic aggregation compared to the 0.047Mn/ZnO one. That limits access to intra crystallite pores, in comparison with pure ZnO the number and the size of intra aggregate pores decrease, leading to certain homogeneity in structuring of intra aggregate space.

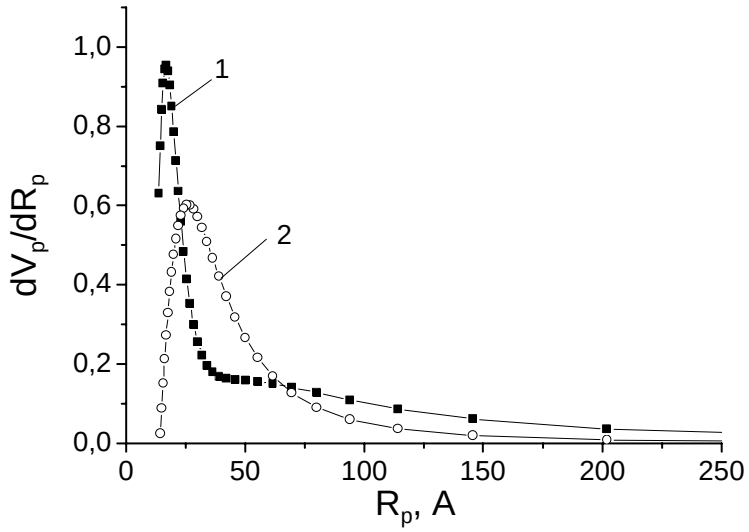

Figure 5. Size distribution of mesopores for 0.047 Mn/ZnO – (1); 0.011Mn/ZnO – (2) samples.

The influence of copper ions over porous texture of ZnO present some differences compared to manganese ions. For 0.034 Cu/ZnO sample porous texture is analogous to 0.047Mn/ZnO (Fig. 5) – there is well defined mesopores (Rp =20-25Å) and not clear peak at Rp =40-60 Å. The influence of copper ions is stronger and different in parallel with Mn ions for 0.015 Cu/ZnO. While the addition of Mn ions for 0.011Mn/ZnO show tendency to homogeneity in the structure of intra aggregate space. Contrariwise for 0.015 Cu/ZnO it was observed restructuring of intra aggregate space and partial restriction of access to intra crystallite space.

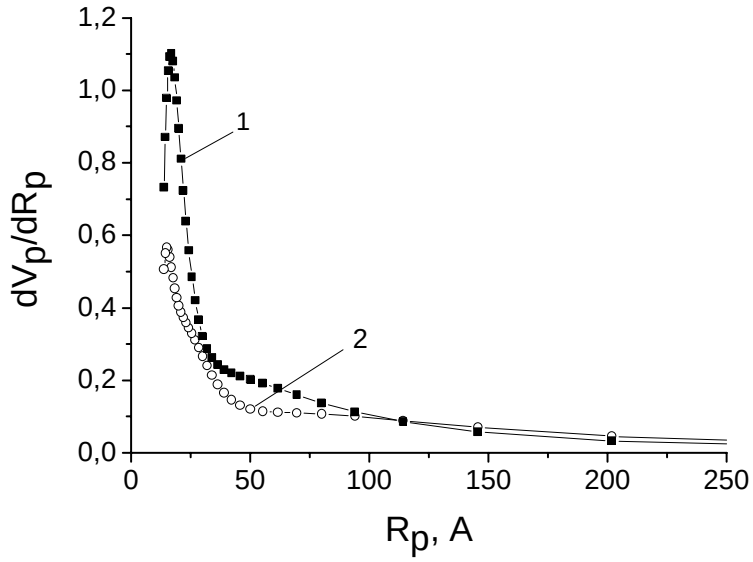

Figure 6. Size distribution of mesopores for 0.034 Cu/ZnO – (1); 0.015 Cu/ZnO – (2) samples.

4. CONCLUSION

The XRD studies revealed that obtained ZnO, Cu-doped and Mn-doped ZnO have hexagonal wurtzite structure. The content of Mn in the samples is 0.011 and 0.047 wt. %, content of Cu - 0.015 and 0.034 wt. %. Specific surface area of the oxides is 24 ÷ 25 m^2/g, the size of the crystallites is up to 50 nm for copper doped samples, 20 nm for manganese ones. Adsorption isotherms for all of the investigated samples are from IV type with hysteresis loops from H1 type. Inclusion of manganese and copper ions into the structure of zinc oxide influenced the porous texture. The accomplished investigation lead to conclusion, that the obtained oxides are characterized with texture build of intra crystallite pores and intra aggregate pores. Pore distribution curves show that doping with Cu and Mn and their concentration affects both – the size of initial aggregates of the particles ZnO and their ordering.

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