Generation of Pb/PbO_x nanoparticles for inhalation experiments

P. Moravec, J. Smolík, J. Ondráček, P. Vodička and R. Fajgar

Institute of Chemical Process Fundamentals AS CR, v.v.i., Prague, 16502, Czech Republic
Keywords: evaporation/condensation, externally heated tube reactor, MOCVD, nanoparticle generation.
Presenting author email: moravec@icpf.cas.cz

Health aspects of nanoparticles (NP′s) on living beings are considered to be important. However, the real data of the impact of NP′s inhalation are rather rare. A study of allocation of MnO_x nanoparticles in organs of laboratory animals in inhalation chamber was presented by Večeřa and Mikuška (2012). For these experiments a source of continual generation of nanoparticles in duration of days or even weeks and in appropriate concentration is necessary. In this work a study of continual generation of Pb/PbO_x nanoparticles in hot wall tube reactor are presented.

NP′s were synthesized in an externally heated tube flow reactor with i. d. 25 mm and length of heated zone 1 m. Three methods of NP′s generation were tested: i) thermal decomposition of lead bis(2,2,6,6,-tetramethyl-3-5heptanedionate) (PbTHD2) in inert atmosphere (pyrolysis), ii) thermal decomposition of PbTHD2 in oxidizing atmosphere (10 vol. % O_2, oxidation), iii) evaporation/condensation of metallic Pb. Particle production was studied in dependence on reactor temperature (T_R), precursor concentration (P_{PbTHD2} or P_{Pb}), and reactor flow rate (Q_R). The particle production was monitored by scanning mobility particle sizer (SMPS, TSI model 3936L75) and samples for particle characterization were deposited onto TEM grids using nanometer aerosol sampler (NAS, TSI model 3089) and on Sterlitech Ag filters. Particle characteristics were studied by transmission/scanning electron microscopy (TEM/SEM), energy dispersive spectroscopy (EDS), atomic mass spectroscopy (AMS), elemental carbon organic carbon (ECOC), X-ray diffractometry (XRD) and X-ray photoelectron spectrometry (XPS).

Production of NP′s by pyrolysis was stable at reactor temperature up to 550 °C with number concentration above $1.5 \cdot 10^7$ #/cm^3. With increasing T_R NP′s concentration at the reactor outlet decreases possibly due to deposition on the reactor wall. Size of primary particles specified by TEM was in the range from 5 to 15 nm. The content of Pb in samples determined by AMS varied between 46 and 61 mass %. ECOC analysis detected no EC and 22 mass % of OC. NP′s generated by oxidation have higher content of Pb (84 mass %) and almost zero content of both EC and OC. However, number concentration of generated particles was lower ($\leq 1.1 \cdot 10^7$ #/cm^3 at T_R 480 °C) and with increasing T_R the production of NP′s decreased rapidly. By evaporation/condensation method the production of NP′s was performed at T_R ranging from 840 to 860 °C. Number concentration of generated particles was above $1.5 \cdot 10^7$ #/cm^3 and mean particle/cluster size was between 20 and 30 nm (Figure 1) and the content of Pb in the samples was 80 mass %. XRD analysis (performed with a lag of about three weeks) showed diffraction pattern of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$, PDF 00-013-0131), which indicates that Pb NP′s are not long-term stable in the air and react with oxygen, CO_2 and air humidity. XPS analysis showed that lead is present in NP′s in bonds Pb-O.

From the three tested methods the evaporation/condensation of metallic Pb seems to be the most suitable for long lasting inhalation experiments due to its simplicity, unambiguous mechanism of NP′s formation and well defined composition. Even so, NP′s can change their composition during the lag between their formation and inhalation.

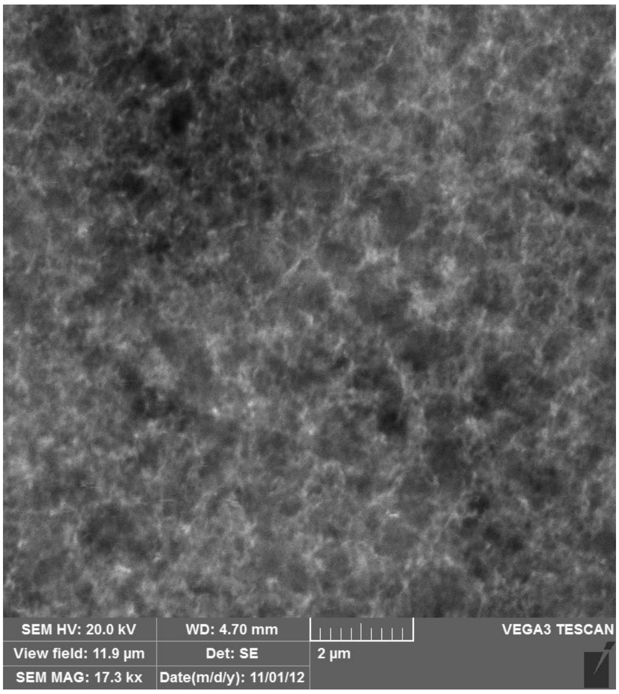

Figure 1. SEM image of NP′s generated by evaporation/condensation of metallic Pb at T_R=860 °C, Q_R=1000 cm^3/min.

This work was supported by the Grant Agency of the Czech Republic under grants P503/11/2315 and P503/12/G147. XPS analyses were performed by Dr. Josef Zemek, Institute of Physics AS CR, v.v.i., AMS analyses by MSc. Ludmila Soukupová, ICPF AS CR, v.v.i. and XRD analyses by Dr. Roman Skála, Geological Institute AS CR, v.v.i.

Večeřa, Z., and Mikuška, P. (2012) *Proc. 13th An. Conf. of the Czech Aerosol Soc., October 2012, Třeboň*.