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In Situ In-House Powder X-ray Diffraction Study of Zero-Valent Copper Formation in Supercritical Methanol

Panpan Sun,^{1,2} Frederik H. Gjørup,² Jakob V. Ahlburg,² Aref Mamakhel,² Shuzhong Wang,¹ Mogens Christensen.^{2*}

¹Key Laboratory of Thermo-Fluid Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

²Department of Chemistry & iNANO, Aarhus University, Aarhus C 8000, Denmark

Abstract: Nano/micro crystalline copper is widely used in catalysts and it has potential for being used as conductive additive to ink for inkjet printed electronics. Copper is attractive, because it has excellent electrical conductivity and low cost compared to noble metals. The nucleation and phase transitions from the precursor to the final micrometer sized Cu in supercritical methanol have been studied for the first time using in-house *in situ* powder X-ray diffraction (PXRD). Temperatures have a significant impact on the reduction process of Cu²⁺, at low synthesis temperature (250 °C), it was observed how the Cu²⁺ precursor initially formed copper hydroxy nitrate (Cu₂(OH)₃NO₃) and transformed to copper(II)oxide (CuO) *i.e* no reduction took place. At 300 °C multiple phase transformation could be observed from initial copper hydroxy nitrate to zero-valent copper, the *in situ* investigations reveal the following phase transitions; Cu^{II}₂(OH)₃NO₃ → Cu^{II}O → Cu^I₂O → Cu⁰. Increasing the synthesis temperature causes the pure Cu⁰ to form much faster; at 350 °C, it takes 8.7 min to produce phase pure Cu⁰, while at 450 °C, the formation takes ~0.7 min. Increasing the initial concentration of Cu²⁺ in the precursor causes formation of larger Cu⁰ crystallites in the final product. Finally, the *in situ* observations were used as guidance for making Cu⁰ using a supercritical flow setup.

Corresponding Author:

Name: Mogens Christensen. Address: Aarhus University, Langelandsgade 140, 8000, Aarhus C, Denmark. Phone: +45 8715 5339. Fax: +45 8619 6199. E-mail: mch@chem.au.dk. Web addresses: <http://pure.au.dk/portal/en/mch@chem.au.dk>

Introduction

Nano and micro crystalline copper have attracted more and more interests from researchers and engineers, due to the excellent performances in optics, catalysts, electrical conduction and as additives in lubricating oil¹⁻⁴. Copper nanoparticles are especially attractive in application of printed circuit boards (PCBs) compared with noble metals (silver and gold), due to high electrical conductivity, low-cost and low electrochemical migration probability⁵. Various methods have in recent years been applied for synthesis of nano/micro copper crystals, such as thermal decomposition^{6, 7}, microwave heating^{8, 9}, solvothermal¹⁰, polyol^{11, 12}, sol-gel¹³ and supercritical water^{14, 15}. Among these synthesis methods, supercritical fluids have become increasingly popular, because of the potential for large-scale commercial manufacturing and upholding green chemistry concepts^{16, 17}.

Supercritical fluids are a fascinating reaction medium, owing itself to low density, low dielectric constant, low viscosity and other unique properties. A huge number of inorganic oxides have been successfully synthesized in supercritical water, a few examples are ZnO¹⁸, NiO¹⁹, TiO₂²⁰, γ -Fe₂O₃²¹ and CuO²². Supercritical carbon dioxide was used in the preparation of elemental Cu and Ni²³. Supercritical methanol (T > 239.5 °C, P > 8.1 MPa) combines solvothermal synthesis and reduction, as it acts as both solvent and reduction agent. Different species of metals have been synthesized from their corresponding salts, with supercritical methanol acting both as reaction medium and reduction agent, e.g. Ag^{24, 25}, Cu^{24, 25}, Ni^{24, 25}, Co²⁶. It is of great interest to understand the reduction from divalent metal ion into zero-valent metal, as it can potentially improve the reaction process. Different researchers have proposed different reaction pathways,

one being that hydroxide ions (OH^-) dissociated from methanol molecules in supercritical conditions acts as reduction agent through electron transfer from hydroxide ions to dissociated metal ions^{24, 27}. Other experiments have proved that hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) are generated as by-products of methanol reforming in the supercritical state, and all these by-products are all effective reduction agents²⁸, which are proposed to possibly reduce copper ions in supercritical methanol²⁹. In other words, the synthesis of zero-valent metals in supercritical methanol from higher valent metal salt are a complicated process.

In situ synchrotron powder X-ray diffraction (PXRD) experiments have been used to shed light on the formation of nanocrystallites e.g. $\gamma\text{-Fe}_2\text{O}_3$ ^{30, 31} and $\text{SrFe}_{12}\text{O}_{19}$ ³². Recently, the robustness of the methods was investigated in a reproducibility study on $\gamma\text{-Fe}_2\text{O}_3$.³³ Synchrotrons are great tools for these studies as the high flux and large area detectors gives a very high time resolution, albeit access to beamtime can be a challenge. Here we demonstrate the use of a newly developed *in situ* in-house supercritical synthesis setup.³⁴

In situ PXRD is applied to explore the reduction process of Cu^{2+} ions to Cu^0 and the crystallization mechanism in supercritical methanol. The reaction kinetics were analyzed using the Gualtieri kinetic model, and a reaction mechanisms for the crystallite formation were proposed³⁵. The information obtained from the *in situ* experiment has been exploited in the design of a supercritical flow synthesis to scale-up the synthesis of zero-valent copper particles.

Experimental

***In situ* synthesis:** All reagents were used without purification; copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Sigma Aldrich, analytical grade, purity >98%), Methanol (CH_3OH , Merck KGaA Corporation, analysis grade). A precursor solution with 2 M concentration of $\text{Cu}(\text{NO}_3)_2$

was prepared by dissolving the appropriate amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in methanol. Lower concentrations were made by diluting the 2 M Cu^{2+} solution.

A schematic diagram of the experimental *in situ* setup is shown in Fig. 1. The capillary reactor (inner and outer diameter are 0.75 mm and 0.85 mm, respectively) was made of silica and coated with polyamide. The precursor was injected into the capillary reactor using a syringe and the capillary tube was subsequently connected to an HPLC pump (Prep Pump, LabAlliance) through Swagelok fittings and stainless steel tubing, the pressure was set to 11.4 MPa. A heat gun (HiHeater, Miyawaka Corporation, Japan) heated the silica capillary reactor with a jet of hot air to a preset temperature. The heat gun allowed for a fast heating, capable of reaching 450 °C within 25 seconds, reaching 415 °C inside the capillary within the first 15 seconds (~28 K/s), and stabilizing to 450 °C within the next 10 seconds.

Fig. 1 Schematic diagram of the in-house *in situ* setup. The capillary reactor is heated by a jet of hot air from the heat gun. The capillary is illuminated by monochromatic X-rays and an area detector records the diffracted pattern at set intervals. The obtained detector images are integrated and plotted as function of reaction time. (Courtesy of Henrik Lyder Andersen)

The actual temperature inside the capillary was slightly lower than the set temperature on the controller, the time evolution of the temperature inside capillary can be found in the supporting information. Five different reaction temperatures in the interval from 250 °C to 450 °C in steps of 50 °C were investigated regarding the formation of Cu⁰ from copper (II) nitrate trihydrate (Cu(NO₃)₂•3H₂O) in supercritical methanol. The capillary tube with the precursor material was mounted on a special designed sample holder inside a Smartlab diffractometer (Rigaku, Japan). The diffractometer was equipped with a Cu rotating anode and Johnson monochromator to extract Cu K_{α1} radiation. A cross beam optics unit CBO-E provided a convergent beam used in Debye-Scherrer geometry. The heat gun was placed under the capillary reactor at a fixed calibrated distance of about 2 mm. *In situ* data frames were recorded using a HyPix-3000 2D detector fixed at a sample/detector distance of 135.5 mm and covering the angular interval $2\theta = 29.8 - 61.9^\circ$. A commercially available 5° Soller slit in the incident beam combined with a special designed large area 5° Soller slit in front of the detector allowed using a 15 mm wide X-ray beam, without significant peak-broadening. The images were collected with a 10 s exposure time. An additional 9 s for saving data and opening/closing the shutter gave a total time resolution of 19 s per frame. For the experiment at 250 °C, a low angle data set was collected to reveal the low angular peaks for the Cu₂(OH)₃NO₃ phase, this was obtained by placing the detector at a $2\theta_{center} = 24^\circ$ (corresponding to the 2θ range of 7.8 - 39.7°).

Flow synthesis: Based on the *in situ* experiments, a range of supercritical flow synthesis experiments were conducted to investigate the possibility of large-scale synthesis of elemental copper and copper oxide nanoparticles. Two high pressure pumps were used to supply precursor (0.01 M Cu(NO₃)₂ in methanol, 5 ml/min) and solvent methanol (10 ml/min) continuously. In order to increase the heating rate the methanol was heated by two pre-heaters to reach the

intended reaction temperature of 350 and 400 °C, after which the precursor and solvent were mixed in the flow apparatus. The reaction pressure was kept at 11 MPa throughout the flow reaction. The two fluids mixed through a T-piece mixer and caused almost instantaneous heating of the precursor. The mixture was kept at the reaction temperatures of 350 and 400 °C for 3.2 and 2.7 s, respectively. Finally the product passed through a water cooled jacket and a pressure relief valve. Detailed information and a schematic diagram of the continuous flow reactor can be found in the literature³⁶. The products were washed several times with deionized water and ethanol to remove impurities. Powder products were obtained after vacuum drying at 60 °C for 24 h.

Characterization of flow product: Phases characterization and crystallite size and morphology of the flow reactor products were performed using powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). PXRD data were collected with the same Smartlab diffractometer as the *in situ* experiment, however with a zero background flat silicon single crystal sample holder in Bragg-Brentano geometry and using a silicon strip detector D/teX Ultra 250. Samples for electron microscopy were prepared by adding droplets of ultrasonically dispersed powder in ethanol on a nickel grid. TEM images were captured using a Philips CM20 microscope.

Rietveld refinements: The collected 2D images were integrated using a Python script, converting the data into 2θ positions (°) and intensities. Rietveld refinement was performed on the integrated data using the *Fullprof Suite* software.³⁷ During refinement, a large amount of data were analyzed taking advantage of sequential Rietveld refinement in *Fullprof Suite*. The refinements included the observable phases of copper hydroxy nitrate, cupric oxide, cuprous oxide and copper with chemical formula; $\text{Cu}_2(\text{OH})_3\text{NO}_3$, CuO , Cu_2O , and Cu using the

spacegroups $P2_1$, $C2/c$, $Pn\bar{3}m$ and $Fm\bar{3}m$, respectively. The peak profiles were described by the Thompson-Cox-Hasting pseudo-Voigt function and the backgrounds were determined by a linear interpolation between a series of background points. In the refinements the following factors were refined; the scale factor, 2θ zero point, unit cell parameters, background and peak shape parameters. In all cases the Cu atoms are occupying special positions without refinable coordinates and the atomic occupancies were fixed to be fully occupied, in other words, the atomic positions and atom occupancies were fixed to literature values³⁸⁻⁴¹. Thermal vibration parameters were strongly correlated with the scale factor, due to the limited number of peaks within the detection range. Debye-Waller factors were therefore fixed to B values extracted from the literature corresponding to the temperature of the respective experiment⁴²⁻⁴⁴. Crystallite size were calculated based on the full width at half maximum intensity (FWHM) obtained from the Rietveld refinements by using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where D represents crystallite size, $K = 0.89$ represents the Scherrer constant, λ represents the wavelength, β is FWHM, and θ is the Bragg angle. In the refinement the term $\beta \cos(\theta)$ is refined as one angle-independent parameter for all peaks of a given phase.

The peak broadening observed in the X-ray powder diffraction pattern is a convolution of the contribution from the sample microstructure and the instrument resolution. The instrumental peak broadening was corrected using data from a NIST LaB₆ 660B standard sample⁴⁵. Peak broadening, which may arise from microstrain in the lattice is neglected due to the low reaction temperature. Strain broadening could be investigated if high angular and q resolution could be obtained from e.g. synchrotron powder diffraction instruments. The normalized scale factors

obtained from the refinements were used for reaction kinetics investigations using the Gualtieri kinetic model.

Results and discussion:

***In situ* investigations:** Four different crystalline phases were observed in the *in situ* investigations depending on synthesis temperature and time. In order to give an impression of the time-evolution of the different phases a 3D plot is shown of the diffraction patterns collected at 350 °C in Fig. 2. The three dimensions are time (min), Bragg angle $2\theta(^{\circ})$, and intensity (arb. units). Fig. 2 (b) is the 2D projection of the 3D plot in Fig. 2 (a), where the intensity is given by the color scale. By comparison with a crystallographic database it was possible to determine the obtained crystallographic phases. The heating was started at time equal 0 min, no diffraction peaks are observed until 0.8 min. At 0.8 min, five peaks belonging to CuO and Cu₂O are observed. The CuO peaks quickly disappears and after persistent heating for 2.0 min, two new peaks are observed belonging to Cu.

Fig. 2 (a) 3D *in situ* diffraction data collected at 350 °C, with color scale demonstrating the intensity and heating started at 0.08 min. (b) 2D projection of the plot, clearly revealing three phases, first CuO, followed by Cu₂O and finally Cu.

Three representative diffractograms illustrating all of the observed phases are shown in Fig. 3, where the observed data and the refined Rietveld model are shown together with the difference between the observed data and the calculated model. Fig. 3 (a) shows the Cu₂(OH)₃NO₃ (JCPDS NO. 45-0594) phase appears after ~20 s at a reaction temperature of 250 °C. The main diffraction peak of Cu₂(OH)₃NO₃ is observed around $2\theta = 15^\circ$, which was collected by placing the detector at $2\theta_{\text{center}} = 24^\circ$. The low angle diffraction data helped to confirm the presence of Cu₂(OH)₃NO₃. The corresponding low angle diffraction data collected at 250 °C and ~20 s can be found in the supporting information. Fig. 3 (b) and (c) show diffraction patterns collected at 300 °C after 4.8 and 40 min, respectively. The peaks obtained after 4.8 min are indexed to CuO (JCPDS NO. 48-1548) and Cu₂O (JCPDS NO. 05-0667), while at 40 min the observed peaks are Cu₂O and Cu (JCPDS NO. 04-0836). The reliability factors (R_{wp} , χ^2) for the sequential Rietveld refinements are shown in supporting information.

Fig. 3 Powder diffraction patterns obtain from linear integration of the 2D image collected by the Hypix-3000. The integrated data (black open circle) is shown along with the Rietveld model fit (red), the difference curve $I_{\text{obs}} - I_{\text{calc}}$

(blue), and the indexed peak positions (vertical lines). The data is shown for (a) 250 °C, 0.4 min (b) 300 °C, 4.8 min (c) 300 °C, 40.0 min.

The evolution of the different phases and the corresponding weight fractions are shown in Fig. 4. For the reaction at 250 °C only two phases were observed within the duration of the experiment, which lasted nearly 1 hour, as shown in Fig. 4 (a). Initially $\text{Cu}_2(\text{OH})_3\text{NO}_3$ is observed as the only phase after heating for 0.4 min, but it rapidly disappears after 1.4 min. At 0.7 min, the CuO phase starts to emerge and increases fast in weight fraction. The CuO is the only observable phase after 1.4 min and until the experiment is ended after almost 1 hour. The experiments at 300 °C reveals four different crystalline phases during the experiment as seen in Fig. 4 (b). $\text{Cu}_2(\text{OH})_3\text{NO}_3$ and CuO appear in the first frame after initiating the heating, however $\text{Cu}_2(\text{OH})_3\text{NO}_3$ is converted completely to oxide products in the next frame, where Cu_2O also starts appearing. The CuO is converted into Cu_2O as time progresses. At 10.9 min, the pure Cu^0 starts to appear. The reduction of Cu_2O to Cu^0 slowed down after approx. 20 min at 300 °C in supercritical methanol, even after 52.0 min a full conversion is not obtained. For the reaction taking place at 350 °C the $\text{Cu}_2(\text{OH})_3\text{NO}_3$ is not observed. It is either bypassed or the time resolution is insufficient to observe the presence of the phase. In the first frame diffraction peaks from CuO crystallites appear, but it is quickly converted into Cu_2O , which again relatively quickly converts into elemental Cu after less than 2 min. It takes 6.7 min from the emergence of Cu^0 to complete conversion of Cu_2O into pure Cu^0 . For the reaction temperatures of 400 °C and 450 °C, the conversion into elemental Cu^0 is very fast and takes 62 s and 43 s, respectively, as shown in Fig. 4 (d) and (e).

Fig. 4 Evolution of phase weight fraction with time at different reaction temperatures (a) 250 °C (b) 300 °C (c) 350 °C (d) 400 °C (e) 450 °C with 11.4 MPa of reaction pressure

In order to obtain smaller crystallites, precursors with lowered concentrations were also investigated and the same phase evolution trends were observed. For all the reactions at temperatures of 350 °C and higher, elemental Cu^0 were obtained as the final crystalline phase.

Temperature and Crystallite size: The crystallite size of the copper particles calculated from the Scherrer equation is generally >100 nm, therefore the size cannot be trusted from the Scherrer equation⁴⁶. The size is inversely proportional to the peak width β , the full width at half maximum of the peak. In Fig. 5 the time evolution of $1/\beta$ is plotted to show the trend of crystallite size as function of time for the different reaction temperatures and precursor concentrations. The Cu^0 crystallite size reaches a constant size at the reaction temperature of 350 °C. When increasing reaction temperature to 400 °C and 450 °C, it is observed how prolonged heating time resulted in an increase of the average crystallite size. Beside crystallite size, unit cell parameter can also be extracted from refinement, the evolution of unit cell with time can be found in supporting information.

Concentration and crystallite size: Decreasing the Cu^{2+} concentration in the precursor has a significant effect regarding the size of the formed crystallites. For the powder patterns collected

for 1 M of Cu^{2+} , a slight increase in average crystallite size is observed as time progresses. Decreasing Cu^{2+} concentration to 0.5 M, no significant change was observed during the 10 min of the experiment. In the case of the low concentration, crystallites appear to be too far apart to cause significant Oswald ripening.

Fig. 5 The evolution of $1/\beta$ with heating time at different temperatures and different Cu^{2+} concentrations calculated from the instrument corrected peak widths

Kinetics: In order to quantify the reaction kinetics of the phases formed during the supercritical synthesis of Cu particles in methanol, the Gualtieri model has been fitted to the refined XRD data. The Gualtieri model³⁵ assumes that the probability P that N nuclei has formed to the time t can be expressed by a simple Gaussian distribution:

$$P_N(t) = \exp\left(-\frac{(t-a)^2}{2b^2}\right) \quad (2)$$

Where a is the position of the maximum of the Gaussian curve and b is the variance of the distribution, related to the width of the curve. The total number of nuclei N at time t can then be expressed as the cumulative distribution function:

$$N(t) = \frac{1}{1 + \exp\left[-\left(\frac{t-a}{b}\right)^2\right]} \quad (3)$$

Furthermore, a is related to the rate of nucleation, $k_n = 1/a$.

An expression very similar to the Johnson-Mehl-Avrami-Kolmogorov (JMAK)⁴⁷⁻⁴⁹ equation is used to describe the nuclei growth process and the total expression for the extent of reaction, α , is then the combination of available nuclei and their growth:

$$\alpha(t) = N(t - t_0) \cdot \left\{ 1 - \exp \left[- \left(k_g(t - t_0) \right)^n \right] \right\} \quad (4)$$

Where k_g is the rate of growth and n is growth dimension ($n = 1$ for rods and needles, $n = 2$ for plates, and $n = 3$ for isotropic particles). Furthermore the variable t_0 has been introduced to account for the time before the reaction is initiated.

In the analysis presented here, the scale factors obtained from sequential Rietveld refinement, normalized to the $[0,1]$ range, are used to describe the extent of reaction α . In the case where the scale factor decrease over time, the extend of reaction is simply described by $1 - \alpha$. Furthermore $n = 3$ is assumed for all reactions, as TEM images and Rietveld refinements indicate isotropic particles. The normalized scale factors along with the Gualtieri fits are shown in Fig. 6, together with the angle-independent integral breadths, $\beta \cdot \cos(\theta)$, obtained from Rietveld refinement. The kinetic analysis has been omitted for the experiments performed at 400 °C and 450 °C, as the reactions occur faster than the time resolution allows to follow. A summary of the kinetic analysis is provided in Table 1.

Fig. 6 Normalized scale factor and angle independent integral breadth as function of time for the 250 °C, 300 °C, and 350 °C reactions. The fitted Gualtieri models are superimposed on the corresponding scale factors. The Coefficients of determination, R^2 , are summarized in Table 1. Error bars have been omitted, as they are insignificant compared to the spread of the data points.

At 250 °C the growth rate appears to be the rate-determining step, as $k_g < k_n$. This fits with the “bend” observed at 10 min; the majority of the CuO nuclei form within the first 10 min, at which point the reaction is limited by the growth of the existing nuclei. It is noticed that α starts decreasing slightly after 35 min, which could be explained by sedimentation of the particle at the bottom of the capillary. If the capillary were not fully illuminated by the X-ray beam, this would lead to a decrease in the available volume of scattering particles. The angle-independent integral breadths, and inversely the particle size, appear more or less constant for the CuO phase at 250 °C and fluctuations are deemed insignificant compared to the data point spread.

The reaction kinetics behave quite differently at 300 °C, where the three phases CuO, Cu₂O, and Cu can be followed. The formation of CuO happens very fast and only the decrease in scale factor can be followed, corresponding to the reduction to Cu₂O. The normalized scale factors of

the CuO and Cu₂O phases intersect at $\alpha = 0.5$, which indicates that the Cu₂O phase is formed from the existing CuO. It is postulated that the CuO particles are re-dissolved before being reduced to Cu₂O, which fits the observed trend for the integral breadths in Fig. 6 at 300 °C, namely that the CuO particles decrease in size while the Cu₂O particles appear to increase in size. At about 12 min the increase in the Cu₂O scale factor stops, coinciding with the appearance of Cu. The Cu scale factor increases rapidly from 12 min to 25 min, where the rate stagnates. This is close to the point where CuO is no longer visible in the XRD pattern. After this point Cu₂O decreases slowly and Cu increases slowly, but without reaching full conversion. The following explanation is provided: Small CuO particles form fast, beyond the time resolution, and are then steadily re-dissolved and reduced to Cu₂O. The concentration of Cu₂O increases and some of the particles grow large due to Ostwald ripening. After roughly 10 min Cu particles start forming, possibly due to a sufficiently high Cu₂O concentration. At 15 min a steady-state is achieved, where Cu particles form from small Cu₂O particles as fast as CuO is reduced, which is also confirmed by the kinetic analysis, showing that k_n is significantly larger than k_g . At 25 min new Cu₂O is no longer formed, and readily reducible Cu₂O is depleted, leaving large Ostwald ripened Cu₂O particles. This is supported by TEM and EDX images (Fig. 8), where clusters of Cu₂O particles are observed alongside large cubic Cu₂O particles.

At 350 °C very small particles of Cu₂O form rapidly, and are quickly reduced to Cu. The scale factor of Cu₂O and Cu intersect at $\alpha = 0.5$ within few minutes. From the decrease in integral breadths it is suggested that the smallest Cu₂O particles are reduced first, as this would lead to an increase in the average particle size. From the kinetic analyses, it can be deduced, that a surplus of Cu nucleation sites are available, meaning that the reaction is only limited by the particle growth rate.

It is difficult to distinguish whether the reactions are solid state transformation or solution-mediated nucleation, or perhaps a combination. For a two-phase phase transformation one would expect the extend-of-reactions to cross at exactly $\alpha = 0.5$, as one is converted to the other in a 1:1 ratio. For a solution-mediated reaction the extend-of-reactions would be expected to cross at $\alpha < 0.5$, as one phase turns amorphous before recrystallizing as the new phase. However, a cross at $\alpha = 0.5$ is not enough to distinguish between the two mechanisms, as the dissolve-recrystallize mechanism might be faster than the XRD time-resolution so that the crossing occurs at $\alpha \lesssim 0.5$.

Table 1 Summary of the kinetic analysis.

Temperature	Phase	R^2	t_0 (min)	a (min)	b (min)	k_n (1/min)	k_g (1/min)
250 °C	CuO	0.889	0(1)	4(2)	15(2)	0.2(1)	0.15(3)
300 °C	CuO	0.994	1.7(2)	5.2(2)	3.5(1)	0.192(9)	0.42(5)
	Cu ₂ O	0.986	0.0(8)	5.4(8)	3.2(1)	0.19(3)	0.23(5)
	Cu	0.996	7.7(4)	6.8(6)	12.9(5)	0.15(1)	0.084(3)
350 °C	Cu ₂ O	0.998	1.7(3)	2.8(3)	0.25(2)	0.36(4)	0.23(1)
	Cu	0.985	2.4(2)	0	2.41(8)	--	0.30(2)

The performed *in situ* powder X-ray diffraction experiment cannot identify the reduction mechanism, responsible for reducing Cu²⁺ to Cu⁰, whether it is hydrogen (H₂), carbon monoxide (CO), methane (CH₄), or hydroxide ion (OH⁻) dissociated from supercritical methanol. For further understanding the reduction mechanism of copper (II) nitrate in supercritical methanol, *in situ* powder X-ray diffraction could be combined with complementary techniques, for instance infrared spectroscopy.

Supercritical flow synthesis: The *in situ* crystallization study of Cu can be regarded as guidance for the up-scaled synthesis using a supercritical continuous flow apparatus, which may be used for industrial scale production of copper nanoparticles. In order to verify the application of the *in*

situ research, two flow synthesis experiments were carried out at 350 and 400 °C. At 350 °C the reaction time is expected to be too short in the flow setup to produce pure elemental Cu, while at 400 °C an almost pure Cu⁰ phase is expected. The PXRD patterns and the corresponding Rietveld models are shown in Fig. 7. The main crystalline phase produced at 350 °C is Cu₂O, and a small amount of CuO phase, disclosed by the peak at $2\theta = 38.7^\circ$, as seen in Fig. 7. Increasing the reaction temperature to 400 °C results in elemental copper as the main product, with an apparent size of 29.9(1) nm and a minute impurity of Cu₂O (<0.1 wt%), observed at $2\theta = 36.4^\circ$. The peak width of Cu₂O suggest very small crystallites and they could originate from an incomplete reduction or from re-oxidization of the Cu nanocrystallites. The results of the flow synthesis generally corresponding very well with the expectations from the *in situ* experiments. It is worth noting that the flow reactor and *in situ* setup deviated at two important points; 1) heating rate and 2) residence time. The heating rate for the *in situ* setup is about 28 K/s, while that of the flow reactor is in the order of 500 K/s. In the flow synthesis, the residence time is decided by the flow rate and the reactor volume, but also in part from the reaction temperature and pressure. The following equation can be used to calculate the residence time t :

$$t = \frac{V_r}{F} \cdot \frac{\rho_T}{\rho_{298}} \quad (5)$$

Where V_r is reactor volume, F is total flow rate inside reactor, ρ_T and ρ_{298} are the fluid densities at the reaction temperature and room temperature at the reactor pressure. The density of supercritical methanol at 11 MPa is determined from a linear interpolation based on values from literature⁵⁰ to 0.087 g/cm³ (350 °C) and 0.073 g/cm³ (400 °C). The calculated residence time is underestimated compared to the real residence time, because the mixed fluid temperature is gradually changed. Calculated residence time at 350 °C and 400 °C gives 3.2 s and 2.7 s, respectively. By comparing the calculated residence time of the flow reactor to the reaction time

found from the *in situ* experiments, it is possible to understand the observed Cu₂O phase formed at 350 °C and it could also explain the minute amount of Cu₂O in the 400 °C experiment. According to the *in situ* experiments, a slightly longer reaction time or higher temperature would result in pure elemental Cu. There are several methods to prolong residence time, *e.g.* reduce the flow rates from the pumps, increase the length of the reactor, or using a larger tubing diameter.

Fig. 7 PXRD and Rietveld refinement results of products synthesized from continuous flow reactor at different reaction temperatures and at 11 MPa. The raw data are shown as black open circle, along with the Rietveld model fit (red) and the difference curve $I_{\text{obs}} - I_{\text{calc}}$ (blue). In order to show data at 350 °C clearly it has been scaled by a factor of two. The reliability factors at 350 °C are R_{wp} : 15.3 %, χ^2 : 1.74, and at 400 °C are R_{wp} : 16.1 %, χ^2 : 2.14.

TEM pictures are presented in Fig. 8 showing the morphology and size distribution of the products synthesized at 350 °C and 400 °C. For products synthesized at 350 °C, a spherical morphology is observed with 'tentacles' surrounding the core and at higher magnification the 'tentacles' are revealed to be constituted of a large amount of nano size particles, as seen in Fig. 8 (a). At 400 °C an interesting conversion of the morphology occurs, as shown in Fig. 8 (b). Irregular aggregates form from relatively small nanoparticles, as shown in Fig. 8 (c). Energy-Dispersive X-ray spectroscopy (EDX) and High Angle Annular Dark Field (HAADF) collected

on the sample prepared at 350 °C, see Fig. 8 (d), is affirming the presence and the morphology of the Cu_2O , the ratio between Cu and O is 2.3:1.0, although it is acknowledge that the accuracy of the EDX elemental analysis is generally low for light elements. The elemental EDX analysis is summarized in the supporting information. The size distribution of copper nanoparticles obtained at 400 °C is measured by hand from 128 particles and the result is plotted in Fig. 8 (e). TEM gives an average number weighted particle size of 21.4(3) nm, obtained from log-normal distribution fit, this value is in good agreement with volume weighted crystallite sizes extracted from PXRD (29.9(1) nm).

Fig. 8 TEM results of products synthesized at (a) 350 °C, (b) and (c) 400 °C (d) EDX scanning map of products collected at 350 °C and (e) size distribution of products synthesized at 400 °C and 11 MPa

Conclusion

Zero-valent copper crystallites were synthesized from Copper (II) nitrate in supercritical methanol. During the process, three different intermediate crystallite phases were observed using *in situ* in-house X-ray powder diffraction with a 19 s time resolution, allowing to follow the evolution of phase transformations: $\text{Cu}^{\text{II}}_2(\text{OH})_3\text{NO}_3 \rightarrow \text{Cu}^{\text{II}}\text{O} \rightarrow \text{Cu}^{\text{I}}_2\text{O} \rightarrow \text{Cu}^0$. The crystallite size increased with increasing reaction temperature and with increasing Cu^{2+} concentration in the precursor.

The Gualtieri kinetic model was used to investigate the reaction kinetics of the reduction process, using the normalized scale factors obtained from Rietveld refined *in situ* PXRD data as the extend-of-reaction. The reaction kinetics and pathway were found to depend strongly on reaction temperature for the experiments performed at 250 °C, 300 °C, and 350 °C, however, at high temperatures (400 °C and 450°C), a higher time resolution is needed to explore their kinetics.

The *in situ* results were successfully used as guidance for an up-scaled synthesis using a continuous supercritical flow reactor. Copper nanoparticles were confirmed by PXRD and TEM images with a number weighted average size of 21.4(3) nm.

The work has demonstrated the power of *in situ* X-ray diffraction investigations and the ability to perform these experiments in the home laboratory, without the use of synchrotron radiation. The simple methods demonstrated here can be spread more widely and significantly speed up the discovery and tailoring of advanced functional materials.

Conflicts of interest

There are no conflicts of interest to be declared.

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Associated content:

Supporting Information. Additional description of methods and results along with crystallographic data are available free of charge via the Internet at <http://pubs.acs.org>

References:

1. Shao, L.-Y.; Coyle, J. P.; Barry, S. T.; Albert, J., Anomalous permittivity and plasmon resonances of copper nanoparticle conformal coatings on optical fibers [Invited]. *Opt. Mater. Express* **2011**, *1*, 128-137.
2. Toyir, J.; de la Piscina, P. R. r.; Fierro, J. L. G.; Homs, N. s., Highly effective conversion of CO₂ to methanol over supported and promoted copper-based catalysts: influence of support and promoter. *Appl. Catal., B* **2001**, *29*, 207-215.
3. Athanassiou, E. K.; Grass, R. N.; Stark, W. J., Large-scale production of carbon-coated copper nanoparticles for sensor applications. *Nanotechnology* **2006**, *17*, 1668-1673.
4. Yu, H. L.; Xu, Y.; Shi, P. J.; Xu, B. S.; Wang, X. L.; Liu, Q., Tribological properties and lubricating mechanisms of Cu nanoparticles in lubricant. *Trans. Nonferrous Met. Soc. China* **2008**, *18*, 636-641.
5. Lee, Y.; Choi, J. R.; Lee, K. J.; Stott, N. E.; Kim, D., Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics. *Nanotechnology* **2008**, *19*, 415604.
6. Kenfack, F.; Langbein, H., Synthesis and thermal decomposition of freeze-dried copper-iron formates. *Thermochim. Acta* **2005**, *426*, 61-72.
7. Salavati-Niasari, M.; Davar, F.; Mir, N., Synthesis and characterization of metallic copper nanoparticles via thermal decomposition. *Polyhedron* **2008**, *27*, 3514-3518.

8. Zhu, H.; Zhang, C.; Yin, Y., Novel synthesis of copper nanoparticles: influence of the synthesis conditions on the particle size. *Nanotechnology* **2005**, *16*, 3079.
9. Zhu, H.-t.; Zhang, C.-y.; Yin, Y.-s., Rapid synthesis of copper nanoparticles by sodium hypophosphite reduction in ethylene glycol under microwave irradiation. *J. Cryst. Growth* **2004**, *270*, 722-728.
10. TANG, X.-l.; Ling, R.; SUN, L.-n.; TIAN, W.-g.; CAO, M.-h.; HU, C.-w., A solvothermal route to Cu₂O nanocubes and Cu Nanoparticles. *Chem. Res. Chin. Univ.* **2006**, *22*, 547-551.
11. Carroll, K. J.; Reveles, J. U.; Shultz, M. D.; Khanna, S. N.; Carpenter, E. E., Preparation of Elemental Cu and Ni Nanoparticles by the Polyol Method: An Experimental and Theoretical Approach. *J. Phys. Chem. C* **2011**, *115*, 2656-2664.
12. Park, B. K.; Jeong, S.; Kim, D.; Moon, J.; Lim, S.; Kim, J. S., Synthesis and size control of monodisperse copper nanoparticles by polyol method. *J. Colloid Interface Sci.* **2007**, *311*, 417-424.
13. Huang, Z.; Cui, F.; Kang, H.; Chen, J.; Zhang, X.; Xia, C., Highly dispersed silica-supported copper nanoparticles prepared by precipitation–gel method: a simple but efficient and stable catalyst for glycerol hydrogenolysis. *Chem. Mater.* **2008**, *20*, 5090-5099.
14. Ziegler, K. J.; Doty, R. C.; Johnston, K. P.; Korgel, B. A., Synthesis of organic monolayer-stabilized copper nanocrystals in supercritical water. *J. Am. Chem. Soc.* **2001**, *123*, 7797-7803.
15. Kubota, S.; Morioka, T.; Takesue, M.; Hayashi, H.; Watanabe, M.; Smith, R. L., Continuous supercritical hydrothermal synthesis of dispersible zero-valent copper nanoparticles for ink applications in printed electronics. *J. Supercrit. Fluids* **2014**, *86*, 33-40.
16. Aymonier, C.; Loppinet-Serani, A.; Reveron, H.; Garrabos, Y.; Cansell, F., Review of supercritical fluids in inorganic materials science. *J. Supercrit. Fluids* **2006**, *38*, 242-251.
17. Adschiri, T.; Lee, Y. W.; Goto, M.; Takami, S., Green materials synthesis with supercritical water. *Green Chem.* **2011**, *13*, 1380-1390.
18. Sue, K. W.; Kimura, K.; Yamamoto, M.; Arai, K., Rapid hydrothermal synthesis of ZnO nanorods without organics. *Mater. Lett.* **2004**, *58*, 3350-3352.
19. Sue, K.; Kawasaki, S.; Suzuki, M.; Hakuta, Y.; Hayashi, H.; Arai, K.; Takebayashi, Y.; Yoda, S.; Furuya, T., Continuous hydrothermal synthesis of Fe₂O₃, NiO, and CuO nanoparticles by superrapid heating using a T-type micro mixer at 673 K and 30 MPa. *Chem. Eng. J.* **2011**, *166*, 947-953.
20. Mi, J. L.; Johnsen, S.; Clausen, C.; Hald, P.; Lock, N.; So, L.; Iversen, B. B., Highly controlled crystallite size and crystallinity of pure and iron-doped anatase-TiO₂ nanocrystals by continuous flow supercritical synthesis. *J Mater Res* **2013**, *28*, 333-339.
21. Andersen, H. L.; Jensen, K. M. O.; Tyrsted, C.; Bojesen, E. D.; Christensen, M., Size and Size Distribution Control of gamma-Fe₂O₃ Nanocrystallites: An in Situ Study. *Cryst. Growth Des.* **2014**, *14*, 1307-1313.
22. Sun, P. P.; Wang, S. Z.; Zhang, T.; Li, Y. H.; Guo, Y., Supercritical Hydrothermal Synthesis of Submicrometer Copper(II) Oxide: Effect of Reaction Conditions. *Ind. Eng. Chem. Res.* **2017**, *56*, 6286-6294.
23. Blackburn, J. M.; Long, D. P.; Cabanas, A.; Watkins, J. J., Deposition of conformal copper and nickel films from supercritical carbon dioxide. *Science* **2001**, *294*, 141-145.
24. Choi, H.; Veriansyah, B.; Kim, J.; Kim, J. D.; Kang, J. W., Continuous synthesis of metal nanoparticles in supercritical methanol. *J. Supercrit. Fluid.* **2010**, *52*, 285-291.
25. Jaehoon, K.; Daewoo, K.; Veriansyah, B.; Jeong Won, K.; Jae-Duck, K., Metal nanoparticle synthesis using supercritical alcohol. *Mater. Lett.* **2009**, *63*, 1880-1882.
26. Shin, N. C.; Lee, Y.-H.; Shin, Y. H.; Kim, J.; Lee, Y.-W., Synthesis of cobalt nanoparticles in supercritical methanol. *Mater. Chem. Phys.* **2010**, *124*, 140-144.
27. Veriansyah, B.; Kim, J. D.; Min, B. K.; Kim, J., Continuous synthesis of magnetite nanoparticles in supercritical methanol. *Mater. Lett.* **2010**, *64*, 2197-2200.

28. Bondesgaard, M.; Becker, J.; Xavier, J.; Hellstern, H.; Mamakhel, A.; Iversen, B. B., Guide to by-products formed in organic solvents under solvothermal conditions. *J. Supercrit. Fluid* **2016**, *113*, 166-197.
29. Gadhe, J. B.; Gupta, R. B., Hydrogen production by methanol reforming in supercritical water: Catalysis by in-situ-generated copper nanoparticles. *Int. J. Hydrogen Energy* **2007**, *32*, 2374-2381.
30. Jensen, K. M.; Andersen, H. L.; Tyrsted, C.; Bøjesen, E. D.; Dippel, A.-C.; Lock, N.; Billinge, S. J.; Iversen, B. B.; Christensen, M., Mechanisms for iron oxide formation under hydrothermal conditions: an in situ total scattering study. *ACS nano* **2014**, *8*, 10704-10714.
31. Bremholm, M.; Felicissimo, M.; Iversen, B. B., Time-Resolved In Situ Synchrotron X-ray Study and Large-Scale Production of Magnetite Nanoparticles in Supercritical Water. *Angew. Chem.* **2009**, *121*, 4882-4885.
32. Granados-Miralles, C.; Saura-Muzquiz, M.; Bojesen, E. D.; Jensen, K. M. O.; Andersen, H. L.; Christensen, M., Unraveling structural and magnetic information during growth of nanocrystalline SrFe₁₂O₁₉. *J. Mater. Chem. C* **2016**, *4*, 10903-10913.
33. Andersen, H. L.; Bøjesen, E. D.; Birgisson, S.; Christensen, M.; Iversen, B. B., Pitfalls and reproducibility of in situ synchrotron powder X-ray diffraction studies of solvothermal nanoparticle formation. *J. Appl. Crystallogr.* **2018**, *51*, 526-540.
34. Gjørup, F. H.; Ahlburg, J. V.; Christensen, M., Laboratory setup for rapid *in situ* powder X-ray diffraction elucidating Ni particle formation in supercritical methanol. *Rev. Sci. Instrum.*, submitted for publication, **2019**.
35. Gualtieri, A. F., Synthesis of sodium zeolites from a natural halloysite. *Phys. Chem. Miner.* **2001**, *28*, 719-728.
36. Hellstern, H. L.; Becker, J.; Hald, P.; Bremholm, M.; Mamakhel, A.; Iversen, B. B., Development of a Dual-Stage Continuous Flow Reactor for Hydrothermal Synthesis of Hybrid Nanoparticles. *Ind. Eng. Chem. Res.* **2015**, *54*, 8500-8508.
37. Rodríguez-Carvajal, J., Recent advances in magnetic structure determination by neutron powder diffraction. *Phys. B* **1993**, *192*, 55-69.
38. Effenberger, H., Verfeinerung der Kristallstruktur des monoklinen Dikupfer(II)-trihydroxynitrates Cu₂(NO₃)(OH)₃. *Z. Kristallogr. Cryst. Mater.* **1983**, *165*, 127-135.
39. Massarotti, V. C., D.; Bini, M.; Altomare, A.; Moliterni, A.G.G., X-ray powder diffraction ab initio structure solution of materials from solid state synthesis: the copper oxide case. *Z. Kristallogr. Cryst. Mater.* **1998**, *213*, 259.
40. Nilius, N.; Fedderwitz, H.; Groß, B.; Noguera, C.; Goniakowski, J., Incorrect DFT-GGA predictions of the stability of non-stoichiometric/polar dielectric surfaces: the case of Cu₂O(111). *Phys. Chem. Chem. Phys.* **2016**, *18*, 6729-6733.
41. Fortes, A. D.; Suard, E.; Lemee-Cailleau, M. H.; Pickard, C. J.; Needs, R. J., Crystal Structure of Ammonia Monohydrate Phase II. *J. Am. Chem. Soc.* **2009**, *131*, 13508-13515.
42. Dewames, R. E.; Wolfram, T.; Lehman, G. W., Temperature Dependence of the Debye-Waller Factor for Copper and Aluminum. *Phys. Rev.* **1963**, *131*, 528-529.
43. Purushotham, E., Effect of Particle Size and Lattice Strain on the Debye-Waller Factors of Copper (Cu) Powder Using High Energied Ball Mill. *J. Eng. Sci. Technol. Rev.* **2013**, *6*, 83-86.
44. Singh, N.; Sharma, P. K., Debye-Waller Factors of Cubic Metals. *Phys. Rev. B* **1971**, *3*, 1141-1148.
45. Black, D. R.; Windover, D.; Henins, A.; Filliben, J.; Cline, J. P., Certification of Standard Reference Material 660B. *Powder Diffr.* **2012**, *26*, 155-158.
46. Weidenthaler, C.; Fischer, R. X.; Shannon, R. D., Pitfalls in the powder diffraction analysis of zeolites ZSM-5 and ZSM-8. *Powder Diffr.* **1994**, *9*, 204-212.
47. Avrami, M., Kinetics of phase change I - General theory. *J Chem Phys* **1939**, *7*, 1103-1112.

48. Johnson, W. A.; Mehl, R. F., Reaction kinetics in processes of nucleation and growth. *T. Am. I. Min. Met. Eng.* **1939**, *135*, 416-442.
49. McHenry, M. E.; Johnson, F.; Okumura, H.; Ohkubo, T.; Ramanan, V. R. V.; Laughlin, D. E., The kinetics of nanocrystallization and microstructural observations in FINEMET, NANOPERM and HITPERM nanocomposite magnetic materials. *Scr. Mater.* **2003**, *48*, 881-887.
50. Goodwin, R. D., Methanol Thermodynamic Properties From 176 to 673 K at Pressures to 700 Bar. *J. Phys. Chem. Ref. Data* **1987**, *16*, 799-892.

For table of contents use only

Title:

In Situ In-House Powder X-ray Diffraction Study of Zero-Valent Copper Formation in Supercritical Methanol

Author list:

Panpan Sun,^{1,2} Frederik H. Gjørup,² Jakob V. Ahlburg,² Aref Mamakhel,² Shuzhong Wang,¹ Mogens Christensen.^{2*}

TOC graphic:

Synopsis: The evolution of different copper phases with changing valence in supercritical methanol is observed *in situ* using an in-house powder X-ray diffraction setup. Varying the reaction temperature between 250 °C and 450 °C result in different observable phases, and based on the results the following phase transitions are observed: $\text{Cu}^{2+}_2(\text{OH})_3\text{NO}_3 \rightarrow \text{Cu}^{2+}\text{O} \rightarrow \text{Cu}^+\text{O} \rightarrow \text{Cu}^0$.