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# Copper/Zinc Oxide Catalysts. Part XII. Solid Solution Formation in the CuO/ZnO System. X-Ray Powder Diffraction Study

**Juraj Černák**[1,*], **François Gérard**[2], **Charles Kappenstein**[2],
and **Jozef Chomič**[1]

[1] Department of Inorganic Chemistry, Institute of Chemistry, P.J. Šafárik University,
Moyzesova 11, 041 54 Košice, Slovakia
[2] LACCO, UMR-CNRS-6503, Catalyse par les Métaux, Université de Poitiers,
40, Avenue du Recteur Pineau, 86022 Poitiers, France

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**Summary.** Coordination compounds $Zn(\mathit{mal})(H_2O)_2$ (*ZMH*) (*mal*=maleate anion ($C_2H_2(CO_2)_2{}^{2-}$)), $Cu_{0.06}Zn_{0.94}(\mathit{mal})(H_2O)_2$ (*ZCMH*), $Cu(\mathit{mal})(H_2O)$ (*CMH*), and physical mixtures of *CMH* and *ZMH* were used as precursors for calcination experiments in air at 500 and 1000°C lasting 18 hours. The obtained oxides were investigated by X-ray powder diffraction technique. Calcination at 500°C yielded pure zincite phase (ZnO), tenorite phase (CuO), or their mixtures. The calcination of the Zn-rich sample *ZCMH* at 1000°C lead to zincite phase displaying a slightly lower cell volume than the pure zincite phase obtained from Zn-only containing precursor (*ZMH*). These results suggest that the assumed solid solution $Cu_xZn_{1-x}O$ ($x$=0.01–0.02) exhibits a solubility limit lower than the copper content in the *ZCMH* precursor (6 mol-%). On the other hand, the calcination of the Cu-rich samples at 1000°C, in the presence of Zn(II), yielded tenorite phase exhibiting cell parameters significantly different from those reported for the pure tenorite phase, due to the formation of $Zn_{0.03}Cu_{0.97}O$ solid solutions. All these results are corroborated by intensity analysis of the diffraction peaks.

**Keywords.** Copper oxide; Zinc oxide; Solid solution; XRD; Calcination.

## Introduction

Synthesis of methanol from syngas is a well established industrial process and Cu/ZnO based heterogeneous catalysts are used since 1966. The active catalytic phases are mainly prepared by a co-precipitation method followed by air-calcination and activation under hydrogen [1]. It was claimed by various authors that during the catalyst preparation different types of solid solutions (SS) can be formed: $Cu^{2+}/ZnO$, $Cu^{+}/ZnO$, and $Zn^{2+}/CuO$ [2–7]. Moreover, these solid

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[*] Corresponding author. E-mail: cernakju@kosice.upjs.sk

solutions could play an important role for the catalytic activity of the corresponding materials.

For the first type of SS, *i.e.* $Cu^{2+}/ZnO$, two contradictory opinions concerning its genesis appeared in the literature: (i) formation during low temperature calcination process (350°C) with a high solubility limit of the cupric cations (10 mol-%) [2]; or (ii) formation only after a prolonged calcination at high temperature (at least 900°C) with a much lower limit of solubility of tetrahedral $Cu^{2+}$ in the ZnO framework (about 1 mol-%) [3]. Almost the same limits of solubility of CuO in ZnO were found after calcination of mixed hydroxides at 900°C (1.6 mol-%) [8] and by means of chemical vapour transport using $Cl_2$ as transporting agent at 800–900°C (2 mol-%) [9], respectively.

The $Cu^{+}/ZnO$ SS was claimed to be formed after the reduction of the diphasic system CuO/ZnO by hydrogen at 250°C. The $Cu^{+}$ saturation limit in ZnO was found to be 17 mol-% [4].

Two different suitable temperatures were reported for the formation of the SS of $Zn^{2+}$ in the tenorite phase CuO: 350°C [5] or 1000°C [6, 7]; nevertheless they agree about the solubility limit (5 mol-%). A very similar value (4 mol-%) has been found by *Locmelis et al.* [9] whereas a lower limit of solubility has been claimed recently by *Grygar et al.* [8] (1.2 mol-% of ZnO).

This study was undertaken to check the possibility of solid solution formation in the CuO/ZnO and ZnO/CuO systems from the same class of well defined new bimetallic compounds or mixtures. This purpose can be achieved either by comparison of the cell parameters and by quantitative analysis from diffraction peak intensity of the resulting zincite and tenorite phases; these phases are prepared by prolonged air calcination at two temperatures 500 and 1000°C. The first temperature (500°C) was taken as the lowest possible temperature leading to the total decomposition of the ligands in the precursors in line with their thermal properties [10]. The higher temperature (1000°C) was chosen from previous suggestions for solid solution formation [6–8] with regard to the requirement of adequate diffusion rate of the respective ions in the oxidic phase and stability of CuO [3]. In order to reach an equilibrium state (slow diffusion) the calcination time was chosen to be 18 hours as previously suggested [3]. The precursors used for calcination experiments are: (i) zinc maleate dihydrate $Zn(\mathit{mal})(H_2O)_2$ (*ZMH*) (*mal*=maleate anion ($^{-}O_2C{-}CH{=}CH{-}CO_2{}^{-}$)), (ii) its bimetallic analogue $Cu_{0.06}Zn_{0.94}(\mathit{mal})(H_2O)_2$ (*ZCMH*), (iii) copper(II) maleate monohydrate $Cu(\mathit{mal})(H_2O)$ (*CMH*), and (iv) physical mixtures of *CMH* and *ZMH*. The crystal structures and properties of *ZMH* and *ZCMH* have been already described [10–12]. We present here the results based on X-ray powder diffraction studies of the different samples after calcination.

## Results and Discussion

### *Calcination*

Cu/ZnO based catalysts are usually prepared by calcinations of precursors issued from coprecipitation procedures, but these procedures lead often to polyphasic systems. The phases formed after calcination are generally investigated by various techniques including XRD. In our experiments, the new precursors are coordination compounds containing maleate ligands and exhibiting well-defined composition. The important calcination length (18 hours) was necessary to enable copper or zinc atoms to diffuse into the crystallites of zincite or tenorite phase, respectively [14].

### *CuO in ZnO*

XRD patterns of pure zinc (*ZMH*) and zinc-rich precursor (*ZCMH*) after calcinations are given in Fig. 1. As expected, they indicate the presence of the well crystallized zincite phase for both samples for the two calcination temperatures. In the case of *ZCMH* we observed also the presence of minor tenorite phase (CuO) at both temperatures. Therefore a segregation of copper and zinc containing phases had occurred and the limit of copper solubility in the solid solution – if formed – is significantly lower than the mol percentage of copper in the bimetallic precursor (6 mol-%). No visible shift of the respective diffraction peaks originating from the zincite phase could be detected and the observed intensities agree well with the PDF data (36–1451) [15].

To have a closer view on the influence of copper we have refined the cell parameters of the zincite phase. The results are gathered along with the cell parameters from literature in Table 1. The respective cell parameters and cell volumes of our samples are very close to the PDF value and the differences are small, within $2\sigma$ range. Only parameter $c$ displays a significant lower value (shift higher than $10\sigma$) for sample *ZCMH*-1000. This difference can be explained by a partial substitution of zinc cations by copper cations which will affect more strongly the parameter $c$ corresponding to the packing of the alternate oxygen and zinc layers corresponding to a *hexagonal closed packed* (*hcp*) (wurtzite) type structure. On the

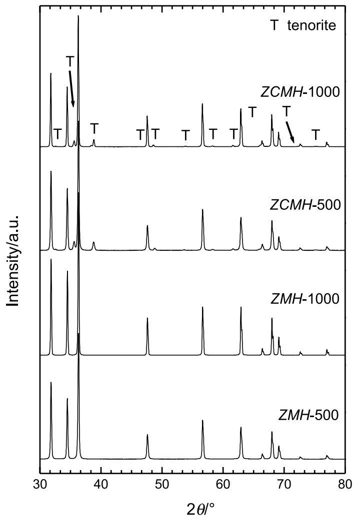

**Fig. 1.** X-Ray powder diffraction pattern of samples *ZMH*-500, *ZMH*-1000, *ZCMH*-500, and *ZCMH*-1000

**Table 1.** Cell parameters of the zincite (ZnO) phase

| Precursor or sample | Temperature of calc./°C | Phase(s) | $a/\text{Å}$ | $c/\text{Å}$ | $V/\text{Å}^3$ | Ref. |
|---|---|---|---|---|---|---|
| ZnO | * | Z | 3.24982(9) | 5.2066(2) | 47.622 | [15] |
| *ZMH*-500 | 500 | Z | 3.24984(9) | 5.2059(2) | 47.615(4) | |
| *ZMH*-1000 | 1000 | Z | 3.25002(7) | 5.2053(2) | 47.615(4) | |
| *ZCMH*-500 | 500 | Z + T | 3.24976(10) | 5.2057(2) | 47.612(5) | |
| *ZCMH*-1000 | 1000 | Z + T | 3.25005(9) | 5.2030(2) | 47.595(5) | |

* Value not given, T=tenorite, Z=zincite

other hand, the cell parameter *a* represents mainly the packing of the oxygen atoms in one layer of the *hcp* structure and will be therefore much less affected by cation substitution. Taking into account the difference in ionic radii of $Zn^{2+}$ (0.74 Å) and $Cu^{2+}$ (0.71 Å), for co-ordination number 4 [16], and the experimental *c* parameters for both samples calcined at 1000°C (*i.e. ZMH*-1000 and *ZCMH*-1000, Table 1), it is possible to obtain, from geometrical considerations, a calculated rough value of the substitution level of the order of 3 mol-%, *i.e.* lower than the current content of copper in the samples *ZCMH* (6 mol-%). This low value is of the same order of magnitude as the reported data (1.6 mol-% [8] and 1 mol-% [3]) and explains the formation of tenorite. Similar qualitative observations, based on volume variations and unit cell shrinkage, have been discussed in Ref. [7].

This result can be compared to a quantitative phase analysis based on diffraction peak intensity. The intensities (taken as the surface area) of the strongest three diffraction peaks of ZnO (101, 100, 002) and CuO (111 + 200, 002 + 11-1, 20-2) have been used to estimate the molar ratio of the two phases. The reference data have been obtained from an equimolar mechanical mixture of both pure precursors *ZMH* and *CMH* after calcination at 500°C (intensity ratio=1.733) and 1000°C (intensity ratio=1.681). The intensity ratio of sample *ZCMH*-500 (=0.092) leads to a molar ratio CuO:ZnO=0.05:0.95, in very good agreement with the data obtained from EDX experiments on the precursor (0.06:0.94) [10] showing a very limited solid solution formation.

After calcination at 1000°C, the corresponding intensity ratio is significantly lowered (0.076) which leads to a lower molar ratio CuO:ZnO=0.04:0.96. This indicates that a part of the copper atoms are incorporated into the zincite structure, in good accordance with the value obtained from the cell parameter variation. The estimated value of copper in the solid solution is in the range 1–2%.

### *ZnO in CuO*

The phases formed during air-calcination of pure copper precursor (*CMH*) and a copper-rich sample have been determined. The Cu-rich precursor is a mechanical mixture of *CMH* and *ZMH* in the molar ratio 9:1 (*CZ*91). This ratio was selected in order to override the expected solubility limit of ZnO in CuO [6, 7]. XRD patterns are given in Fig. 2. They indicate the expected presence of the well crystallized tenorite CuO phase for all samples. In the case of *CZ* samples, the zincite phase

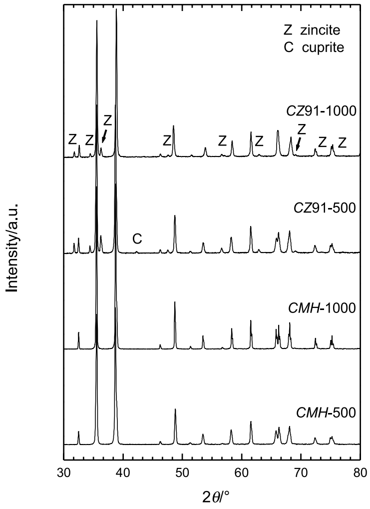

**Fig. 2.** X-Ray powder diffraction pattern of samples *CMH*-500, *CMH*-1000, *CZ*91-500, and *CZ*91-1000

is also present meaning that the limit of zinc solubility in CuO is lower than 10 mol-%. Moreover, in the case of the sample *CZ*91-500, a weak peak, denoted C, at 42.5° is present (Fig. 2) and assigned to the presence of $Cu_2O$ (cuprite) phase in the mixture. This observation suggests that during calcination, a part of the copper atoms is reduced to oxidation number +I by the maleate ion. Calcination at higher temperature leads to a re-oxidation of these $Cu^I$ atoms, as it can be seen by the disappearance of this peak for sample *CZ*91-1000.

Figure 3 shows obvious shifts of the individual diffraction peaks originating from the predominant tenorite phase in the presence of minor zincite phase after calcination at 1000°C, by comparison with a sample originating from pure copper containing precursor (*CMH*). In order to obtain more accurate data, we have refined the cell parameters of the tenorite phase and the results are gathered in Table 2. The respective cell parameters and cell volumes after calcination at 500°C are very

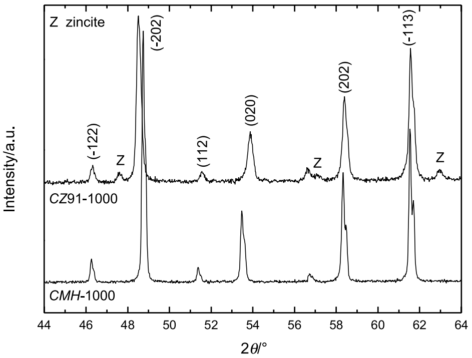

**Fig. 3.** X-Ray powder diffraction pattern of selected region of samples *CMH*-1000 and *CZ*91-1000 showing important shifts in peaks' positions; the numbers over some peaks are the *Miller* indices of the tenorite phase

**Table 2.** Cell parameters of the tenorite (CuO) phase

| Precursor or sample | Calcin. temp./°C | Phase(s) | Cell parameters [Å, °] | | | | Vol./Å$^3$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | $a$/Å | $b$/Å | $c$/Å | $\beta$/° | | |
| *HN* | 1000 | T | 4.68830 | 3.42290 | 5.13190 | 99.51 | 81.22 | [15] |
| *CMH*-500 | 500 | T | 4.6834(3) | 3.4252(2) | 5.1328(4) | 99.38(1) | 81.24(8) | |
| *CMH*-1000 | 1000 | T | 4.6864(3) | 3.4246(2) | 5.1314(3) | 99.53(1) | 81.22(2) | |
| *CZ*91-500 | 500 | T+Z | 4.6877(5) | 3.4229(4) | 5.1319(5) | 99.46(1) | 81.22(3) | |
| *CZ*91-1000 | 1000 | T+Z | 4.7069(2) | 3.4026(2) | 5.1299(4) | 99.85(1) | 80.95(1) | |

T=tenorite, Z=zincite, *HN*=hydroxynitrate

close to those given in the PDF database for a tenorite sample issued from calcination of pure hydroxynitrate precursor at 1000°C [15, 17]. On the other hand, significant differences for $a$ (elongation by ~0.02 Å), $b$ (shortening by ~0.02 Å), and $\beta$ (opening of the angle by ~0.4°) cell parameters are observed for the sample calcined at higher temperature (*CZ*91-1000). These differences result in the lowering of the volume of the tenorite unit cell by about 0.2 Å$^3$. The same phenomenon was observed by *Porta et al.* for the tenorite phases obtained by calcination at 1000°C of hydroxynitrate (Cu:Zn=2:1 molar ratio) or malachite phase type precursors (Cu:Zn=2:1 molar ratio). Moreover, they have observed that the shrinkage of the tenorite unit cell volume is more pronounced in the case of malachite type precursor [7].

The ionic radius of hexacoordinated Zn$^{2+}$ ions (0.88 Å) is slightly higher than the ionic radius of Cu$^{2+}$ ions (0.87 Å), in disagreement with the experimental cell volume shrinkage. But we have to take into account the strong coordination plasticity of Cu(II) due to the *Jahn-Teller* effect. The copper environment in the tenorite phase displays four Cu–O bonds (1.96 Å) in the CuO$_4$ plane, while two oxygen atoms are at longer distances (2.78 Å) roughly perpendicular to the CuO$_4$ plane (inclination angle is 17°) [18]. Therefore, the substitution of Cu$^{2+}$ by Zn$^{2+}$ ions leads to local modification of the metal ion coordination sphere from strongly distorted octahedral (copper in tenorite) toward more regular octahedral (preferred by zinc), resulting in a slightly more compact structure. This is also supported by a comparison of the calculated volumes of the CuO$_4$O$_2$ and ZnO$_6$ (*e.g.* Zn–O 2.11 Å taken from smithsonite [19]) bipyramids: 14.2 Å$^3$ and 12.5 Å$^3$, respectively. This explanation is in line with the explanation given by *Porta et al.* [7].

From the value of the intensity ratios $I$(CuO)/$I$(ZnO) (13.86 at 500°C and 20.14 at 1000°C) the following quantitative phase analysis can be obtained (see above): molar ratios CuO:ZnO=0.89:0.11 at 500°C and 0.92:0.08 at 1000°C. The first value agrees well with the expected ratio (0.90:0.10). The calcination at 1000°C leads to a significant diminution of the ZnO phase content, which parallels the shift of the CuO diffraction peaks. The observed diminution of the zincite phase content in the case of the 9:1 initial mixture suggests a value of 3% for incorporated zinc in the tenorite. This value is between the reported values of Zn$^{2+}$ solubility in tenorite phase: 5 mol-% [6, 7] or 1.2 mol-% [8].

## Conclusions

Calcination of new well-defined zinc, copper, or Cu–Zn bimetallic coordination compounds containing maleato ligands, yielded zincite, tenorite, and a mixture of zincite and tenorite phases. The calcinations at low temperatures (500°C) gave pure zincite and tenorite phases or their mixtures with possible presence of the cuprite phase. The calcinations at higher temperatures (1000°C) lead to modified phases, due to the formation of solid solutions. Variations of the unit cell dimensions are more important in the case of the tenorite phase indicating formation of the well crystallized $Zn_xCu_{1-x}O$ solid solution based on the tenorite phase. Intensity measurements gave $x=0.03$. The precise determination of the zincite phase cell parameters showed a small shrinking of the zincite unit cell volume, which was at the borderline of significance. From diffraction peak intensity the formula $Cu_xZn_{1-x}O$ ($x=0.01$–$0.02$) is proposed.

## Experimental

### *Preparation and Calcination*

The precursors *ZMH*, *ZCMH*, and *CMH* were prepared as described elsewhere [10–12]. They were ground and calcined in ceramic crucible at 500 and 1000°C during 18 hours in static air. The calcined samples are designed S-500 and S-1000, where S represents the precursor. Moreover, a mechanical mixture of *CMH* and *ZMH* (Cu:Zn=9:1 molar ratio) has been prepared and treated as described above and the calcined samples are called *CZ*91-500 and *CZ*91-1000.

### *X-Ray Powder Diffractometry*

X-Ray powder diffraction (XRD) pattern were taken from a computerized Siemens-Bruker D-500 diffractometer using backmonochromatized CuK$\alpha$ radiation ($\lambda$ ($K_{\alpha 1}$)=1.540981 Å, graphite monochromator) in the $2\theta$ range 30–120° with sieved samples (less than 20 $\mu$m). The diffractograms were recorded in step mode (0.02°, 10–20 s). Data handling was carried out by using the software package EVA and FIT (Socabim, France). The cell parameters were refined using the program U-FIT [13].

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