Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 451–455

www.elsevier.com/locate/jeurceramsoc

Coprecipitation of copper/zinc compounds in metal salt–urea–water system

Zorica Crnjak Orel[a,*], Jadran Maček[b,1], Marjan Marinšek[b,2], Stane Pejovnik[b,3]

[a] *National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*
[b] *Faculty of Chemistry and Chemical Technology, Aškerčeva 5, SI-1000 Ljubljana, Slovenia*

Abstract

A study of composite and structural changes of particles prepared by coprecipitation in solutions of Cu^{2+} and Zn^{2+} salts at different starting molar ratios of the corresponding metal nitrates (4:1, 2:1, 1:1, 1:2, 1:4) in the presence of urea is described. The effects of the initial concentration ratios and the ageing time on the final product were discussed in some detail. The final solids were characterized by SEM–EDS, XRD. On ageing at 85 °C, the change from initially amorphous particles to crystalline structure takes place and the results depend on the metal ratio used.

Keywords: Coprecipitation; Spectroscopy; X-ray methods; Grain size; Nanocomposites

1. Introduction

The composite Cu/Zn-oxide particles have been used as catalysts for water-gas shift reaction and methanol synthesis.[1–3] These solids were mostly prepared by precipitation in aqueous solutions of the corresponding metal nitrates in the presence of either sodium or ammonium carbonates that yielded hydroxy-carbonate precursors. The later were then converted to mixed oxides by calcination. The importance of identifying phases of the intermediates and products with different Cu/Zn ratios was stressed by Stone and Waller[1]

The homogeneous alkalization of metal salt solutions by hydrolysis of urea was widely explored for the preparation of pure or mixed metal oxides.[4–7] In mixed systems, various phases can form. Such solids composed of spherical particles were always amorphous, while particles of other morphologies were crystalline.[5]

Whittle et al.[2] showed the morphological and composite changes of non calcined precursors of copper zinc oxide (Cu:Zn = 2:1) formed during the coprecipitation from metal nitrate solutions by sodium carbonate, the influence of aging, and its effect on catalyst properties. By reducing the concentration of carbon dioxide with air which was passed through the reaction mixtures, they reported about Cu-rich nanoparticles formation. The number and size of the product particles were strongly dependent on the ageing time.

Two methods of preparation of Cu/Zn-oxide catalyst were compared in the study of Shishido et al.,[3] i.e., coprecipitation with sodium carbonate in aqueous solutions of metal nitrates, and homogeneous precipitation using urea hydrolysis. The latter method yielded a better catalyst for hydrogen production by steam reforming of methanol.

Saler-Illia et al.[6] also explore a homogeneous precipitation method for the mixed copper–zinc basic carbonate in order to prepare precursors of binary Cu/ZnO catalyst. The composition of the obtained solids depended on the initial reactant concentration and ageing time. At low zinc concentration, a mixture of zincian–malachite and Zn doped tenorite were obtained. With prolonged ageing zincian–malachite dissolves and zinc-doped tenorite was formed. Depending on the quantity of each metal ion aurichalcite (A), zinc–malahite and Zn-doped tenorite were formed.

This work describes the preparation of mixed Cu/Zn basic carbonates prepared from different molar copper to zinc ratios in the starting solutions (4:1, 2:1, 1:1, 1:2 and 1:4) by ageing aqueous solutions of zinc and copper nitrates in the presence of urea at temperatures up to 85 °C. These materials have been characterized by various techniques.

---

[*] Corresponding author. Tel.: +386 1 476 0 236; fax: +386 1 476 0 300.
E-mail addresses: zorica.crnajk.orel@ki.si (Z.C. Orel), jadran.macek@fkkt.uni-lj.si (J. Maček), marjan.marinsek@fkkt.uni-lj.si (M. Marinšek), stane.pejovnik@fkkt.uni-lj.si (S. Pejovnik).
[1] Tel.: +386 1 241 9 200; fax: +386 1 241 9 220.
[2] Tel.: +386 1 241 9 204; fax: +386 1 241 9 220.
[3] Tel.: +386 1 241 9 202; fax: +386 1 241 9 220.

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.04.071

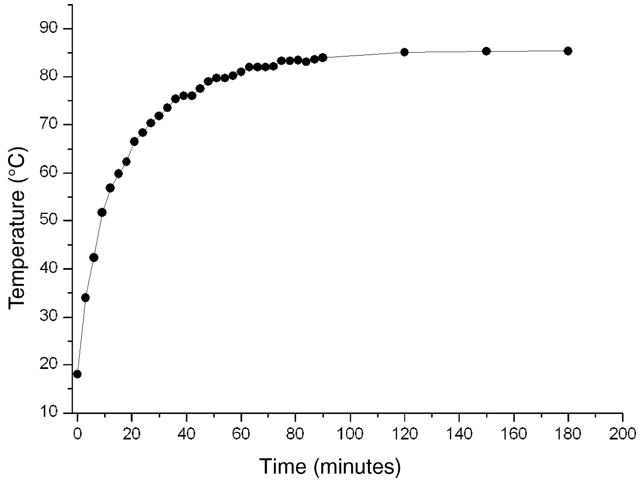

Fig. 1. Temperature profile in the test tube as a function of time.

2. Experimental

All reagents were analytical grade. To avoid hydrolysis on storage, fresh stock solutions were prepared from $Cu(NO_3)_2{\cdot}2.5H_2O$ (Aldrich) and $Zn(NO_3)_2{\cdot}2H_2O$ (Aldrich) and urea (Aldrich). All precipitation experiments were carried out in 14 cm^3 tightly sealed screw-capped borosilicate test tubes.

Predetermined volumes of Cu(II)-, Zn(II)-nitrate, and urea stock solutions, and water were used to obtain desired metal ion ratios and reactants concentrations. In all experiments, 10 cm^3 of these solutions were poured into 14 cm^3 screw-capped borosilicate test tubes which were placed into a preheated oven (90 °C) and kept for various time intervals. After 90, 120 and 180 min, the tubes were quenched to room temperature in cold water. During these experiments, the temperature was measured in the center of test tubes with a Fluke 54 II thermocouple type K with thickness of 1 mm. The resulting temperature profile in the test tube is reproduced in Fig. 1.

In all experiments, the total concentration of urea and metal ions were kept constant at 0.5 and 5×10^{-3} mol dm^{-3}, respectively. Five different molar ratios of Cu/Zn were prepared, e.g., 4:1, 2:1, 1:1, 1:2 and 1:4. The resulting solids were characterized by scanning field emission electron microscopy (SEM, Zeiss Supra 35 VP with EDS analyzer), while X-ray diffraction analyses (XRD) were carried out on a Siemens D-5000 X-ray diffractometer.

3. Results and discussion

Scanning electron micrographs in Figs. 2–4 illustrate the effect of the reaction time on the formation of particles at different Cu/Zn ratios. In all three systems, at first somewhat polydisperse spheres are formed which eventually change into much larger spheres of composite structure (formation of dandelions). In addition to these three systems, experiments were carried out with two other metal ion ratios and some general observations during the formation of particles in all five cases, together with the results of the EDS analyses are summarized in Table 1.

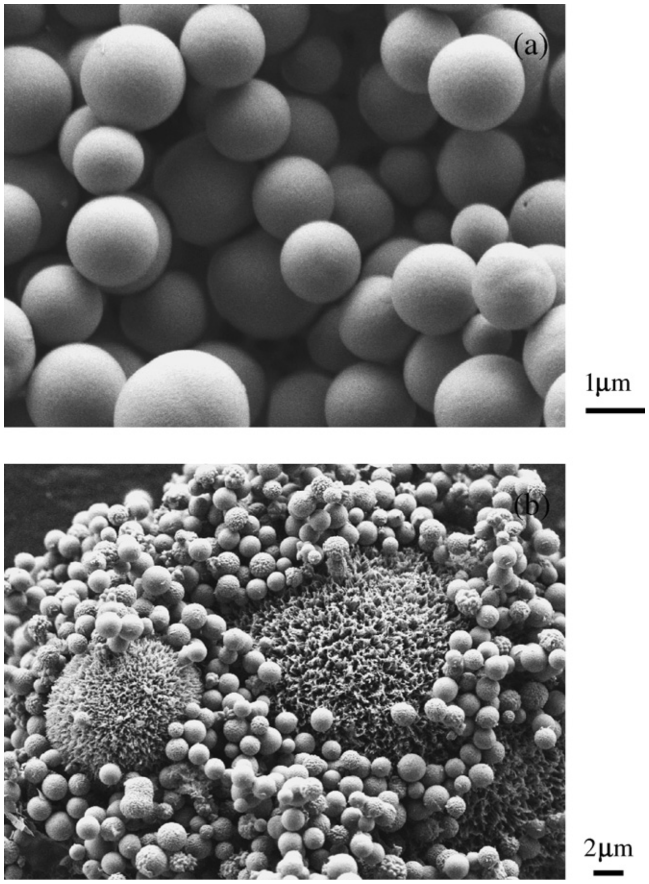

Fig. 2. SEM images of samples prepared at Cu:Zn 2:1: (a) aged 90 min, (b) aged 180 min.

The XRD (Fig. 5) of all studied systems confirmed that these solids are basic carbonates as listed in Table 1.

The electron micrographs show rather dramatic changes of the originally precipitated solids, with time both in terms of particle structure and size. The conversion from amorphous to crystalline solids seems to proceed through a solution/re-precipitation process with the formation of uniform large composite dispersed solids. This mechanism is further corroborated by XRD (Fig. 5). The XRD analysis of the prepared coprecipitates has shown that the initial spherical particles, generated at 90 min are amorphous with a modal size of 1 μm. The chemical composition of these original particles was essentially the same regardless of the ratio of $Cu(NO_3)$ and $Zn(NO_3)$ in the starting solution. Thus, the EDS spot analysis showed that the solids are always Cu-rich consisting of 81–99 at.% Cu and 19–1 at.% of Zn (Table 1). Only at four times excited Zn^{2+} concentration in reacting solutions ($Cu^{2+}/Zn^{2+} = 1{:}4$) XRD spectra reviled weak bands, most likely copper zinc carbonate hydroxide even at ageing times of 90 min. High Cu/Zn molar ratio in particles formed during early stages of ageing is in general agreement with the results obtained by Soler-Illia et al.[6] According to their work amorphous Cu phase, due to lower solubility constant, precipitates first, adsorbs Zn(II) but does not trigger the heterogeneous nucleation of mixed coprecipitate such as aurihalcite which takes place at the expense of hydroxylated Zn(II) aqueous species and already formed amorphous Cu phase. Further crystal growth

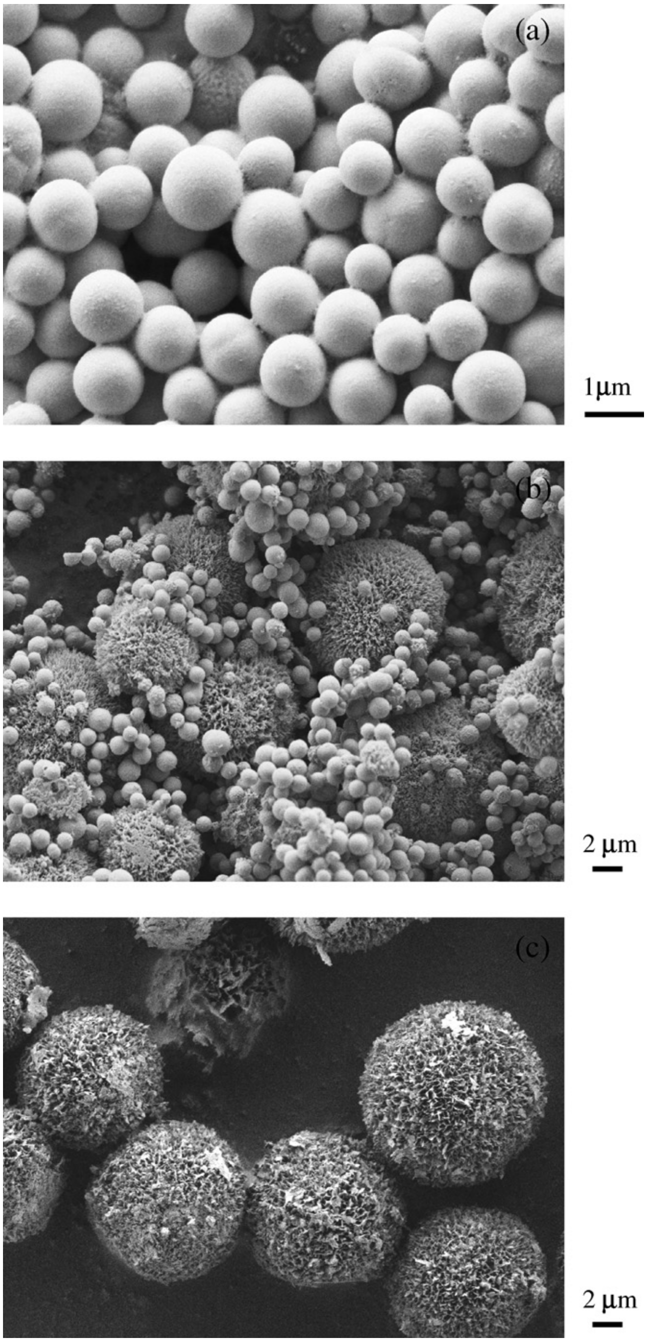

Fig. 3. SEM images of samples prepared at Cu:Zn 1:2: (a) aged 90 min, (b) aged 120 min, (c) 180 min.

yields mixed Cu/Zn hydroxycarbonates. With increasing ageing time two major effects are observed, i.e., the size of particles change and the formation of new phase take place. Details of this conversion depend on the ratio of the two metal nitrates in the initial reactant solutions as displayed in Table 1 and Figs. 5 and 6.

Thus, after 120 min at the Cu^{2+}/Zn^{2+} 4:1 and 2:1 (Fig. 2a), still only the amorphous spheres are observed, while at other concentrations, much larger structurally composite spheres are already formed. The latter represents a small fracture of the particles at the Cu^{2+}/Zn^{2+} 1:1 and 1:2 (Fig. 3b), while the conversion is completed at the ratio of 4:1 (Fig. 4b). The converted

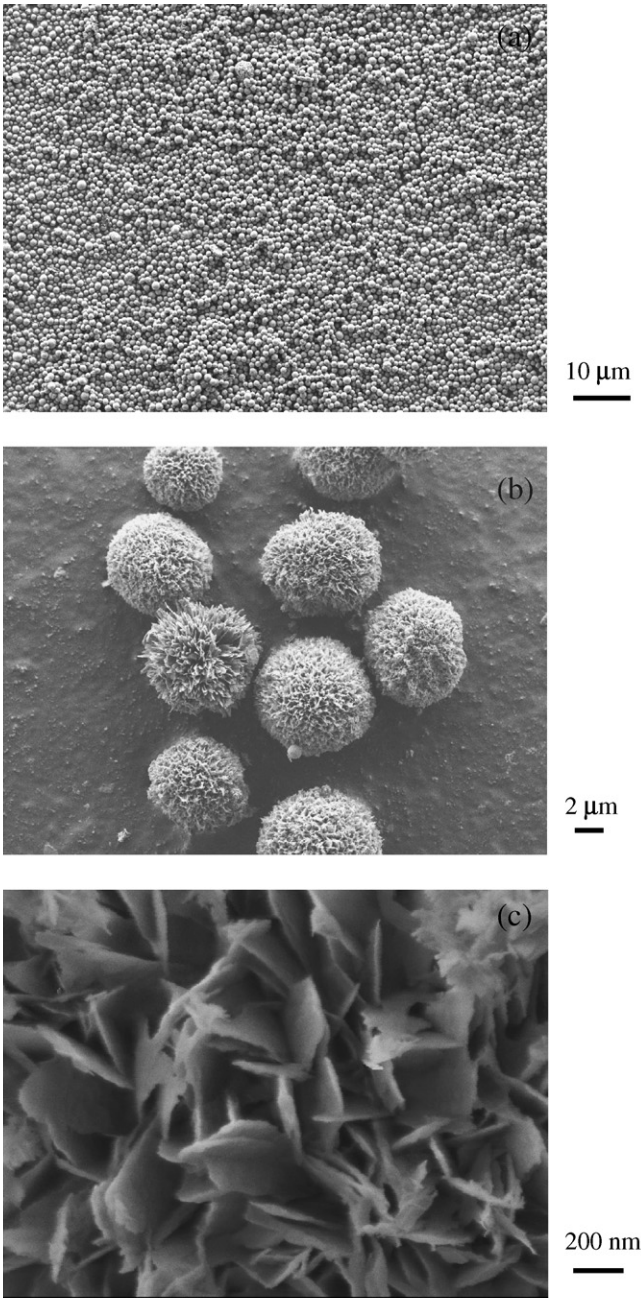

Fig. 4. SEM images of samples prepared at Cu:Zn 1:4: (a) aged 90 min, (b) aged 120 min.

large particles are crystalline (Fig. 6 with peaks characteristics of aurichalcite A). At still higher zinc to copper ratio, the entire content of amorphous particles is transformed into the larger rather complex spheres consisting of copper zinc carbonate hydroxide (H). A detailed SEM of the surface of these particles (Fig. 4c) clearly displays their external complex nature. This finding is consistent with the present understanding that many larger (colloidal) particles are formed by aggregation of small (nano-size) precursors,[8–10] which appears to be the case in the described system.

With subsequent aggregation final particles are formed. X-ray diffractograms of samples prepared after ageing of 180 min

Table 1
Samples prepared by homogeneous precipitation from solutions of copper nitrate and zinc nitrate with urea at temperature up to 85 °C at urea = 0.5 M, $Cu^{2+} + Zn^{2+} = 5 \times 10^{-3}$ M

Sample Cu:Zn ratio	Ageing (min)	pH	XRD	EDS at.% Cu	EDS at.% Zn
4:1	90	6.3	Amorphous	~99	~1
	120	6.8	Amorphous	~99	~1
	180	7.9	M (predomantly) + A	~98	~2
2:1	90	6.2	Amorphous	~98	2.4
	120	6.6	Amorphous	~97	2.8
	180	7.7	Amorphous	~97	~3
			M + A	~37	~63
1:1	90	6.5	Amorphous	~96	~4
	120	6.7	Amorphous	~91	~9
			A	~22	~78
	180	7.9	Amorphous	~94	~6
			M + A	~48	~52
1:2	90	6.6	Amorphous	~92	~8
	120	7.1	Amorphous	~91	~9
			A	~30–40	~70–60
	180	8.0	A, M (some)	~43	~57
1:4	90	6.9	Amorphous	~81	~19
			H	~17	~83
	120	6.9	H	~40	~60
	180	7.8	H	~32	~68

(M) Malachite; (H) $(Cu_{0.2}Zn_{0.8})_5(CO_3)_2(OH)_6$ copper zinc carbonate hydroxide; (A) aurichalcite.

are presented in Fig. 6. In the system obtained from the initial solutions $Cu^{2+}/Zn^{2+} = 4{:}1$ the particles are predominantly malachite (M) with some aurichalcite (A). At $Cu^{2+}/Zn^{2+} = 2{:}1$ ratio larger particles of about 20 μm in size consist of 37 at.% of Cu and 63 at.% of Zn, which are a mixture of malachite and aurichalcite. Peaks corresponding to malachite (M) are slightly shifted to higher 2θ values, probably due to the some replacement of Cu^{2+} with Zn^{2+} at cation sites in the malachite structure.[1]

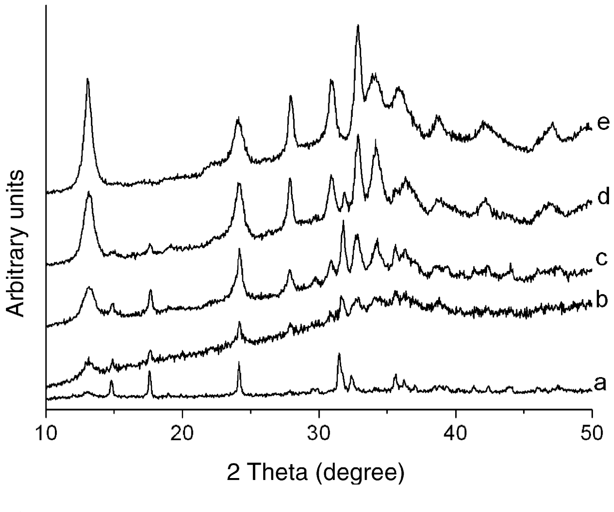

Fig. 5. XRD spectra for samples at Cu/Zn ratios of: (a) 4:1, (b) 2:1, (c) 1:1, (d) 1:2 and (e) 1:4 after ageing for 180 min at 85 °C.

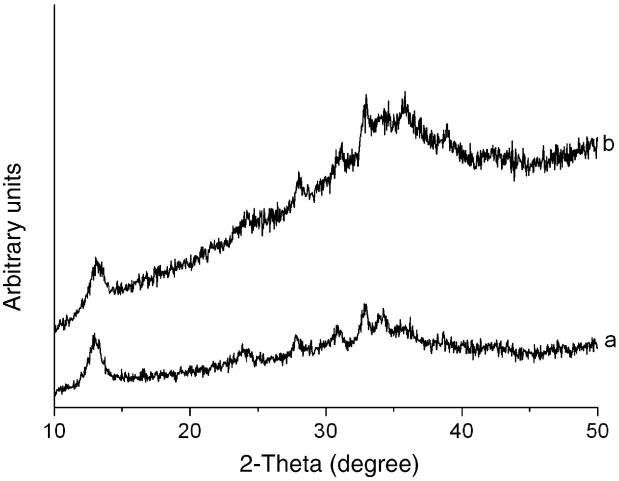

Fig. 6. XRD spectra for samples with Cu/Zn ratio: (a) 1:1, (b) 1:2, prepared after ageing for 120 min at 85 °C.

Samples at $Cu^{2+}/Zn^{2+} = 1{:}1$ and 1:2, are composite of A and M. Spectra presented in Fig. 6 indicate that the crystallization started with the formation of aurichalcite but with progressed ageing, the malachite appeared. The size of larger particles was up to 12 μm (Fig. 3) in both systems. By EDS analysis of samples prepared at $Cu^{2+}/Zn^{2+} = 1{:}1$ we confirmed that the ratio in final solids was ~1.

At Cu^{2+}/Zn^{2+} 1:4, XRD spectra show the formation of copper zinc carbonate hydroxide. Closer examination of the peak intensities at $2\theta = 22°$, 24°, 28° and 33° (Fig. 5), can be used to distinguish between aurichalcite from hydrozincite. The surface of the particles presented is same as shown in Fig. 4b and c.

The characteristic bands of the IR spectra of all five samples prepared after ageing for 180 min (not presented) clearly indicate the presence of hydroxyl and carbonate groups. Samples prepared at Cu/Zn ratios equal to 4:1, 2:1 and 1:1 gave similar IR bands for carbonate groups (600–1500 cm^{-1}) and a broad band at about 3330 cm^{-1}, corresponding to the stretching vibration of nonstructural H_2O, without the presence of any stretching vibration for structural OH groups.[11] The relative intensities of the IR bands of carbonate groups, their positions and splitting are in correlation with the chemical bonding and crystalline structure. Spectroscopic investigations were mostly reported of pure carbonates,[12] and only few studies deal with mixed carbonates. A detailed infrared study of monophase mixed copper–zinc hydroxycarbonate was presented by Stoilova et al.[13] Our results are in good agreement with the IR spectra of aurichalcite [14] and Cu–Zn-hydrochalcite, where the absorption bands at 1550 and 1425 cm^{-1} were used to characterize carbonate species in a malachite-like environment.[11,14]

4. Conclusion

The formation of the particles at different initial ratios of Cu^{2+}/Zn^{2+}as 4:1, 2:1, 1:1, 1:2 in the presence of urea show dramatically changes with time in term of particles structure and size. Details of these conversions depend on both, the ratio of the two metal nitrates in the initial reactant solutions and ageing time. The starting concentration of Cu/Zn = 4:1, 2:1, 1:1, 1:2 have no influence on shape of the particles obtained after 90 min of ageing. In all cases amorphous particles of around 1 μm are formed with the concentration of Cu (at.%) ranging from 99 to 81 at.%. The conversion from amorphous to crystalline solids seems to proceed through a solution/re-precipitation process. The formation of H crystalline phase was observed by XRD. With prolonged ageing larger particles were formed with complex surface characteristics. Most interesting was the formation of mixed Cu/Zn ribbon like particles.

Acknowledgements

This work was supported by the Ministry of Higher Education and Science and Slovenian Research Agency of the Republic of Slovenia (J2-.6027). The authors are gratefully acknowledged to Prof. Egon Matijević for useful discussions.

References

1. Stone, F. S. and Waller, D., Cu–ZnO and Cu–ZnO/Al_2O_3 catalysts for the reverse water-gas shift reaction. The effect of the Cu/Zn ratio on precursor characteristics and on the activity of the derived catalysts. *Top. Catal.*, 2003, **22**, 305–318.
2. Whittle, D. M., Mirzaeli, A. A., Hargreaves, J. S. J., Joyner, R. W., Kiely, C. J., Taylor, S. H. *et al.*, Co-precipitated copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation: effect of precipitate ageing on catalyst activity. *Phys. Chem. Chem. Phys.*, 2002, **4**, 5915–5920.
3. Shishido, T., Yamamoto, Y., Morioka, H., Takaki, K. and Takehira, K., Active Cu/ZnO and Cu/ZnO/Al_2O_3 catalysts prepared by homogeneous precipitation method in steam reforming of methanol. *Appl. Catal. A: Gen.*, 2004, **263**, 249–253.
4. Kratohvil, S. and Matijević, E., Preparation of copper compounds of different compositions and particle morphologies. *J. Mater. Res.*, 1991, **6**, 766–776.
5. Matijević, E. and Sapieszko, R. S., *Formation of Monodispersed Metal (Basic) Carbonates in the Presence of Urea, in Fine Particles: Synthesis, Characterization, and Mechanism of Growth*, ed. T. Sugimoto. Marcel Dekker, New York, 2000, pp. 386–395.
6. Soler-Illia, G. J. A. A., Candal, R. J., Regazzoni, A. E. and Blesa, M. A., Synthesis of mixed copper-zinc basic carbonates and Zn-doped tenorite by homogeneous alkalinization. *Chem. Mater.*, 1997, **9**, 184–191.
7. Castellano, M. and Matijević, E., Uniform colloidal zinc compounds of various morphologies. *Chem. Mater.*, 1989, **1**, 78–82.
8. Privman, V., Goia, D. V., Park, J. *et al.*, Mechanism of formation of monodispersed colloids by aggregation of nanosize precursors. *J. Colloid Interf. Sci.*, 1999, **1**, 36–45.
9. Libert, S., Goia, D. V. and Matijević, E., Internally composite uniform colloidal cadmium sulfide spheres. *Langmuir*, 2003, **26**, 10673–10678.
10. Libert, S., Gorshkov, V., Goia, D. *et al.*, Model of controlled synthesis of uniform colloid particles: cadmium sulfide. *Langmuir*, 2003, **26**, 10679–10683.
11. Musić, S., Popović, S., Maljković, M. and Dragčević, Đ., Influence of synthesis procedure on the formation and properties of zinc oxide. *J. Alloys Compd.*, 2002, **347**, 324–332.
12. Sterzel, W. and Chorinsky, E., Die Wirkung schwerer Kohlenstoffisotope auf das Infrarot-spektrum von Carbonaten. *Spectr. Acta*, 1968, **24A**, 353–360.
13. Stoilova, D., Koleva, V. and Vassileva, V., Infrared study of some synthetic phases of malachite ($Cu_2(OH)_2CO_3$)–hydrozincite ($Zn_5(OH)_6(CO_3)_2$) series. *Spectr. Acta*, 2002, **58A**, 2051–2059.
14. Reddy, B. J., Nieto, F. and Sanchez Navas, A., Spectroscopic characterisation of rosasite and aurichalcite. *N. Jb. Miner. Mh.*, 2004, 302–316.