Nanoparticle Generation for Follow-Up Exposure Studies by Oxidation of Copper Acetylacetonate.

Moravec, Pavel
2017

NANOPARTICLE GENERATION FOR FOLLOW-UP EXPOSURE STUDIES BY OXIDATION OF COPPER ACETYLACETONATE

Pavel MORAVEC[1], Jaroslav SCHWARZ[1], Petr VODIČKA[1], Jaroslav ŠVEHLA[1], Jaroslav KUPCÍK[2]

[1] Institute of Chemical Process Fundamentals of the CAS, v.v.i., Prague, Czech Republic, moravec@icpf.cas.cz
[2] Institute of Inorganic Chemistry of the CAS, v.v.i., Husinec-Řež, Czech Republic, kupcik@iic.cas.cz

Keywords: Exposure studies, MOCVD, Nanoparticle generation, Nanoparticle characterization

INTRODUCTION

The exposure to nanoparticles (NPs) represents a severe problem to human health, because they are becoming more widely used and their number of applications continually increases. Particles containing copper are emitted from smelters, iron foundries, power stations and municipal incinerators (WHO, 1998), as well as from brake linings during braking, Kukutschova *et al.* (2011). Copper and copper oxide NPs are frequently used as catalysts, heat transfer fluids in machine tools (Kim *et al.*, 2011), inks, anode material in lithium-ion batteries (Guo *et al.*, 2002) and many others. Even though CuO NPs were found highly toxic, Karlsson *et al.* (2008) and it is likely that NPs enter human body via respiratory tract, the inhalation exposure experiments of CuO NPs with laboratory animals are still rather rare (Pettibone *et al.*, 2008; Lebedova *et al.*, 2016). The exposure chamber for long lasting inhalation experiments was constructed at the Institute of Analytical Chemistry of the CAS (Večeřa *et al.*, 2011) and some methods of NPs generation for these experiments were already tested in our laboratory (Moravec *et al.*, 2015; Moravec *et al.*, 2016a). The generation of Cu/Cu_2O NPs by thermal decomposition of copper acetylacetonate (CuAA) was reported by Moravec *et al.* (2016b) and here we present the results of long lasting generation of NPs by oxidation of CuAA.

EXPERIMENTAL SETUP

NPs generation was studied in an externally heated work tube with i. d. 25 mm and the length of heated zone 1 m. Total length of the work tube made from impervious aluminous porcelain (IAP) was 1.5 m. Experimental setup was described in more detail at Moravec *et al.* (2015). A stream of nitrogen carrier gas, saturated by precursor vapours in a saturator (Q_S), was fed into the reactor, where it was mixed with a stream of a mixture of nitrogen and air. A stream of particle laden gas (Q_R) was diluted at the outer part of the work tube by a diluting stream of air (Q_{Dil}). The particle production was studied in dependence on reactor (T_R) and saturator temperature (T_S) and on flow rates Q_R, Q_S and Q_{Dil}. Precursor vapour pressure (P_{CuAA}) was controlled by saturator temperature and/or saturator flowrate and its values in the reactor were calculated from the equation (Teghil *et al.*, 1981):

$$P_{CuAA}(Pa) = 1000 \times 10^{\left(4.8 - \frac{2828}{T_S(K)}\right)} \times \frac{Q_S}{Q_R}, \quad (1)$$

valid in the temperature range from 43 to172 °C. NPs production was monitored using scanning mobility particle sizer (SMPS, TSI model 3936L75). Samples for NPs characterization were deposited onto TEM grids using a nanometer aerosol sampler (NAS, TSI model 3089) and on cellulose, quartz, Zefluor and Sterlitech Ag filters. Filters were weighted before and after sampling on scales Sartorius M5P-000V001 with readability 1 μg. The particle characteristics were studied with high resolution transmission electron microscopy HRTEM, *JEOL 3010*, samples on TEM grids), energy dispersive spectroscopy (EDS, *INCA/Oxford* connected to *JEOL 3010*, TEM grids), inductively coupled plasma – optical emission spectrometry (ICP-OES, *Agilent 4200 MP-AES,* cellulose filters), elemental and organic carbon analysis (EC/OC, *Model 4, Sunset Laboratory*, quartz filters) and X-ray diffraction (XRD, *Bruker D8 Discover Diffractometer*, Ag filters). Interpretations of selected area electron diffraction (SAED) patterns were performed using program ProcessDiffraction (Lábár 2008; Lábár 2009).

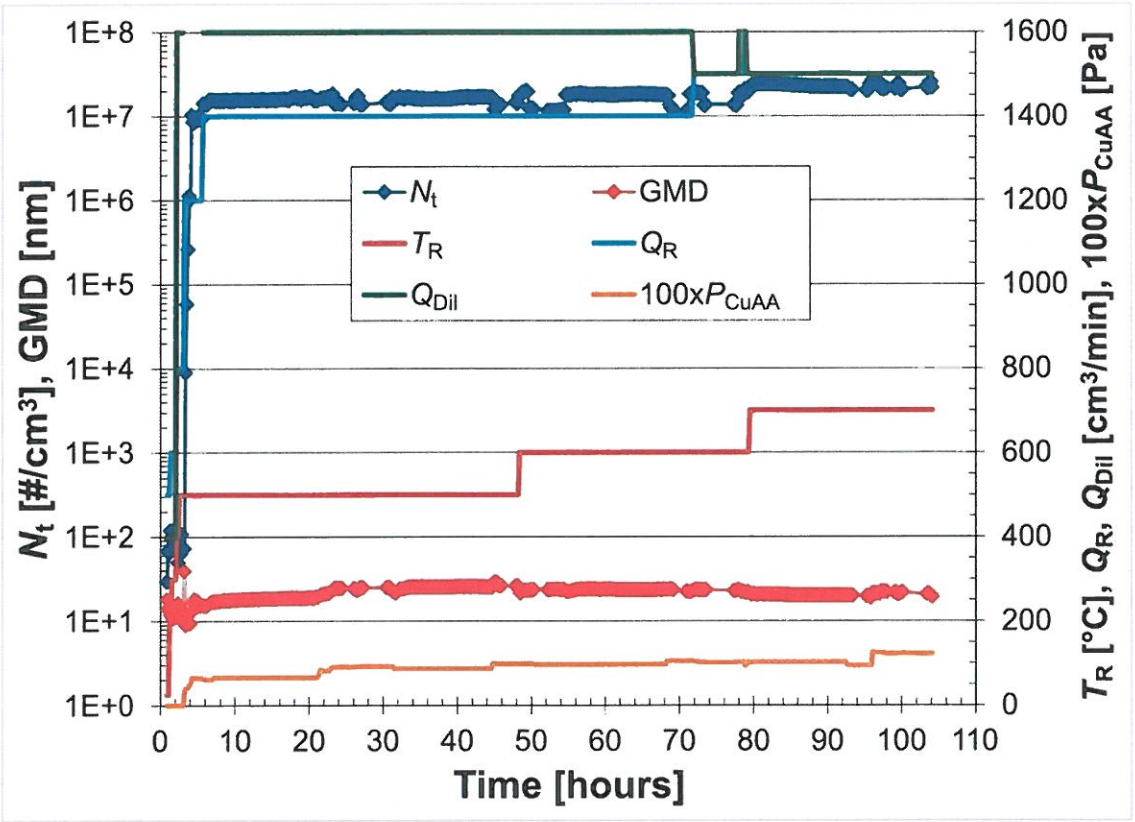

Fig. 1: N_t and GMD of NPs generated by oxidation of CuAA at various experimental conditions T_R, Q_R, Q_{Dil}, and P_{CuAA}. c_O=12 vol. %.

RESULTS AND CONCLUSIONS

NPs production was studied during an experimental campaign with total duration 104 h in dependence on experimental parameters T_R (500-700 °C), T_S (120-134 °C), Q_R

(1400-1500 cm^3/min), Q_S (150-300 cm^3/min) and Q_{Dil} (1500-1600 cm^3/min). Oxygen concentration (c_O) was kept on the value 12 vol. %. For this experimental campaign we used the same batch of precursor we already used in the 102 h long campaign for NPs generation by thermal decomposition of CuAA (Moravec *et al.*, 2016b). An example of NPs production in the form of total number concentration (N_t) and geometric mean diameter (GMD) is shown in Figure 1, but we have also available NPs production in mass total concentration M_t (μg/m^3) and surface total concentration S_t (nm^2/cm^3). It is obvious that NPs production is stable at steady state conditions and increases with increasing P_{CuAA}. With increasing T_R, N_t increases while GMD decreases, see Figure 1.

Total mass concentrations and, subsequently, emission rates (ER) were calculated both from SMPS data and also from filter measurements. The results are summarized in Table 1. Maximum NPs production rate from filter measurements 2000 μg/m^3, which corresponds with emission rate 6 μg/min, was achieved at T_R=600 °C. The values obtained from SMPS were several times lower. SMPS mass concentrations were calculated for default value of particle density 1.2 g/cm^3 in Aerosol Instrument manager software. In our former studies (Moravec *et al.*, 2016a, Moravec *et al.*, 2016b), where agglomerated very small primary particles were produced, the density 1.2 g/cm^3 proved to be quite good approximation, even though this value was far from bulk density of synthesized NPs (titania or copper/copper oxide). In this study, NPs detected by SMPS were larger and less agglomerated, see following paragraph, and therefore, default particle density 1.2 g/cm^3 was rather far from reality.

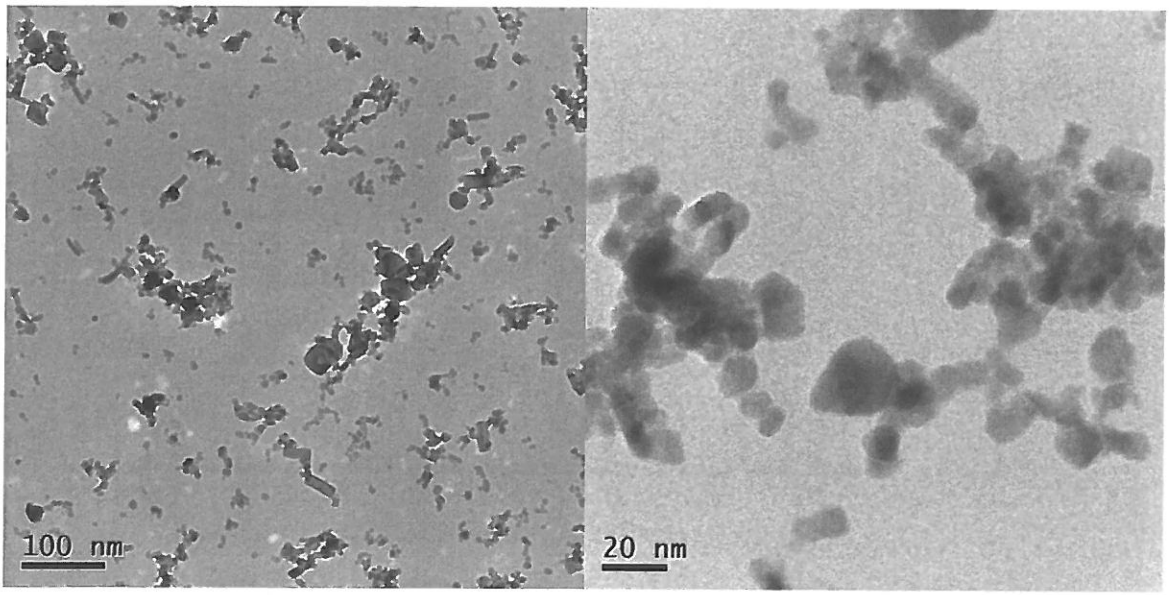

Fig. 2: TEM images of the sample of NPs synthesized at T_R=500 °C, Q_R=1400 cm^3/min, Q_{Dil}=1600 cm^3/min, P_{CuAA}=0.82 Pa and c_O=12 vol. %.

Morphology of NPs was studied by HRTEM and an example of NPs images, synthesized at T_R=500 °C, is shown in Figure 2. As can be seen, NPs are often faceted with typical size 10-30nm, but there is also some portion of larger particles with sizes up to 100 nm. We did not observe significant differences in NPs morphology synthesized at various T_R. From a comparison of GMD detected by SMPS (typically 20-25 nm, see Figure 1), with typical NPs size from TEM images, one can conclude that SMPS detected mostly individual particles and agglomeration occurred mainly during deposition of NPs on TEM grids. The true density of particles/agglomerates detected by SMPS was then close to the bulk density of material the particles consist of.

Table 1: NPs production and emission rates as a function of T_R.

T_R [°C]	500	600	700
M_t, SMPS [μg/m³]	420-510	330-380	370-540
M_t, Filters [μg/m³]	1220-1490	1500-2020	1400-1820
ER, SMPS [μg/min]	1.3-1.5	1.0-1.1	1.1-1.6
ER, SMPS [μg/min]	3.7-4.5	4.5-6.0	4.2-5.5

EDS analyses confirmed, besides nickel and carbon from TEM grids, presence of copper and oxygen in the samples. Cu to O ratio was close to one in most of spectra. Total concentration of Cu in the samples on cellulose filters was almost independent on T_R, varied between 69.1 and 73.9 mass % with maximum value at T_R=600 °C, see Table 2. Values of TC concentration, determined from the samples on quartz fibre filters by EC/OC analysis, were independent on T_R, too, see Table 2. However, the values were very low, varied between 1.0 and 1.5 mass %, so that NPs can be considered as carbon free.

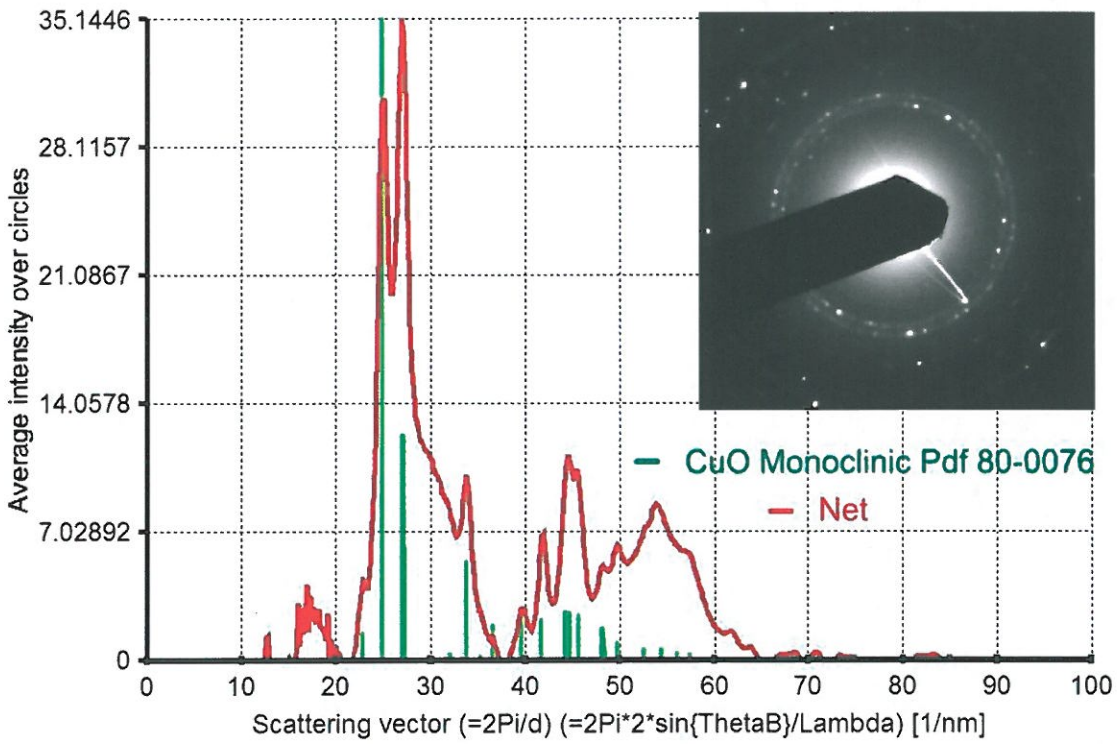

Fig. 3: A comparison of electron diffraction pattern of NPs synthesized at T_R=500 °C, Q_R=1400 cm³/min, Q_{Dil}=1600 cm³/min, P_{CuAA}=0.82 Pa, c_O=12 vol. % (inset and red curve) with model diffraction of monoclinic CuO.

XRD method identified CuO monoclinic crystalline phase (Tenorite) in the samples of NPs synthesized at all three investigated T_R, see Table 2. Mean crystallite size, calculated by Pawley method from integral breadth of peaks (LVol-IB) varied from 20.9 to 27.0 nm with maximum at T_R=600 °C, see Table 2. The results of XRD method were confirmed by SAED analysis, see Table 2 and Figure 3. Crystallite sizes calculated by Pawley method are in very good agreement with primary particle sizes identified from TEM images, see Figure 2, and with GMD monitored by SMPS, see Figure 1.

Table 2: NPs characteristics in dependence on T_R.

T_R [°C]	500	600	700
TC [%], EC/OC	1.5	1.0	1.1
Cu [%], ICP-OES	69.8	73.9	69.1
cryst. phase, SAED	monoclinic CuO	monoclinic CuO	monoclinic CuO
cryst. phase, XRD	monoclinic CuO	monoclinic CuO	monoclinic CuO
cryst. size, XRD [nm]	20.9	27.0	22.8

In conclusion, the study of long-term generation of NPs by oxidation of CuAA in externally heated tube rector has shown that NPs generation at T_R=600 °C seems to be the most suitable for follow-up inhalation exposure experiments. At this T_R, the maximum emission rate 6 µg/min was achieved, NPs contained the highest content of Cu (73.9 mass %, which corresponds with 92.5 % CuO) and the lowest content of TC. NPs are very well defined in terms of composition, size and crystalline structure. The method of NPs generation by CuAA oxidation suits well for follow-up long lasting inhalation exposure experiments with laboratory animals.

ACKNOWLEDGEMENT

This work was supported by the Czech Science Foundation under grant P503/12/G147. XRD analyses were performed by Mgr. Anna Kallistová, Geological Institute of the CAS, v.v.i.

REFERENCES

Guo K., Pan Q., Wang L., Fang S., Nano-scale copper-coated graphite as anode material for lithium-ion batteries, *J. Appl. Electrochem.*, 32, 109-120, (2002).

Karlsson H. L., Cronholm P., Gustafsson J., Möller L., Copper oxide nanoparticles are highly toxic: A Comparison between metal oxide nanoparticles and carbon nanotubes, *Chem. Res. Toxicol.*, 21, 1726-1732 (2008).

Kim J.S., Adamcakova-Dodd A., O'Shaughnessy P.T., Grassian V.H., Thorne P.S., Effects of copper nanoparticle exposure on host defence in a murine pulmonary infection model, *Particle and Fibre Toxicology*, **8**:29.

Kukutschová J., Moravec P., Tomášek V., Matějka V., Smolík J., Schwarz J., Sejdlerová J., Šafářová K., Filip P., On airborne nano/micro-sized wear particles released from low-metallic automotive brakes, *Environmental Pollution* 159, 998-1006 (2011).

Lábár J.L., Electron diffraction based analysis of phase fractions and texture in nanocrystalline thin films; Part I: Principles, *Microscopy and Microanalysis* 14, 287-295 (2008).

Lábár J.L., Electron diffraction based analysis of phase fractions and texture in nanocrystalline thin films; Part II: Implementation, *Microscopy and Microanalysis* 15, 20-29 (2009).

Lebedová J., Bláhová L., Večeřa Z., Mikuška P., Dočekal B., Buchtová M., Míšek I., Dumková J., Hampl A., Hilscherová K., Impact of acute and chronic inhalation

exposure to CdO nanoparticles on mice, *Environ. Sci. Pollut. Res.*, 23, 24047-24060, (2016).

Moravec P., Smolík J., Ondráček J., Vodička P., Fajgar R., Lead and/or lead oxide nanoparticle generation for inhalation experiments, *Aerosol Sci. Technol.*, 49, 655-665 (2015).

Moravec P., Schwarz J., Vodička P., Koštejn M., Study of TiO_2 nanoparticle generation for follow-up inhalation experiments with laboratory animals, *Aerosol Sci. Technol.*, DOI: 10.1080/02786826.2016.1224803; (2016a).

Moravec P., Schwarz J., Vodička P., Kupčík J., Švehla J., Generation of NPs for exposure experiments from copper acetylacetonate, 17th ACCAS, 25.-26.10. 2016, Želiv, Czech Republic, pp 95-100, (2016b).

Pettibone J.M., Adamcakova-Dood A., Thorne P.S., O'Shaughnessy P.T., Weydert J.A., Grassian V.H., Inflammatory response of mice following inhalation exposure to iron and copper nanoparticles, *Nanotoxicology*, 2, 189-204, (2008).

Teghil R., Ferro D., Bencivenni L., Pelino M., A thermodynamic study of the sublimation processes of aluminum and copper acetylacetonates, *Thermochimica Acta*, 44, 213-222, (1981).

Večeřa Z., Mikuška P., Moravec P., Smolík J., Unique exposure system for the whole body inhalation experiments with small animals. Nanocon 2011, 21.-23.9.2011, Brno, Czech Republic, pp 652-654.

WHO (1998) Environmental Health Criteria for Copper, No. 200, International Programme on Chemical Safety, World Health Organisation, Geneva, Switzerland.