Influence of synthesis conditions on particle morphology of nanosized Cu/ZnO powder by polyol method

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Abstract. Cu/ZnO in nanosizes have been synthesized using ethylene glycol at various conditions. The effects of reaction temperature, extent of reduction, various precursors such as $\text{CuX}_2 \cdot n\text{H}_2\text{O}$, $\text{ZnX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-$, NO_3^- , CH_3CO_2^-), the addition of water and the removal of volatile compounds including water were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and dynamic light scattering (DLS). Cu/ZnO powders with an average diameter of as low as 50 nm was obtained with a very low polydispersity in the absence of a protective polymer. Ethylene glycol oxidation products were also identified by Fourier transform infrared (FTIR) spectroscopy. The morphology of Cu/ZnO powders and the yield of powders are found to be strongly dependent on the synthesis conditions.

Keywords. Polyol process; copper/metal oxide; catalysts.

1. Introduction

Considerable attention has been paid to copper metal nanoparticles like other single or bimetallic particles, in the past two decades due to their unusual properties and potential applications in many fields, such as, the manufacture of various electronic devices (Larry *et al* 1988), conductive films (Tani and Oshita 1996), photonic devices (Zhou *et al* 1995) and new types of catalysts. Non-agglomerated, uniform copper/metal oxide particles are highly desirable for many catalytic reactions, such as, low temperature methanol decomposition to selectively produce H_2 for fuel cells (Cheng and Shiau 1998), dehydrogenation of cyclohexanol (Fridman *et al* 2004) and liquid phase direct oxidation of benzene to phenol (Kanzaki *et al* 2004). Best known usage of these catalysts is, perhaps, the synthesis of methanol from synthesis gas. A number of chemical and physical methods in the production of nanosized materials were exploited such as micro emulsion (Qi *et al* 1997), electrochemical deposition (Molarates *et al* 2001), microwave irradiation (Zhao *et al* 2004), reduction of copper salt solutions with various reducing agents such as NaBH_4 , $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (Yedra *et al* 2003; Zhu *et al* 2005), for the preparation of metal and bimetallic powders. Modest effort has been spent to synthesize metal–metal oxides *in situ*. Cable and Schaak (2005) synthesized nanocrystalline powders of many transition-metal and post transition metal intermetallic compounds such as Cu_6Sn_5 by using polyol process. Zhu *et al* (2005) synthesized well

dispersed copper metal nanoparticles with a diameter of 15 nm by reducing CuSO_4 with hydrazine in ethylene glycol under microwave irradiation. This method is characterized by a quick reaction rate but the agglomeration of particles is often substantial when the precursor concentration is above 10^{-2} M (Zheng *et al* 1997). Zhang *et al* (2005) produced submicrometer sized Cu and Ag crystallites by using 0.125 M $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ and AgNO_3 . Thus, it is one of the aims of this study to synthesize copper nanoparticles in higher precursor concentrations on a *in situ* prepared support without using a protective agent. It is known that at higher concentrations, larger particle sizes and hence less surface area is formed (Schwarzer and Peukert 2004).

Solution based synthetic strategies like polyol process offer several important advantages over traditional high-temperature methods. It consists of the reduction of a precursor in a liquid alcohol medium at moderate temperatures of metallic compounds such as oxides, hydroxides and salts. For example, solution route can precipitate nanocrystalline powders at low temperature (Leonard *et al* 2005) and also solution methods often allow control over nanostructure and morphology, providing a convenient medium for size and shape controlled nanocrystals (Wiley *et al* 2005).

In this work, the synthesis of nanosized copper/zinc oxide particles in ethylene glycol without using a protective compound was studied in order to produce nanosized powder in bulk quantities. As the reaction temperature strongly affects the rate of reduction in polyol synthesis, we also studied the effects of temperature to find out the evolution of crystal structure. We also examined the de-

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pendence of morphology on water content and nature of the metal salt. Lastly, the oxidation products of ethylene glycol were characterized too.

2. Experimental

The experiments were carried out using analytical grade $\text{Cu}(\text{acetate})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{acetate})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 as metal precursors and ethylene glycol. The standard procedure was as follows: specified amounts of metal precursors, usually total ion concentration being kept at 0.2 M, were dissolved in 200 ml ethylene glycol. The solution was transferred to a three-necked flask with a distillation attachment and placed on a magnetic stirrer. The solution was then first heated up to 80°C . Then, the reaction was carried out at the boiling point (198°C) of the polyol for 150 min. The first step was dehydration of ethylene glycol giving rise to acetaldehyde. The second step is duplicative oxidation of the acetaldehyde with formation of diacetyl. This transformation was found to take place at the same time as the formation of metallic powder (Fievet *et al* 1989). The overall reaction can be schematized as follows:

During this period, metal precursors underwent complete dissolution and reduced to metal ions and metal oxides form. The volatile compounds of the reaction medium were collected for further analysis. The reaction flask was naturally cooled down to room temperature; the obtained black precipitate was decanted, filtered and washed several times with ethanol. The final product was obtained after it was dried at 80°C for 6 h. Catalysts were labeled using their nominal compositions. For instance, Cu(30)/ZnO(70) refers to 30% copper metal and 70% ZnO by weight.

The structure and morphology of copper on zinc oxide particles were analysed using Rigaku D/max-2200 Ultima X-ray diffractometer with $\text{CuK}\alpha$ radiation. From X-ray diffractograms, phases and crystallite sizes by using Scherrer formula were calculated. The morphology of the final products was determined by scanning electron microscopy (SEM), Jeol JSM-6335F and the oxidation products of ethylene glycol were identified by a Perkin Elmer 100 FT-IR spectroscope. In a typical size distribution analysis, 0.005 g dried sample was re-dispersed in 20 ml distilled water and placed in an ultrasonic bath for 30 s and then particle size distribution was obtained by a Brookhaven 90 Zeta Plus Dynamic Light Scattering Particle Sizing Instrument. Since no surfactant was used either in polyol reduction or in re-dispersion before particle size

analysis, therefore, apparently rather large agglomerate sizes were obtained.

3. Results and discussion

3.1 XRD results

Figures 1 and 2 show the XRD patterns for Cu(70)/ZnO(30) powders prepared with various precursor salts and at various reaction temperatures, respectively. In figure 1, the XRD pattern a is Cu(70)/ZnO(30) sample prepared with acetate anions; three peaks at 2θ angles of 43.30° , 50.44° and 74.10° were assigned to scattering from the 111, 200 and 220 planes of the Cu crystal lattice, respectively. And also in figure 1, the XRD pattern c is Cu(70)/ZnO(30) sample prepared with nitrate anions; three peaks at 2θ angles of 43.31° , 50.45° and 74.11° again were assigned to scattering from the 111, 200 and 220 planes of the Cu cubic lattice. The crystallinity of cubic copper metal was confirmed by comparing the observed XRD pattern with JCPDS card no: 04-0836. The average crystallite sizes (D), shown next to XRD pattern, was calculated using the half width of the (111) diffraction peak by Scherrer formula. No peak assignable to metallic copper was detected when precursor with chlorine anion was used but four peaks at 2θ angles of 28.505° , 32.245° , 47.414° and 56.264° were assigned to scattering from the 111, 200 and 220 planes of the CuCl, Nantokite mineral lattice (JCPDS card no: 06-0344) as shown in figure 1b. The calculated

Figure 1. X-ray patterns of Cu(70)/ZnO(30) with various metal precursor anions.

crystallite sizes of copper metallic powder prepared using acetate anion are almost half of that obtained with nitrate anion. It is demonstrated in the X-ray diffractograms of various Cu/ZnO samples with increasing copper content (Altınçekiç and Boz 2008) that the ZnO phase can be seen when the nominal sample composition is at least Cu(20)/ZnO(80). It is thought that with increasing copper content the ZnO is covered with metallic copper like core-shell model. And so, only dominant metallic copper phase is detected. The unidentified peaks in the diffractograms can be assigned to minor intensities of metallic copper phase. And also energy dispersive scanning (EDS) analyses of sample Cu(30)/ZnO(70) showed that solids are Cu-rich and this finding signals that copper exists over zinc oxide support (Altınçekiç and Boz 2008). Figure 2 shows the XRD patterns of Cu(70)/ZnO(30) powders prepared at three reaction temperatures and with acetate anions. The reaction temperature strongly affects the rate of reduction in polyol synthesis. Reaction temperature was varied to find the conditions at which highly crystalline copper on zinc oxide was produced. XRD data clearly demonstrate the growth of copper metallic phase as a function of temperature. Increase in the reaction temperature to 120°C, 154°C and 198°C resulted in the intensification and sharpening of the diffraction peaks for the powders as shown in figure 2, respectively. Thus it is an electrochemical reduction reaction; the decrease in the oxidation potential of ethylene glycol as the temperature increases indicates that this reaction is favoured at high temperature. This increase in reaction temperature showed that 6CuO·Cu₂O phase

disappeared, copper metallic and ZnO phases have grown steadily and the crystallinity has improved as the reaction temperature increased. It should be noted that because of the mild reducing power of ethylene glycol, it is unable to reduce a cation of an electropositive metal such as zinc ($E^0 = -0.763$) so the less electropositive element, copper ($E^0 = +0.337$) is reduced.

3.2 FT-IR results

In order to identify the oxidation products of ethylene glycol as the reduction proceeds, aliquots of samples from Cu(80)/ZnO(20) preparation media are taken for every half an hour. Changes in FT-IR peaks are shown in figure 3. The typical vibration peaks of interest are presented and labelled in figure 3. First spectrum belongs to pure ethylene glycol. The band at 1452 cm⁻¹ is due to vibration of -CH₂ group. The strong adsorption band at about 1720 cm⁻¹ is attributed to absorption of C=O stretching. It is shown that carbonyl group existed from beginning to end and it was inferred that ethylene glycol was partially transformed to aldehyde in the beginning and then finally it was oxidized. The band at 1252 cm⁻¹ corresponds to the stretching of C-O-C in -CH₃COO⁻ groups. FT-IR studies confirmed that the ethylene glycol is totally oxidized.

3.3 DLS results

Typical agglomerate size of Cu(70)/ZnO(30) sample in which 3 moles of water added to the reaction medium was

Figure 2. X-ray patterns of Cu(70)/ZnO(30) at different reaction temperature.

Figure 3. FT-IR spectra of Cu(70)/ZnO(30); with the time of reaction.

Figure 4. SEM micrographs of **a.** Cu(70)/ZnO(30), **b.** Cu(30)/ZnO(70), **c.** Cu(70)/ZnO(30) (water distilled off), **d.** Cu(70)ZnO(30) 1 micron (water distilled-off), **e.** Cu(70)ZnO(30) 100 nm (water distilled-off), **f.** Cu(70)ZnO(30) water added, **g.** Cu(70)ZnO(30) with NO_3^- anion and **h.** Cu(70)/ZnO(30) with Cl^- anion.

Table 1. Particle size analysis results from DLS.

Catalyst sample	Effective agglomerate diameter (nm)	Half width (nm)	Polydispersity index (PD)
Cu(70)/ZnO(30)	184.9	45.2	0.060
Cu(30)/ZnO(70)	240.4	60.8	0.064
Cu(70)/ZnO(30) water added	308.5	21.8	0.005
Cu(70)/ZnO(30) Cl ⁻ anion	831.2	58.8	0.005
Cu(70)/ZnO(30) water distilled off	905.8	64.1	0.005
Cu(70)/ZnO(30) NO ₃ ⁻ anion	1134.2	80.2	0.005

found to be 308.5 nm with a polydispersity (PD) index of 0.005. For the other samples, agglomerate sizes were given in table 1. Highest value observed was for Cu(70)/ZnO(30) sample prepared with NO₃⁻ metal salt and it was 1134.2 nm with PD being 0.005.

3.4 SEM results

Figures 4a and b present the SEM micrographs of the Cu(70)/ZnO(30) and Cu(30)/ZnO(70) powders dried at 80°C for 6 h, respectively. It can be observed that the powders are composed of non-agglomerated spherical particles. Copper particle sizes range between 50 and 350 nm. The dependence of morphology on the water content and type of metal precursor anion, while keeping reaction temperature and reaction time constant, was also examined. Figures 4c and f show the SEM micrographs of the Cu(70)/ZnO(30) powder in which the volatile compounds are distilled off from the reaction medium and 3 moles of water per precursor are added to the reaction medium, respectively. When volatile compounds are distilled off from the reaction medium and the temperature reaches the boiling point of the polyol, the reducing power of EG increases and the reaction leads to the formation of metal. The mechanism of formation of metal particles consists of two separate steps: dissolution of the intermediate phase and then nucleation and growth of particles from solution. Decreasing the hydrolysis ratio and increasing the reaction temperature increases the rate of reduction and spontaneous nucleation rate. Thus, the particles were found to be more uniform and monodisperse with a polydispersity index, 0.005. When water remained in the reaction medium the reduction was inhibited. In figures 4g and h Cu(70)/ZnO(30) powders were prepared with NO₃⁻ and Cl⁻ anions containing precursors. It is clearly observed that detrimental nitrate and chlorine groups could not be removed during vigorous boiling of ethylene glycol or by washing with pure alcohol. The typical spherical copper particles with a low polydispersity obtained with acetate anion now disappeared.

4. Conclusions

In summary, we have produced nanosized copper/zinc oxide particles in bulk quantities by a simple polyol pro-

cess which has several advantages compared to other conventional synthesis methods. Only ethylene glycol is used and no further reducing agent, surfactants or protective compounds are used and this made the process easy to scale-up for mass production. Study of experimental conditions revealed that crystallite size and particle morphology totally depends on reaction temperature and metal precursor anion being used. SEM micrographs showed that the synthesized powders in which acetate anions were used and when volatile compounds were distilled off are rather uniform and spherical. Particle sizes obtained are in between 100 and 160 nm calculated from SEM micrographs. The crystallite sizes were for copper (111) metallic peak found to be in the range of 27–41 nm. Size distribution of the nanoparticles is much narrower than the particles produced by traditional methods. Polyol synthesis offers a facile route to replace the traditional co-precipitation method for the preparation of copper/zinc oxide catalysts and also it allows a certain control of the morphological characteristics that is useful for several applications.

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References

- Altınçekiç G T and Boz I 2008 *J. Nanosci. & Nanotechnol.* **8** 874
- Cable Robert E and Schaak Raymond E 2005 *Chem. Mater.* **17** 6835
- Cheng W H and Shiau C -Y 1998 *Appl. Catal. B: Environ.* **18** 63
- Fievet F, Lagier J P and Blin B 1989 *Solid State Ionics* **32/33** 198
- Fridman V Z, Davydov A A and Titievsky K 2004 *J. Catal.* **222** 545
- Kanzaki Hiroshi, Kitamura Takahiro, Hamada Rei, Nishiyama Satoru and Tsuruya Shigeru 2004 *J. Mol. Catal. A: Chem.* **208** 203
- Larry J R, Rosenberg R M and Uhler R G 1988 *IEEE Trans. Comp. Hybrids & Manuf. Technol.* **CHMT-3** 211
- Leonard B M, Bhuvanesh N S P and Schaak R E 2005 *J. Am. Chem. Soc.* **127** 7326
- Molarates M E T, Buschmann V and Dobrev D 2001 *Adv. Mater.* **13** 62

- Qi L M, Ma J M and Shen J L 1997 *Colloid. Interf. Sci.* **186** 498
- Schwarzer H C and Peukert W 2004 *Chem. Eng. Commun.* **191** 580
- Tani H and Oshita K 1996 US Patent Specification No. 5,588,098
- Wiley B, Sun Y, Mayers B and Xia Y 2005 *Chem. Eur. J.* **11** 454
- Yedra A, Fernandez Barquin L, Gomez Sal J C and Pankhurst Q A 2003 *J. Magn. & Magn. Mater.* **14** 254
- Zhang Yong Cai, Wang Gui Yun, Hu Xiao Ya and Xing Rong 2005 *J. Solid State Chem.* **178** 1609
- Zhao Yu, Zhu Jun-Jie, Hong Jian-Min, Bian Nigsheng and Chen Hong-Yuan 2004 *Eur. J. Inorg. Chem.* **20** 4072
- Zheng H G, Li Y D, Li C W, Zhao H Z, Liu Y H and Qian Y T 1997 *Acta Phys. Chim. Sin.* **11** 974
- Zhou S, Wada T and Sasabe H 1995 *J. Chem. Soc., Chem. Commun.* 1525
- Zhu Haitao, Zhang Canying and Yin Yansheng 2005 *Nanotechnology* **16** 3079