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An application of microemulsion method for synthesis of copper-zinc materials

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Microemulsion method was used for preparation of copper-zinc mixed oxides. Samples were prepared from the solutions containing zinc and copper nitrates. Sodium carbonate was used as a precipitant and hydrazine as reducing agent. Water-in-oil (W/O) microemulsions were formed by the application of cyclohexane, isopropyl alcohol, and hexadecyltrimethylammonium bromide (CTAB) as surfactant. The aim of the studies was determination of the influence of the sequence of synthesis stages on the formation of materials, their surface and structural properties. Thermal decomposition studies of materials were carried out by infrared spectroscopy. The physicochemical properties were characterized by nitrogen adsorption-desorption method, X-ray diffraction (XRD) and temperature-programmed reduction (TPR).

1. INTRODUCTION

Nanotechnology gained a huge increase of interest in the recent years. New nanomaterials may find wide application in many fields in the

near future, ranging from common goods to advanced technologies. Much attention has been paid to new synthesis methods, which allow better control of the size or shape of nanoparticles. For this reason it is understandable why the development of microemulsion method for new nanomaterials synthesis enjoys great interest.

This method enables in easy way to control the size of reversed micelles, and thereby the particle size, by changing water-to-surfactant molar ratio (W_0). Not only the particle size, but also their shape or composition of materials can be readily modified. Various intermetallic nanoparticles can be obtained just by changing the composition of water cores of micelles. Microemulsion method has been used for the synthesis of many types of materials, including metals, alloys, metal oxides, sulfides and selenides, metal borides, halides, carbonates and hydroxides of metals. The microemulsion method might be used for preparation of oxide materials of suitable chemical composition on nanometer level, porosity and specific surface area [1]. Usually such colloidal templates give smaller particles than those produced by precipitation method in aqueous system. It has been observed that the type and concentration of surfactant, the nature of oil phase and alcohol, the reaction temperature and rate of microemulsion mixing strongly influenced particle size, shape and growth rate, however the mechanism of the control of the size and shape of formed particles is still under debate [2]. Moreover the sequence of precipitation or reduction stages in complex microemulsion systems has not been well documented.

Zinc oxide is a very interesting material. It is widely used in the ceramic industry, the manufacture of tires, cement, pigments, and cosmetics. It shows unique optical, electronic and photo-catalytic properties, such as those connected with high energy band gap. ZnO is also a component of many adsorption and catalytic systems, including low-temperature CO conversion catalyst, methanol synthesis, steam reforming of methanol [3-4]. Mechanical, optical, sensory, catalytic, electrical and thermal conductivity of ZnO depends on the size, shape and even nanomaterials morphology. Additionally ZnO holds the possibility of dilute magnetic semiconductor with a Curie temperature above room temperature. It has been predicted that Cu-ZnO is a ferromagnetic and shown signs of magnetic behavior. Because of that, various chemical and physical methods have been used for preparation of copper-zinc oxide systems and nowadays its examination enjoys huge interest [5].

Microemulsions are normally transparent, isotropic solutions, and are divided into two types, oil-in-water (O/W) and water-in-oil (W/O). The

reverse microemulsion – W/O type, consists of at least three components: the continuous phase – an organic solvent, dispersed phase – water and surfactants (ionic or nonionic), accumulated at the interface which stabilize the system. The resulting micelles create specific microenvironment for chemical reactions, where precipitation or reduction can occur. As a result, the nanoparticles could be formed inside small confinements. Micelles during synthesis play complex role, both they serve as nano-reactors, and also they control the growth of formed nanoparticles. When the dimensions of the crystallite approaches the size of entire micelles, surfactant molecules are adsorbed on its surface, preventing agglomeration. This result in the formation of very small crystallites of similar size [6-7]. The synthesis of nanomaterials often refers to the combination of two microemulsions containing the appropriate reagents, e.g., metal salts and reducing substances or precipitants. After mixing, micelles collision occurs, which results in the exchange of content and percolation [7]. The size and shape of the micelles can be controlled in several ways. The most common way is changing of the ingredients proportions of the mixture or introducing various external factors (such as temperature or electric field).

The aim of the studies was to determine the influence of the sequence of synthesis stages on the formation of copper-zinc mixed oxides by water-in-oil (W/O) microemulsion method, and the surface and structural properties of obtained materials.

2. MATERIALS AND METHODS

Copper-zinc oxides, have been prepared by reverse microemulsion method. The assumed copper content was 30 wt. %. Different sequence of particular stages of synthesis was applied. The scheme is shown on Fig. 1. The microemulsion systems was consisted of cyclohexane (44 wt. %) as continuous oil phase, aqueous solution as dispersed phase (36 wt. %), hexadecyltrimethylammonium bromide (CTAB) as surfactant (10 wt. %) and isopropanol (10 wt. %) as cosurfactant.

The CuO-ZnO-1 sample was obtained by co-precipitation method in microemulsion. The aqueous phase of first microemulsion was a 0.01 M of copper nitrate and 1.25 M of zinc nitrate solution. The microemulsion was then mixed with another microemulsion containing precipitation agent (sodium carbonate 1.25 M solution).

Preparation of CuO-ZnO-2 sample was preceded by reduction of copper using ten-fold excess of hydrazine prior mixing with microemulsions containing zinc and carbonate ions. CuO-ZnO-4 was prepared by the same way, while using double amount of surfactant.

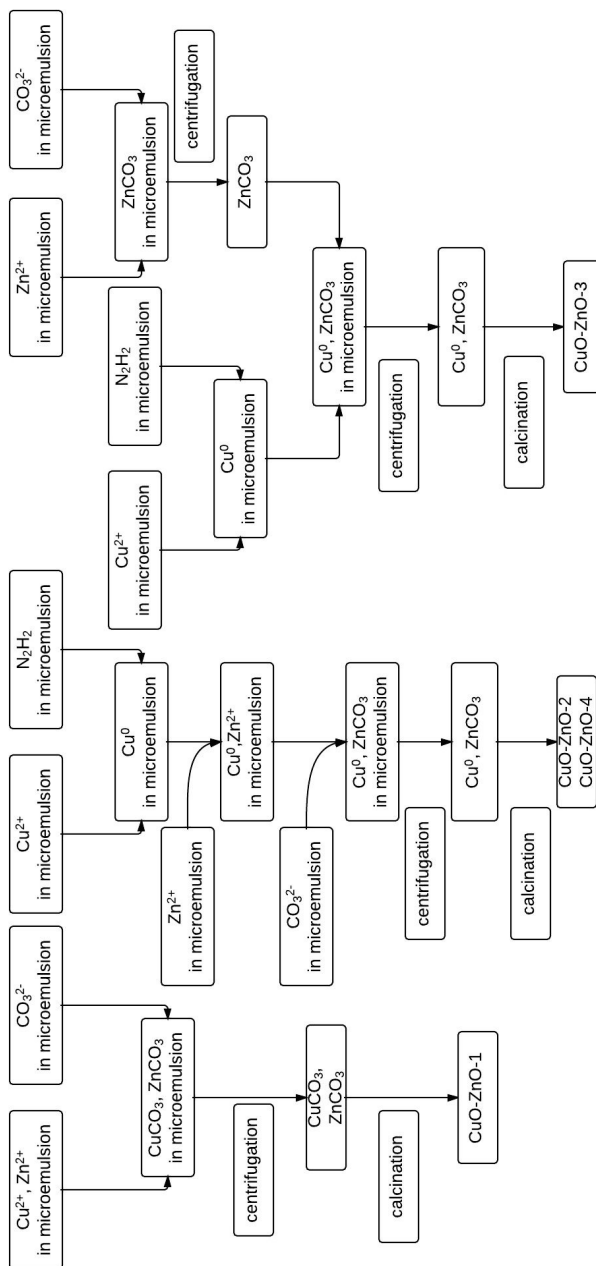


Fig. 1. Schema of the samples preparation.

During the synthesis of CuO-ZnO-3 sample, the reduced copper nanoparticles obtained by microemulsion method with application of hydrazine were deposited on the precipitate, formed from microemulsions containing $\text{Zn}(\text{NO}_3)_2$ and Na_2CO_3 .

The synthesis was carried out at room temperature for 3 h under vigorous stirring. The microemulsions were destabilized with a few ml of tetrahydrofuran (THF). The precipitates were as separated by centrifugation and were washed with chloroform, water and methanol-water mixture. Samples were dried at room temperature overnight, and then calcined in air at 350°C for 1h.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) studies were performed using Nicolet 6700 (Thermo Scientific) spectrometer equipped with high-temperature reaction chamber (Harrick). FT-IR spectra were recorded in the mid-IR region ($400 - 4000 \text{ cm}^{-1}$) with resolution of 4 cm^{-1} . Samples were heated in the flow of ~8% of oxygen in argon with the rate $30 \text{ cm}^3/\text{min}$. The spectra were recorded every 50°C from room temperature to 450°C .

The specific surface area and porosity were calculated from nitrogen adsorption-desorption isotherms gained on a Micromeritics ASAP 2405 instrument after outgassing of the samples at 200°C . The BET method was used to calculate the specific surface areas. The adsorption branch of isotherms was used to obtain BJH pore size distribution.

Microscopic images were obtained using Scanning Electron Microscope Phenom FEI Company with magnification range from 120x to 24,000x and 5kV accelerating voltage.

Powder X-ray diffraction (XRD) studies were carried out in an Empyrean (PANalytical) diffractometer, using CuK_α radiation.

Temperature-programmed reduction (TPR) with hydrogen was carried out on the Autochem II Micromeritics instrument. About 50 mg of sample was introduced into the quartz U-tube microreactor. Sample was heated in the flow of $\text{H}_2(5 \text{ vol.}\%)/\text{Ar}$ mixture with the rate $10^\circ\text{C}/\text{min}$ from -30°C to 600°C .

1. RESULTS AND DISCUSSION

The DRIFTS spectra (Fig. 2) of the samples, before calcination, were collected during heating from 25°C to 450°C . Wide band at about 3400 cm^{-1} can be seen for all samples, which is characteristic of the stretching vibrations of O-H groups, coming from surface hydroxyl

groups and water adsorbed. Small differences in the number and band position within this region in the spectra of dried samples recorded at 25°C indicate on the different chemical nature of CuO-ZnO precursor phases. Samples prepared by different methods show also different thermal stability.

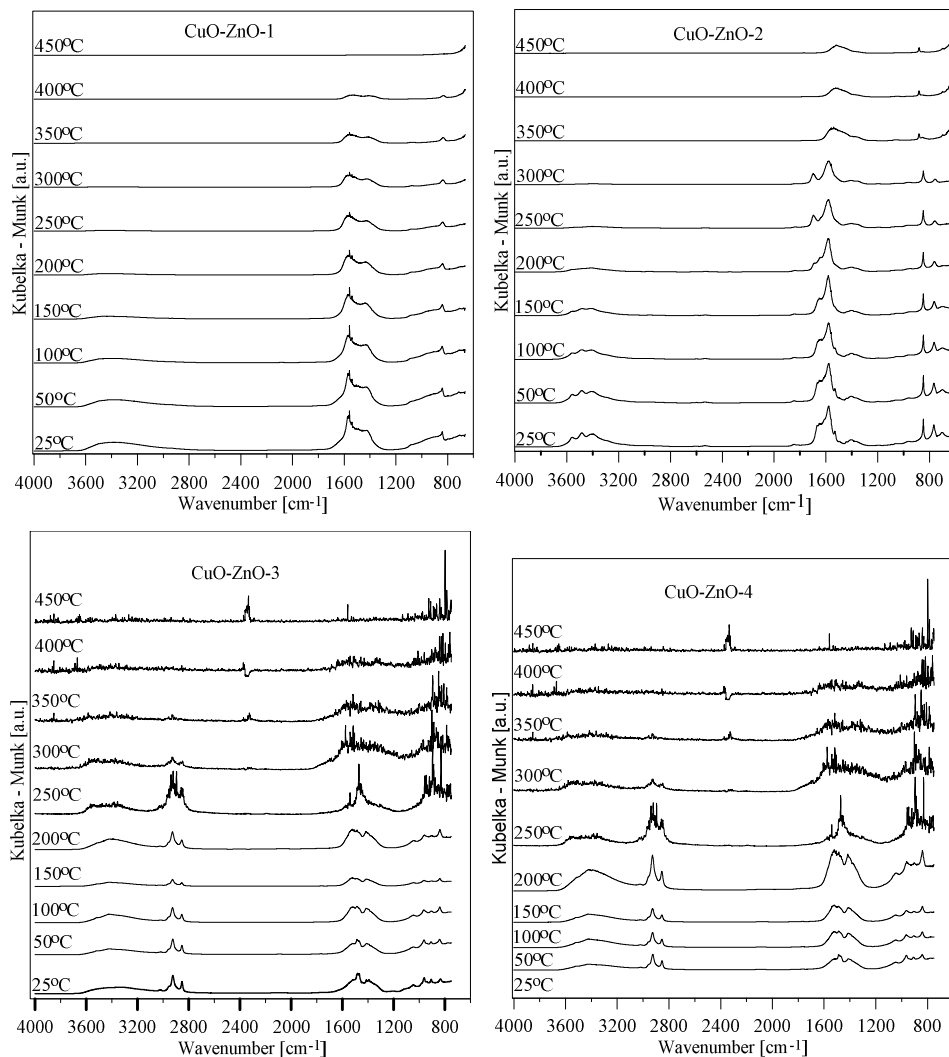


Fig. 2. DRIFTS spectra of CuO-ZnO (dried) samples, recorded during thermal decomposition in the flow of oxygen/argon mixture from 25 to 450°C.

The transformation of the species can be observed by comparison of the intensity of hydroxyl group vibration. The large disappearance of hydroxyl groups vibrations takes place in the case of CuO-ZnO-1 sample

between 150°C and 200°C, while this effect in the case of Cu-ZnO-2 is observed between 200-250°C. The samples CuO-ZnO-3 and CuO-ZnO-4 show higher stability, and disappearance of pronounced amounts of hydroxyl groups is observed above 350°C.

The two bands at 2950 cm^{-1} and 2850 cm^{-1} on the spectra of CuO-ZnO-3 and CuO-ZnO-4 result from stretching vibrations of C-H hydrocarbon groups, which decline at temperature around 350°C for both samples. Their presence is connected with the traces of surfactant molecules left on the surface after washing.

The bands at 1550 cm^{-1} and 1400 cm^{-1} , which are present on the spectra of all samples before thermal treatment, come mostly from C=O stretching vibrations. Small differences indicate different chemical bonding. The shape of the spectra is changing during thermal treatment. However these vibration bands do not completely disappear at 350°C (at applied calcination temperature). Large interferences in two last samples are caused by high gas evolution during samples decompositions [8].

The sequence of preparation stages influences structural and surface properties of materials. The BET specific surface areas of the samples after calcination, pore volume and mean pore diameter are presented in the Table 1. The largest specific surface area is observed for the sCuO-ZnO-1 sample, which was obtained by the co-precipitation in microemulsion of Zn^{2+} and Cu^{2+} by sodium carbonate (in microemulsion). Similar values were observed by Hingorani and coworkers [9]. This sample shows also relatively small mean pore diameter. Similar surface area is observed for the CuO-ZnO-2 sample, obtained by precipitation of Zn^{2+} with Na_2CO_3 , with deposited Cu nanoparticle formed in a separate microemulsion. This sample shows also relatively large pore volume and large mean pore diameter.

Table 1. Physicochemical properties of prepared samples.

Sample	Specific surface area [m^2/g]	Total pore volume [cm^3/g]	Mean pore diameter [nm]
CuO-ZnO-1	27.3	0.08	14.3
CuO-ZnO-2	23.3	0.13	26.0
CuO-ZnO-3	13.3	0.05	16.8
CuO-ZnO-4	8.0	0.03	21.0

It is interesting that CuO-ZnO-3 sample, which was prepared by deposition of copper nanoparticles on the surface of isolated zinc containing solid shows much lower specific surface area and smaller pore volume. The influence of surfactant concentration is well reflected in the changes of the surface and structural properties of CuO-ZnO-2 and CuO-ZnO-4 samples. The latter one shows smaller surface area and pore volume.

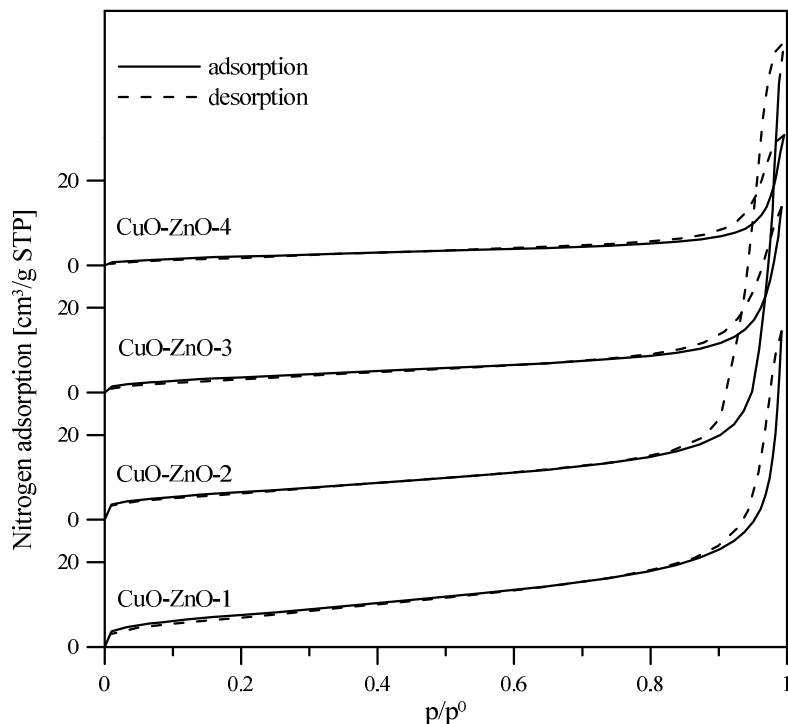


Fig. 3. Low temperature adsorption-desorption of nitrogen.

The shape of isotherm (Fig. 3.) indicates on the presence of slit-shaped pores formed by regular interconnected species.

The CuO-ZnO-4 sample shows different morphology from that observed for remaining samples. The changes are evidenced on SEM images (Fig. 4). The samples prepared in the presence of the smaller amount of surfactant show sponge-like morphology. Small species are connected together in rather random way, forming empty voids. In the case of CuO-ZnO-4 these species are linked into thin regular belts, which are deposited on more amorphous part of material.

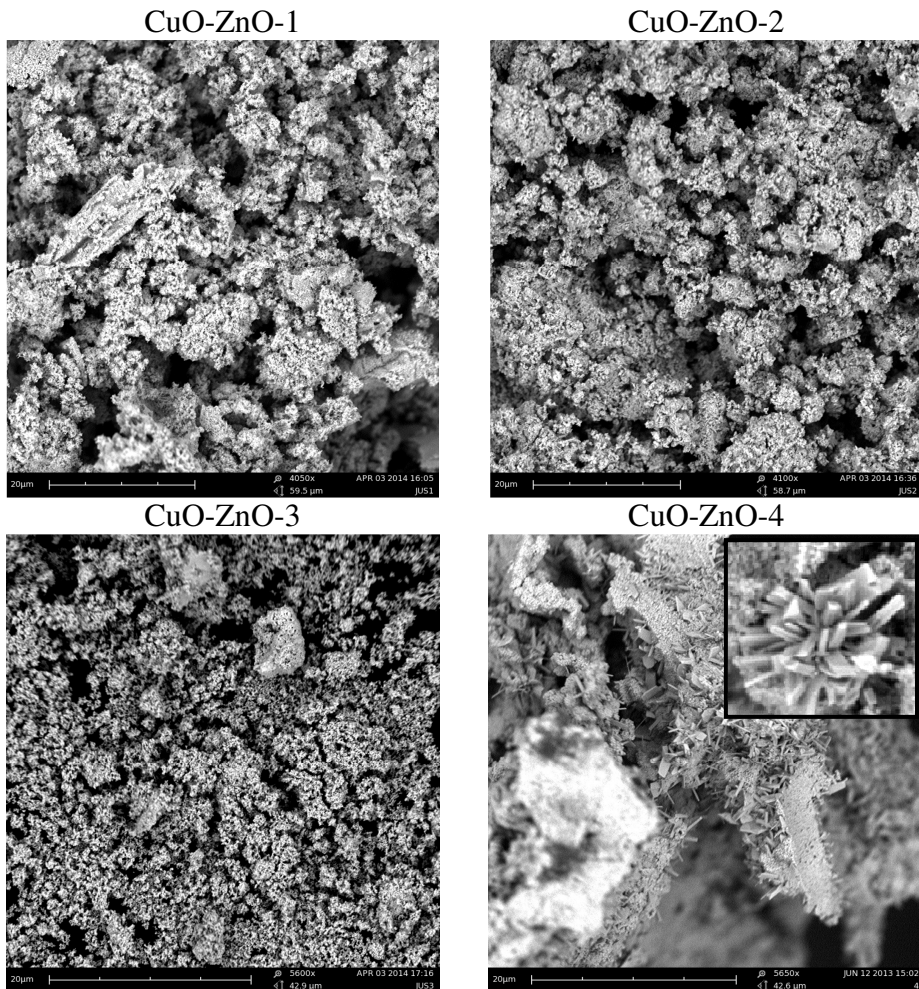


Fig. 4. SEM images of CuO-ZnO samples. Scale bars: 20 μm.

The XRD pattern for CuO-ZnO-1 sample (Fig. 5) shows diffraction peaks, located at $2\theta = 31.8, 34.5, 36.3, 47.6, 56.6, 62.9, 66.4, 67.9, 69.0$ and 72.6 , which correspond to ZnO hexagonal P63mc phase (PDF # 80-0074). The main CuO reflection peaks, which are located at $2\theta = 32.5, 35.5, 38.7, 48.8, 58.2, 59.0, 61.6, 65.7$ and 66.4 well correspond to the phase of PDF# 04-0836. Similar phases are identified for all samples. One can observe reflection lines on the spectra of CuO-ZnO-2 and CuO-ZnO-4 samples coming from residual carbon, left on the surface after surfactant decomposition.

The size of ZnO and CuO crystallites was estimated by the application of Scherrer equation (Table 2). The reflections used for

calculations were $2\theta = 36.3$ for ZnO and $2\theta = 38.7$ for CuO. The smallest CuO and ZnO particles are observed for CuO-ZnO-2 sample. The size of ZnO is changed from 13.9 to 35.4 nm as the surfactant concentration is increased. The more pronounced effect is visible for copper oxide crystallites, which size is increased from 11.4 to 20.1 nm.

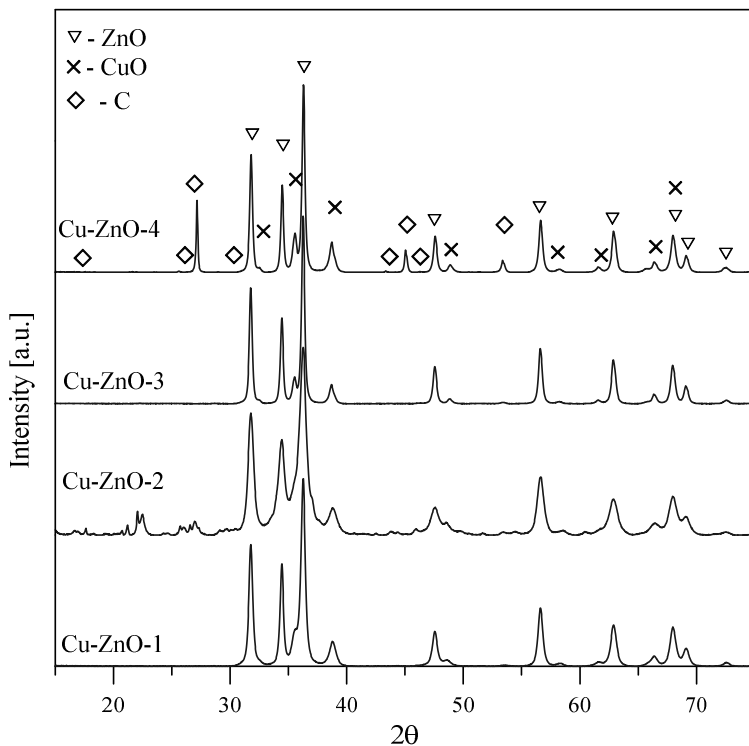


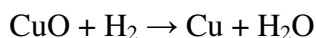
Fig. 5. XRD patterns of the samples after calcination.

Table 2. The size of crystallites of CuO and ZnO calculated from XRD studies.

Sample	CuO [nm]	ZnO [nm]
CuO-ZnO-1	17.6	21.6
CuO-ZnO-2	11.4	13.9
CuO-ZnO-3	19.1	33.1
CuO-ZnO-4	20.1	35.4

Fig. 6 shows temperature-programmed reduction profiles of CuO-ZnO samples. The main peak in CuO-ZnO-1 profile is placed

between 150 and 350°C. Low temperature peaks are usually ascribed to the reduction of copper oxide accordingly to the reaction:



However the reduction temperatures may change due to different chemical environment of copper oxides and their different size. According to Fierro and coworkers the reduction temperature of copper-zinc mixed oxides containing 30% CuO ranges from 150 to 200°C [10]. However pure copper oxide, as well as copper-zinc oxide systems of much lower reducibility were also widely described in the literature [11-13]. Agrell and coworkers prepared copper supported zinc oxide catalysts using microemulsion method, which have similar composition. Reduction peak for similar catalysts was placed between 180-240°C and reducibility decreased after reoxidation to temperatures ranging from 220 to 250°C. High temperature reduction maxima were explained by strong interaction between ZnO and CuO [14]. High temperature peaks on the TPR curves of Cu/ZnO catalysts have been also ascribed to the reduction of ZnO in the vicinity of copper metallic species.

The TPR profile for CuO-ZnO-2 sample is more complex. One can observe several overlapped peaks, which suggest the presence of various copper oxide species. It is visible low-temperature peak located between 150 and 250°C, the peak with similar position as in the CuO-ZnO-1 sample, and sharp peak with maximum at around 350°C. There is also observed high temperature broad peak. Low temperature peak may result from reduction of CuO of different environment, especially located in the vicinity of very small copper metallic species or Cu₂O surface phases, which may remain in the samples after reduction with hydrazine and encapsulation with some oxide or carbonate species. While high intermediate peaks, with maximum at 350°C could be related to the reduction of small crystallites located in the pores of materials or strongly interacted CuO-ZnO mixed oxide phases or zinc oxide layers inhibiting CuO reduction [13]. An increase of surfactant concentration used in the synthesis condition caused the decrease of reducibility of CuO. The stronger decrease of reducibility is observed for CuO-ZnO-3 sample obtained by deposition of copper nanoparticles on the surface of as prepared ZnO-based support. The almost symmetrical and the narrowest reduction peak one can observe for first sample, which indicates a homogenous material and narrow particle size distribution [14].

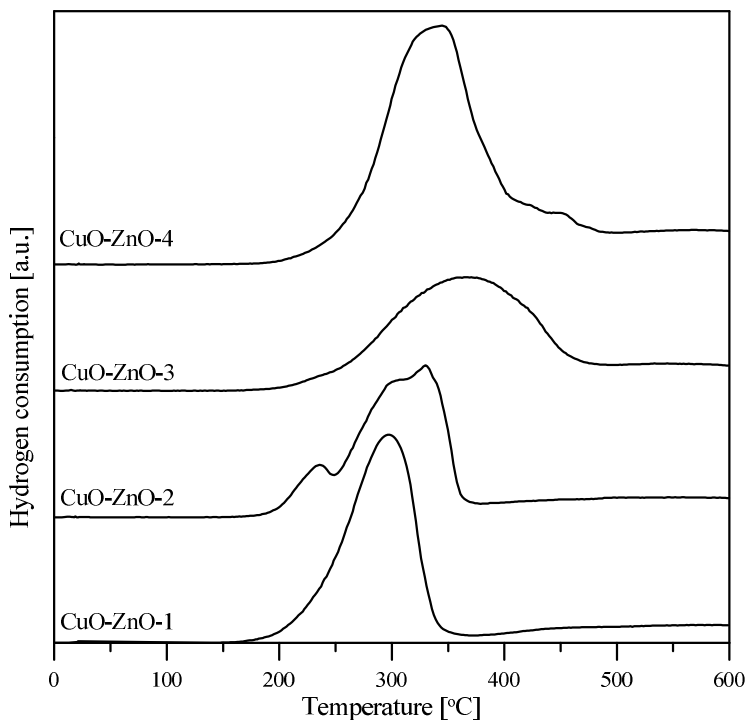


Fig. 6. Temperature-programmed reduction (TPR) of the samples.

4. CONCLUSIONS

Copper-zinc oxides were synthesized by microemulsion method. The sequence of particular stages of preparation have the influence on structural and surface properties of obtained materials. The CuO-ZnO-1 sample, prepared by co-precipitation in microemulsion exhibited the highest specific surface area. The smallest crystals size of both oxides was observed for CuO-ZnO-2 sample. SEM and XRD measurements confirmed formation of CuO and ZnO crystallites of different morphology and size in the samples. DRIFTS and temperature programmed reduction studies shed more light on the formation of and mutual interaction between oxide phases in the samples.

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CURRICULA VITAE

Justyna Pawlonka was born in Pulawy in 1988. She studied Basic and Applied Chemistry on Maria Curie-Skłodowska University, where she obtained the M. Sc. degree in 2012. Her master thesis entitled: “Decomposition of biodegradable polymers in natural conditions” (supervisors: Prof. dr hab. Janusz Ryczkowski and dr Sylwia Pasieczna-Patkowska) was awarded by the Polish Chemical Society. In 2012 she started her Ph. D. studies in Department of Chemical Technology, on Maria Curie-Skłodowska University in Lublin.

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Tadeusz Borowiecki was born in Lublin in 1945. In 1968 he graduated from the Faculty of Mathematics, Physics and Chemistry, Maria Curie-Skłodowska University (MCSU) of Lublin. He received his Ph.D. degree in 1977 and full professor title in 2002. In the period 1996-99 and 1999-2002 he was a Dean of the Faculty of Chemistry. Moreover, from 2005 to 2008 he was a Vice-Rector of MCSU. He is the author of above 150 original papers and 13 patents. His research areas are: heterogeneous catalysis and chemical technology. The studies are focused on: physicochemical properties of catalysts, temperature-programming techniques in catalysts characterization, catalysts deactivation process, processes for obtaining synthesis gas and hydrogen.