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PHYSICO-CHEMICAL CHARACTERIZATION OF THERMAL DECOMPOSITION COURSE IN ZINC NITRATE-COPPER NITRATE HEXAHYDRATES

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This study reports experimental investigations by non-isothermal TG/DSC analysis of $Zn(NO_3)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}4H_2O$ and their mixtures of known compositions in the temperature range 30–1200°C. Solid/liquid transitions in the sealed samples of the hexahydrate salts and their mixtures were also studied by DSC in the temperature range 0–60°C. The mixture with composition $0.85Zn(NO_3)_2{\cdot}6H_2O+0.15Cu(NO_3)_2{\cdot}6H_2O$ showed single melting peak at 29°C. This mixture was chosen for detailed studies. Melting temperature and heat of fusion of single salt hexahydrates and of the mixture were calculated from DSC endotherms.

The different stages in the thermal decomposition processes have been established. The intermediate and the final solid products of the thermal decomposition were analyzed by XRD. The scheme and the decomposition temperature depended on the composition of the starting material. The final decomposition products were CuO (monoclinic), Cu_2O (cubic), ZnO (hexagonal) and their mixtures with the defined crystalline structures. Possible influence of the addition of $CuCl_2{\cdot}2H_2O$ into the mixture $0.85Zn(NO_3)_2{\cdot}6H_2O+0.15Cu(NO_3)_2{\cdot}6H_2O$ and a gel combustion technique of the precursor preparation, on the composition and morphology of the solid decomposition products, were also studied. The gel combustion technique, using citric acid added to a mixture of $0.85Zn(NO_3)_2{\cdot}6H_2O+0.15Cu(NO_3)_2{\cdot}6H_2O$, was applied in an attempt to obtain mixed Zn/Cu oxides of a particular mole ratio. The morphology of the solid decomposition products was examined by SEM.

Keywords: *copper nitrate hexahydrate, copper oxide, thermal decomposition, XRD analysis, zinc nitrate hexahydrate, zinc oxide*

Introduction

A very important step in the modern sustainable development is a role of new materials synthesis. Better and less complicated methods for preparing known materials are usually based on the use of suitable catalysts. Many industrial catalysts contain metal particles dispersed in a porous matrix. Transition metal oxides may serve as suitable substitutes for noble metal catalysts or as new catalysts in a variety of application areas. For example, metal oxides are largely used in the field of oxidation-reduction reactions, pollution control, electrochemical and photoelectrochemical cells [1–4].

It has been shown that molten salts, as reaction media, can provide a simple route for the preparation of some dispersed oxides, multi-component compounds, layered intercalation hosts and supported catalysts [5]. Further chemical treatment of the products can lead to the desired structure and morphology of specialized technical demands. Metal nitrates are widely used as precursors in the production of nano scale metal oxides for high surface catalysts [5, 6]. Though molten hydrated salts as reaction media should be more convenient for the soft chemistry preparations, they have been much less studied for the purpose of chemical synthesis of solids. A number of studies on kinetics and mechanisms of thermal decomposition of various metal hydrates showed that final solid decomposition products were metal oxides or metal powders. Most thoroughly studied were decompositions of hydrated oxalates, formates, acetates and sulphates [7–10]. Transition metal nitrates form hydrates with variable number of hydrated water molecules, therefore they do not decompose in simple stages. Very little is known about the processes occurring when hydrated nitrates are thermally converted to the oxides. Few studies in that field have been done so far [11–14].

Different variations of gel-combustion techniques have been used nowadays to synthesize finely dispersed oxides or oxide mixtures, to serve as catalysts, ceramics precursors as well as intercalate electrode materials for Li-ion batteries [15–21]. The technique involves metal nitrates and an organic compound serving as complexing and gel forming agent as well as fuel. Firstly this method was used to synthesize superconducting ceramics with glycine as organic additive [15]. Huang *et al.* [16] synthesized nano-crystalline $BaFe_{12}O_{19}$ powders by low temperature combustion of nitrates and citric acid gel. Mangalaraja *et al.* [17] prepared dielectric ceramic powder $Ni_{1-x}Zn_xFe_2O_4$ by flash combustion of nitrates and carbamide gels. Wang *et al.* [18] prepared ultrafine hexagonal ferrite CoZn powders, by slow oxidation of

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gels formed by acetates and citric acid. Jugovic *et al.* [19] synthesized intercalate compound $LiMn_2O_4$ by glycine-nitrate method. Jiao *et al*. [20] prepared the electrochromic NiO thin film by slow combustion of gel composed of chlorides and citric acid in butanol. Yoshimura *et al.* [21] prepared nickel tungstate catalyst on alumina support impregnated by solutions of nitrates and citric acid.

In this work, the thermochemical studies of the mixtures of $Zn(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 6H_2O$ and their mixtures with and without added $CuCl_2\cdot 2H_2O$ have been performed by non-isothermal TG and DSC measurements.

The gel combustion technique with citric acid gel was applied in this study to obtain mixtures of ZnO and CuO from the mixture containing $0.85Zn(NO_3)_2\cdot 6H_2O+0.15\ Cu(NO_3)_2\cdot 6H_2O$.

The composition and structure of the solid products obtained by thermal decomposition and by gel combustion technique were studied by XRD analysis. The morphology of the decomposition end products was examined using a scanning electron microscope (SEM).

Experimental

Materials

The hydrated salts $Zn(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 6H_2O$ and $CuCl_2\cdot 2H_2O$ used in this work were reagent grade Merck products. They were used without further purification. The mixtures of the desired compositions were prepared from known masses of each compound and melted together in stoppered glass vessels.

The mixtures of the salts were prepared by successive addition of solid $Cu(NO_3)_2\cdot 6H_2O$ into molten $Zn(NO_3)_2\cdot 6H_2O$, melted together and analyzed by DSC. Gradual addition of $Cu(NO_3)_2\cdot 6H_2O$ into molten $Zn(NO_3)_2\cdot 6H_2O$ resulted in gradual lowering of the melting point of $Zn(NO_3)_2\cdot 6H_2O$, due to cryoscopic effect and gradual approach of the melting peaks of the two hydrates. At the molar concentration ratio Zn:Cu= 0.85:0.15 the DSC scan showed a single melting peak, indicating that a complex compound might have been formed. This mixture was chosen for further studies.

The gel-combustion method to synthesize ZnO–CuO mixtures was performed in a following way: zinc nitrate hexahydrate and copper nitrate hexahydrate were dissolved in pure water. The solutions were mixed in the volume ratio to obtain the predetermined Zn/Cu molar ratio (0.85:0.15). A solution of citric acid was then added, in an amount that provides the citric acid/metal nitrate mole ratio of approximately 1:4. The solutions were then heated to remove the solvent, and upon almost all water was evaporated under permanent mixing, a transparent gel remained. The gel was further heated in an open crucible, gradually rising temperature to 400°C, until a combustion of citric acid occurred.

The equation of combustion of citric acid is:

$$2C_6H_8O_7+9O_2=12CO_2+8H_2O \qquad (1)$$

while the decomposition of $Zn(NO_3)_2$ results in ZnO and a mixture of gases NO_2, NO, N_2 and O_2, with exact composition depending on the reaction temperature. Since the combustion temperature is generally unknown, an exact citric acid *vs*. nitrate mole ratio needed to complete organic combustion is in principle also unknown, and in this work an empirically proven mole ratio 1:4 [19] was used. In each case, additional heating in air may level the deviations of stoichiometry, if any, appearing during the very gel combustion. The heating in air at a constant temperature of 400°C was thus prolonged for approximately 1 h, in order to combust possible residues of carbon, or to revert the metal oxides to a stoichiometric composition.

Methods

DSC measurements of the sealed hydrated salts were performed in aluminum sample pans (for volatile samples), using a Perkin Elmer DSC4 calorimeter with an accessory for subambient measurements. The temperature calibration of the instrument and the melting temperature data presentation were made in accordance with recommendations given by GEFTA group (Gesellschaft fur Thermische Analyse e.V., Germany) [22]. The energy scale calibration was made for various range settings using indium standard samples.

Simultaneous TG/DSC scans were performed in open platinum sample pans using a thermal analyzer 2960 SDT (TA, DE, USA), allowing thermal analysis scanning up to 1200°C. The temperature scale was calibrated with silver and zinc calibration standards. Samples of approximately equal mass (≈10 mg) were scanned at heating rate of $10°C\ min^{-1}$ in N_2 atmosphere at gas flow rate of $100\ mL\ min^{-1}$.

Solid decomposition products were analyzed by X-ray diffraction analysis (XRD) using a Siemens-D500 diffractometer with Ni filtered CuK_α radiation (λ=1.54178 Å). An on-line data acquisition system allowed an automatic JCPDS (Joint Committee on Powder Diffraction Standards) library search and data identification.

The morphology of the decomposition end products was examined using SEM (Philips, model XL30). Microstructural characterization of powders was performed on a Zeiss Axiovert 25 optical microscope. To observe the internal powder structure samples with loose powder particles mounted into the epoxy resin were prepared.

Results and discussion

The solid/liquid equilibria in pure hydrated salts $Zn(NO_3)_2\cdot6H_2O$ and $Cu(NO_3)_2\cdot6H_2O$ were first analysed by differential scanning calorimetry (DSC) of hermetically sealed samples. The melting points and the enthalpy of melting were determined from endothermic DSC scans. The melting points for both salts were in agreement with standard reference data [23]. On cooling both salts show supercooling and freezing temperature was lower by 15–20°C. Figure 1 shows the melting curves of $Zn(NO_3)_2\cdot6H_2O$, $Cu(NO_3)_2\cdot6H_2O$ and the mixture $0.85Zn(NO_3)_2\cdot6H_2O+0.15Cu(NO_3)_2\cdot6H_2O$.

The values of the melting points and the enthalpy of melting, calculated from the curves presented in Fig. 1, are given in Table 1.

During dehydration of crystalline hydrates it is assumed that water is evolved on heating in one or more steps. However, release of water from salt hydrates usually includes more than one simple process. That is particularly the case with hydrates of small, highly charged transition metal cations, when water is present as a ligand coordinated to a cation. In these cases dehydration can be regarded as the thermal decomposition of a complex compound.

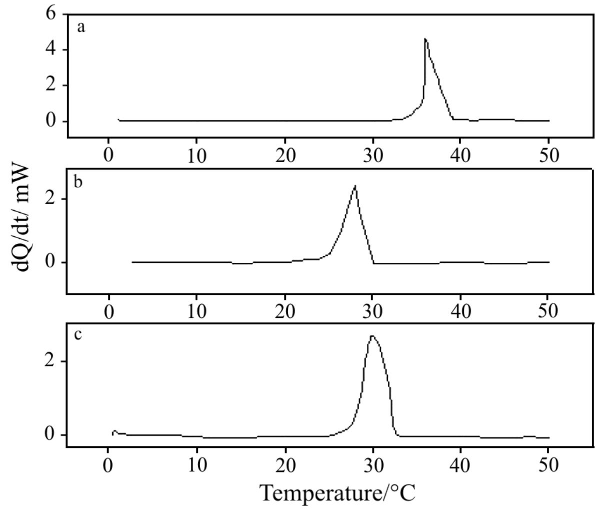

Fig. 1 The melting curves of: a – $Zn(NO_3)_2\cdot H_2O$,
b – $Cu(NO_3)_2\cdot6H_2O$,
c – $0.85Zn(NO_3)_2\cdot6H_2O+0.15Cu(NO_3)_2\cdot6H_2O$

Table 1 The melting points and the enthalpies of melting of the hydrated species

Species	*m.p.*/°C	Δ*H*	
		J g^{-1}	kJ mol^{-1}
$Zn(NO_3)_2\cdot6H_2O$	36.2	156	46.5
$Cu(NO_3)_2\cdot6H_2O$	26.1	111	32.8
$0.85Zn(NO_3)_2\cdot6H_2O$ $+0.15Cu(NO_3)_2\cdot6H_2O$	29.0	165	49.0

Dehydration of $Zn(NO_3)_2\cdot6H_2O$ and $Cu(NO_3)_2\cdot6H_2O$ has not been extensively studied so far. In the tabulated reference data the dehydration of $Zn(NO_3)_2\cdot6H_2O$ was described as simple water release, occurring in the temperature interval 105–131°C [23] and the dehydration of $Cu(NO_3)_2\cdot6H_2O$ as release of 3 moles of H_2O starting at the melting point (26.4°C) and followed by HNO_3 evolution at 170°C [23] or as release of water and mixture of nitrogen oxides in the temperature interval 90–180°C [13].

Our studies, presented in this work showed that the scheme of the thermal decomposition of $Zn(NO_3)_2\cdot6H_2O$ and $Cu(NO_3)_2\cdot6H_2O$ is more complicated and several processes may occur simultaneously or consecutively.

The TG curves of $Zn(NO_3)_2\cdot6H_2O$ and $Cu(NO_3)_2\cdot6H_2O$, scanned from room temperature to 800°C, are shown in Fig. 2. To facilitate readings of the transition temperature the derivative forms of the TG curves are also presented in Fig. 2.

XRD analysis of the solid end products showed that crystalline oxides ZnO (PDF: 36-1451) and CuO (PDF: 05-0661) are obtained as the results of the thermal decomposition of $Zn(NO_3)_2\cdot6H_2O$ above 300°C and $Cu(NO_3)_2\cdot6H_2O$ above 270°C, respectively. From DSC studies no structural changes were observed after the temperatures corresponding to the initial formation of ZnO (300°C) and CuO (270°C). In the same time, XRD patterns of the solid decomposition products, taken at the initial and the final temperature of the TG plateau scans, were identical. The intermediate solid products of the partial thermal decomposition at 200–210°C were also analysed by XRD. The products were identified as $Zn(NO_3)_2\cdot2Zn(OH)_2$ (PDF: 18-1486) and $Cu_2(OH)_3NO_3$ (PDF: 14-687). Due to the limits of the experimental set up the gaseous decomposition products were not analysed.

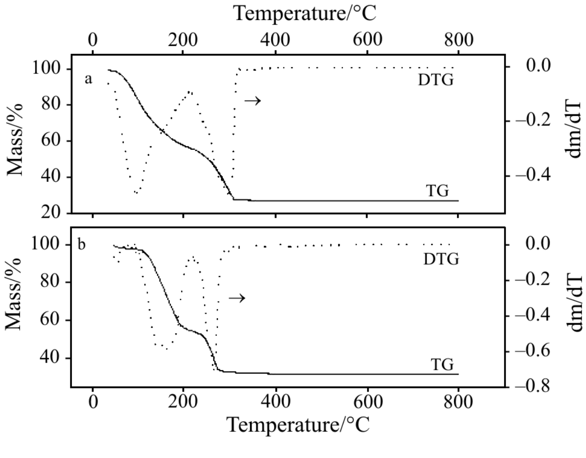

Fig. 2 TG and DTG diagrams of a – $Zn(NO_3)_2\cdot6H_2O$ and b – $Cu(NO_3)_2\cdot6H_2O$

On the basis of the composition of the solid products, the mass loss and the mass balance, the following decomposition schemes are proposed:

$Zn(NO_3)_2 \cdot 6H_2O$

$$3Zn(NO_3)_2 \cdot 6H_2O_{(s)} \rightarrow Zn(NO_3)_2 \cdot 2Zn(OH)_{2(s)} + +4HNO_{3(g)} + 14H_2O_{(g)} \quad (2)$$

between 95–215°C and

$$Zn(NO_3)_2 \cdot 2Zn(OH)_{2(s)} \rightarrow 3ZnO_{(s)} + 2NO_{2(g)} + +H_2O_{(g)} + O_{2(g)} \quad (3)$$

between 205–305°C.

$Cu(NO_3)_2 \cdot 6H_2O$

$$2Cu(NO_3)_2 \cdot 6H_2O_{(s)} \rightarrow Cu_2(OH)_3NO_{3(s)} + +H_2O_{(g)} + HNO_{3(g)} \quad (4)$$

between 150–215°C and

$$Cu_2(OH)_3NO_{3(s)} \rightarrow 2CuO_{2(s)} + HNO_{2(g)} + H_{2(g)} \quad (5)$$

between 215–270°C.

In addition to the processes (2) to (5) melting of lower hydrates, obtained after partial dehydration occur above 100°C. DSC scans taken simultaneously with TG measurements showed multipeak endothermic curves, with superimposed caloric effects.

$0.85Zn(NO_3)_2 \cdot 6H_2O + 0.15Cu(NO_3)_2 \cdot 6H_2O$

It has been described earlier that CuO may react with oxides of some other metals (Co, Fe, Mn) producing mixed oxides with spinel structure [5, 13]. The mixed oxides were obtained by solid–solid interactions, starting from hydrated salts. The composition of the oxides depended on the concentration of single oxides and on the reaction temperature. Formation on mixed oxides of copper with zinc was not reported, except in complexes with hydrotalcites [24].

The aim of our studies of the thermal decomposition of the mixture $0.85Zn(NO_3)_2 \cdot 6H_2O + 0.15Cu(NO_3)_2 \cdot 6H_2O$ was to establish the eventual possibility of formation of Zn/Cu mixed oxides, having in mind an indication of possible mixed complex formation in molten state, from the single DSC endothermic peak, as seen in Fig. 1. Since there was an indication that the presence of chloride ion in some cases may promote formation of mixed oxides via formation of oxychlorides [5], attempts were made with addition of chloride ions into the original melt as 0.02 moles of $CuCl_2 \cdot 2H_2O$.

The thermal decomposition of the mixture $0.85Zn(NO_3)_2 \cdot 6H_2O + 0.15Cu(NO_3)_2 \cdot 6H_2O$ with and without chloride addition was studied by TG analysis from room temperature to 1200°C. In order to obtain more accurate data the TG scans were made in two steps (room temperature to 650°C and 400–1200°C), so that the initial mass of the sample was approximately 10 mg. The TG diagrams were divided in two temperature ranges and presented in Fig. 3.

From Figs 3a and b it can be seen that the mass loss reaches a constant value of 28.2% without and 26.1% with the presence of chloride. The mass losses obtained after thermal decomposition at 650°C correspond to the calculated stoichiometric values for formation of the mixtures of ZnO and CuO (the calculated values are 27.4 and 26.7%, respectively). XRD diagrams of the samples taken after thermal treatment up to 650°C showed presence of ZnO and CuO, Fig. 4, curve a. The ratio of the intensities of the main diffraction lines for ZnO and CuO correspond to the initial Zn/Cu ratio.

However, the shapes of the TG curves a and b were different. Consequently, different compositions of the solid intermediate products of the samples after heating to 200°C were identified by XRD analysis. Partially decomposed samples without chloride addition (Fig. 3, curve a) showed the presence of a mixture of $Zn(NO_3)_2 \cdot 2Zn(OH)_2$ (PDF: 18-1486) and $Cu_2(OH)_3NO_3$ (PDF: 14-687). In the mixture containing chloride additions at 200°C (Fig. 3, curve b) XRD analysis showed the presence of $CuCl_2$ (PDF: 34-0198), CuO (PDF: 05-0661), $Zn(NO_3)_2 \cdot 4H_2O$ (PDF: 19-1467) and $Cu_2(OH)_3NO_3$ (PDF: 14-0687). From Fig. 3, curves c and d, it can be seen that there is an additional transition at 840°C in the mixture without chloride, and at 860°C in the mixture with chlorides. These transitions are identified as reduction of CuO and formation of Cu_2O, as observed in pure $Cu(NO_3)_2 \cdot 6H_2O$, but at higher temperature (930°C). The scheme of the reaction is following:

$$2CuO_{(s)} \rightarrow Cu_2O_{(s)} + 0.5O_{2(g)} \quad (6)$$

From XRD diagrams of the solid products of final thermal decomposition, at 1200°C, Fig. 4, curve b, the presence of Cu_2O (PDF: 05-0667) and ZnO (PDF: 36-1451) was identified. No traces of any chloride species were detected in the final solid products. The same XRD patterns were obtained for the samples with and without chloride addition into the initial salt mixture.

In DSC curves, scanned simultaneously with TG analysis the reaction (5) was revealed as a distinct endothermic peak.

The morphology of the solid decomposition products of the mixture $0.85Zn(NO_3)_2 \cdot 6H_2O + 0.15Cu(NO_3)_2 \cdot 6H_2O$ with and without $CuCl_2 \cdot 2H_2O$ added, were analysed by SEM. Straight rods were built from hexagonally shaped particles when zinc and copper oxide were formed from nitrate melts forming agglomerates of

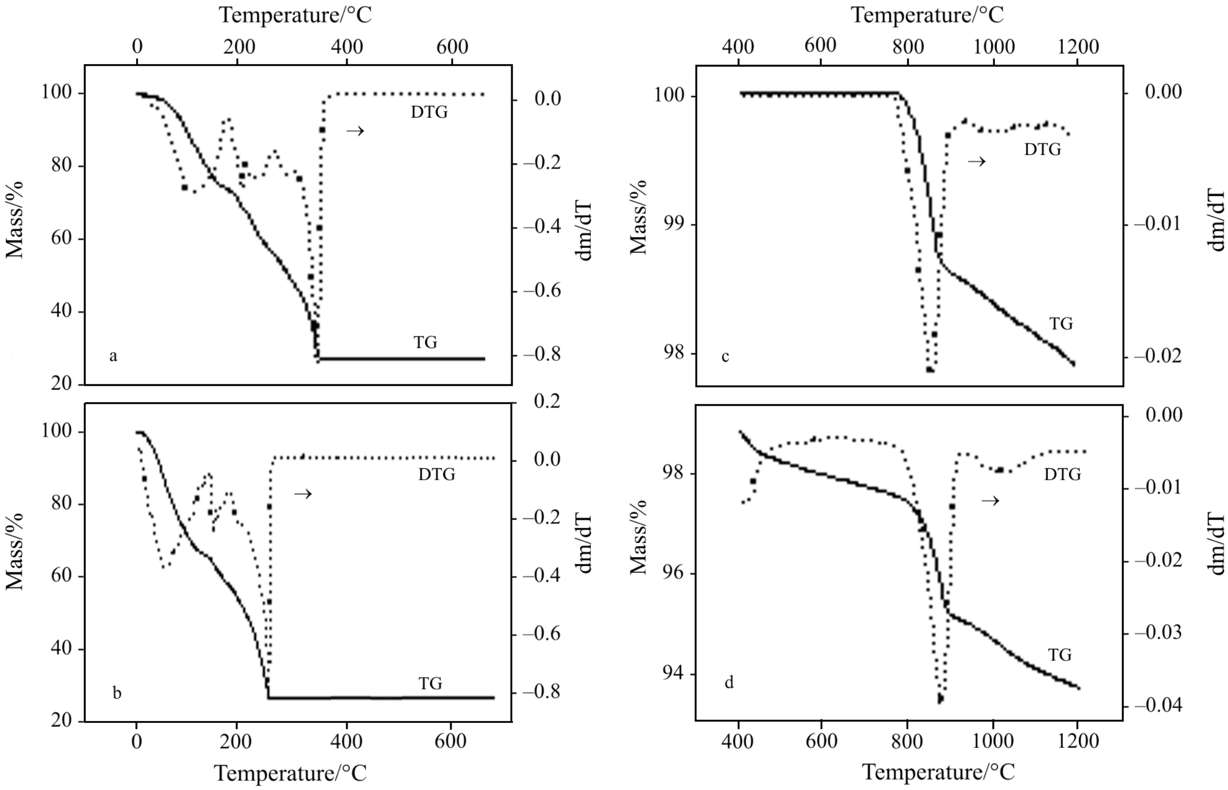

Fig. 3 TG and DTG diagrams of the mixture $0.85Zn(NO_3)_2{\cdot}6H_2O + 0.15Cu(NO_3)_2{\cdot}6H_2O$ scanned up to a – 700 and c – 1200°C; with added 0.02 moles of $CuCl_2{\cdot}2H_2O$ scanned up to b – 700 and d – 1200°C

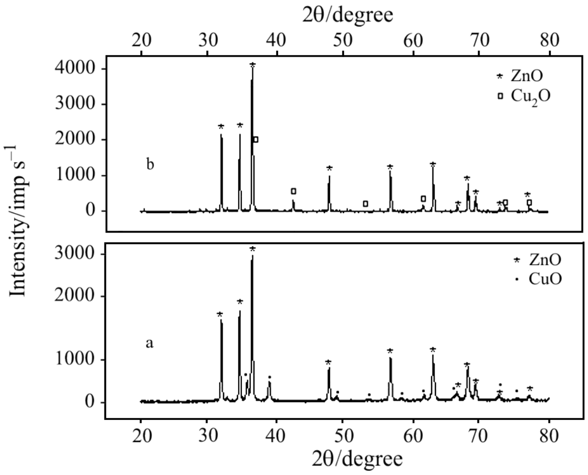

Fig. 4 XRD diagrams of the solid decomposition products at a – 650 and b – 1200°C

comb like structure [25], as shown in Figs 5a and b. The rods were packed in branches when the oxides were prepared from nitrate melts containing chlorides (Fig. 5c). However, preparation of Zn/Cu oxide mixture by gel combustion with citric acid resulted in disrupter to a microporous structure, shown in Fig. 5d. XRD analysis of the latter samples were the same as those presented in Fig. 4a, showing the existence of ZnO and CuO patterns but no Cu_2O_2.

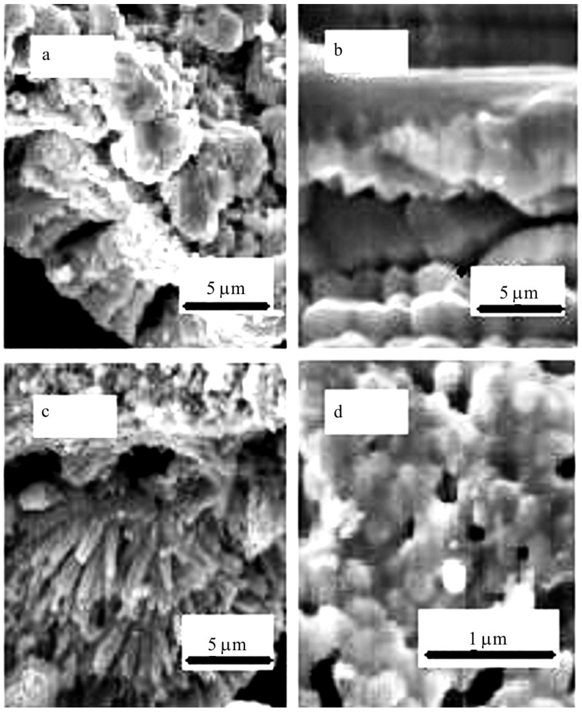

Fig. 5 SEM images of representative structures of ZnO/CuO prepared from: a – and b – mixed nitrates hexahydrates, c – with addition of $CuCl_2$, d – with addition of citric acid

Conclusions

- Solid/liquid equilibria in $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$ and their mixtures were studied by DSC of hermetically sealed samples. Mutual solubility was observed in the entire concentration range
- Single melting peak was assumed as an indication of a complex compound formation in the mixture with composition $0.85Zn(NO_3)_2{\cdot}6H_2O+0.15Cu(NO_3)_2{\cdot}6H_2O$
- Crystalline oxides ZnO, CuO and their mixtures were obtained after thermal decomposition at 650°C of the pure hydrated nitrates and the mixture containing $0.85Zn(NO_3)_2{\cdot}6H_2O+0.15Cu(NO_3)_2{\cdot}6H_2O$
- A mixture of ZnO and CuO with microporous structure was obtained by gel combustion of the $0.85Zn(NO_3)_2{\cdot}6H_2O+0.15Cu(NO_3)_2{\cdot}6H_2O$ mixture with citric acid
- The solid products of thermal decomposition above 840°C are ZnO, CuO and Cu_2O
- Formation of mixed Zn–Cu oxides was not observed, nor has it been known so far, though it is known that oxides of copper can form binary or ternary oxide compounds with other dipositive metal ions from nitrate or nitrate-chloride salts precursors [5, 13]. In this work, addition of chlorides, added as $CuCl_2{\cdot}2H_2O$ resulted only in slight changes of morphology.

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