A Comparison of Titania Nanoparticles Production in Two Different Reactors by MOCVD Method

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A COMPARISON OF TITANIA NANOPARTICLE PRODUCTION IN TWO DIFFERENT REACTORS BY MOCVD METHOD

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INTRODUCTION

Nanoparticles (NP's) have attracted considerable attention, because they show a quantum size effect, for which the physical and chemical properties are strongly dependent on particle size (Nakaso *et al.*, 2003). This change of properties can also affect the toxicity and therefore NP's cannot be treated the same way as bulk material. In spite of that, inhalation studies of NP's are still rather rare, Večeřa *et al.*, 2011. Recently, an exposure system for inhalation experiments was constructed in the Institute of Analytical Chemistry AS CR (Večeřa *et al.*, 2011) and the first experience with this system were reported by Večeřa *et al.*, 2012. For these studies, a method of continual long-term generation of NP's in the gas phase is necessary. Methods for long-term generation of MnO_x (Moravec *et al.*, 2013a) and Pb/PbO_x (Moravec *et al.*, 2013b) NP's have recently been reported. The next task was to test the method for long-term generation of TiO_2 NP's suitable for subsequent inhalation experiments.

Titania NP's are of interest for their unique properties and applications as pigments, cosmetics, catalyst and also photocatalyst for waste water treatments. Recently, titania NP's were used for exposure experiments, Koivisto *et al.*, 2011. However, in different reactors NP's synthesis proceeds in different ways. So, the aim of this study was to perform the long-term generation of TiO_2 NP's in the current high temperature ceramic tube reactor and to compare the results with our previous experiments performed in moderate temperature glass reactor (Moravec *et al.*, 2001)

EXPERIMENTAL SETUP

The current reactor is 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. Titanium tetraisopropoxide (TTIP) was used as a precursor. Vapors of TTIP were decomposed in an inert atmosphere (pyrolysis) or/and in the mixture of nitrogen and air with oxygen concentration 10 vol. % (oxidation). Vapor pressure of TTIP was calculated from the equation (Okuyama *et al.* 1986):

$$P(Pa) = 133.32 \times \exp(21.2 - \frac{7130}{T(K)}). \quad (1).$$

Current experimental setup was described in more detail by Moravec *et al.* (2014). Glass reactor consisted of the tube 55 cm long with ID 2.7 cm. Detailed description of the experimental setup with glass reactor was described by Moravec *et al.*, 2001.

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 PTFE, Zefluor, quartz, cellulose and Sterlitech Ag filters. Particle characteristics were studied by transmission/scanning electron microscopy (TEM, *JEOL 2000FX*/SEM, *TESCAN INDUSEM*), energy dispersive spectroscopy (EDS, *Bruker Quantax*), inductively coupled plasma – optical emission spectrometry (ICP-OES, *IRIS Intrepid II XDL*), elemental and organic carbon analyzer (EC/OC, *Model 4, Sunset Laboratory*), X-ray diffraction (XRD, *Philips X'Pert diffractometer PW3020*) and X-ray photoelectron spectrometry (XPS, *ADES-400, VG Scientific*). Four experimental campaigns were performed in total duration of 264 hours with one batch of precursor. NP's production and their characteristics were studied in dependence on TTIP vapor pressure (P_{TTIP}, 1.6 – 2.8 Pa, controlled both by saturator temperature T_S and by saturator flow rate Q_S), reactor temperature (T_R, 500 – 900 °C), reactor flow rate (Q_R, 800 – 1400 cm^3/min) and oxygen concentration (c_O; 0 or 10 vol. %).

Particle production in the glass reactor was monitored using Differential mobility particle sizer (DMPS, *TSI model 3932C*), and particle characteristics were analyzed by SEM/TEM, *JEOL 2000FX*) and by EDS (*Philips JXA 50A*). In the glass reactor 12 one day (8-10 hours) experiments were performed. One of those was in an oxidizing atmosphere ($c_O \sim 20$ vol. %). The particle production was investigated as a function of P_{TTIP} (0.3 – 2.8 Pa), T_R (300 – 500 °C) and Q_R (300 – 700 cm^3/min).

RESULTS AND CONCLUSIONS

IAP reactor

The requirement for inhalation experiments is to produce 3 liters of aerosol per minute with number concentration (N_t) above 1 x 10^7 #/cm^3 and geometric mean diameter (GMD) below 50 nm. Experiments have shown that particle production can be controlled by T_R, P_{TTIP} and Q_R. Generally, with increasing T_R and Q_R the number

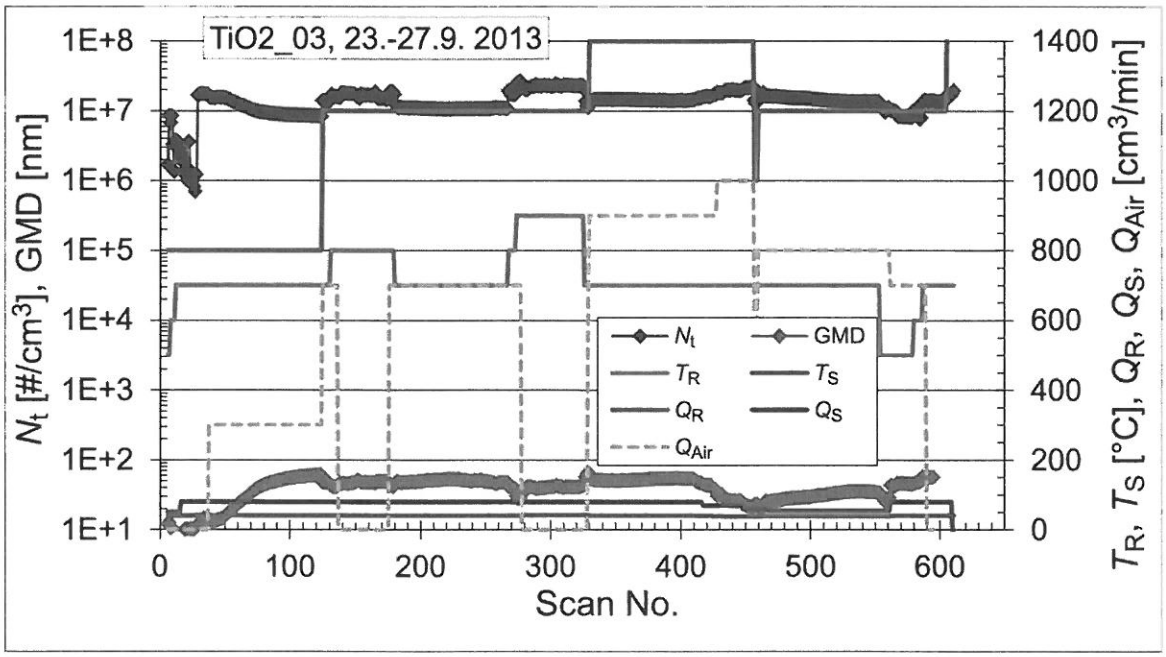

Fig. 1 Time dependence of N_t and GMD at given experimental conditions, one scan = 10 minutes.

concentration increases and the geometric mean diameter decreases, while the influence of the precursor vapor pressure has the opposite direction. At low precursor concentration N_t is high, often higher than 2.0 x 10^7 #/cm^3, but the size distribution is on the left edge of the measuring range of SMPS. With increasing precursor concentration the size distribution shifts to the right (mass concentration increases) but number concentration decreases. Desired N_t and GMD can be achieved in most of experimental conditions tested, which can be seen in Fig. 1.

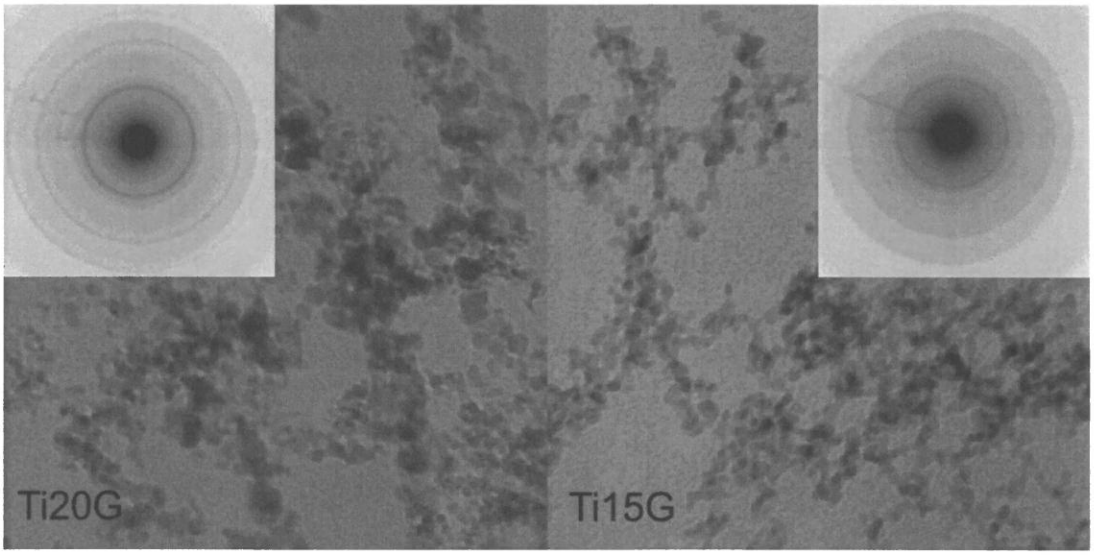

Fig. 2 TEM images and SAED patterns of the samples synthesized at 600 (Ti20G) and 800 °C (Ti15G), respectively. Size of both images is 343x343 nm.

Morphology of NP's was examined mainly by TEM. NP's are typically agglomerated into clusters and chains, see Fig. 2. Typical size of primary particles is increasing from 5 – 8 nm at T_R=500 °C to 12 – 20 nm at T_R=900 °C. However, the maximum NP's size has a minimum at T_R=800 °C, see Table 1. Part of the NP's synthesized at T_R=900 °C is facetted. NP's are monomodal with narrow dispersity in most cases. We did not observe any particles greater than 50 nm. Comparing TEM images with SMPS data it is obvious that SMPS detects already partially agglomerated particles.

Table 1 Morphology and SAED characteristics of NP's synthesized in IAP reactor, [a] estimated values from TEM images

Sample	Description	max. size[a] [nm]	typical size[a] [nm]	SAED [rings]
Ti33G	500 °C, air	16 - 26	5 - 8	4
Ti20G	600 °C, air	24 - 32	8 - 16	8
Ti10G	750 °C, air	16 - 24	8 - 10	8
Ti15G	800 °C, air	16 - 20	8 – 12	7
Ti18G	800 °C, N_2	25	10 - 12	10
Ti23G	900 °C, air	24 - 28	12 - 16	11
Ti25G	900 °C, N_2	24 - 32	12 - 20	11

EDS connected to TEM and/or SEM confirmed presence of Ti and O in the samples and also some other elements as C, Cu, Ag and Au, originating either from TEM grids or filters. The content of Ti on the cellulose filters was determined using ICP-OES method and it was, recalculated on TiO_2, between 74 and 85 weight %. Samples deposited on quartz fiber filters were analyzed on a content of EC and OC using the Eusaar2 thermo-optical protocol for EC/OC analysis (Cavalli *et al.*, 2010). All samples were free of EC and the content of OC was typically between 3 and 6 weight %, extreme values were 1.7 and 11 %. XPS analyses were performed from the surface layers cca 3 and 6 nm (two detection angles) and confirmed presence of Ti in bonds Ti-O (TiO_2) and C in bonds C-C, C-H and also C-O and C=O. That indicates that surface of NP's is contaminated by products of precursor decomposition and also by atmospheric humidity (shift of O^{1s} spectrum to the right) and CO_2.

XRD analysis identified tetragonal anatase crystalline pattern (PDF ICDD 86-1156) in NP's and also cubic silver (87-0717) and cubic chlorargyrite (AgCl; 31-1238) from the filter. The portion of crystalline phase in NP's increases with increasing T_R. In the samples synthesized at T_R=900 °C besides anatase also traces of tetragonal rutile (89-0553) crystalline pattern were detected. In the samples synthesized by oxidation and pyrolysis no visible difference in crystalline patterns was observed. Results obtained by XRD were confirmed by selected area electron diffraction (SAED) patterns. Number (and intensity) of visible rings in electron diffraction patterns is increasing with increasing T_R, see Table 1, and all of them belong to anatase electron diffraction pattern. At T_R=900 °C there were also some visible dots corresponding with rutile electron diffraction pattern.

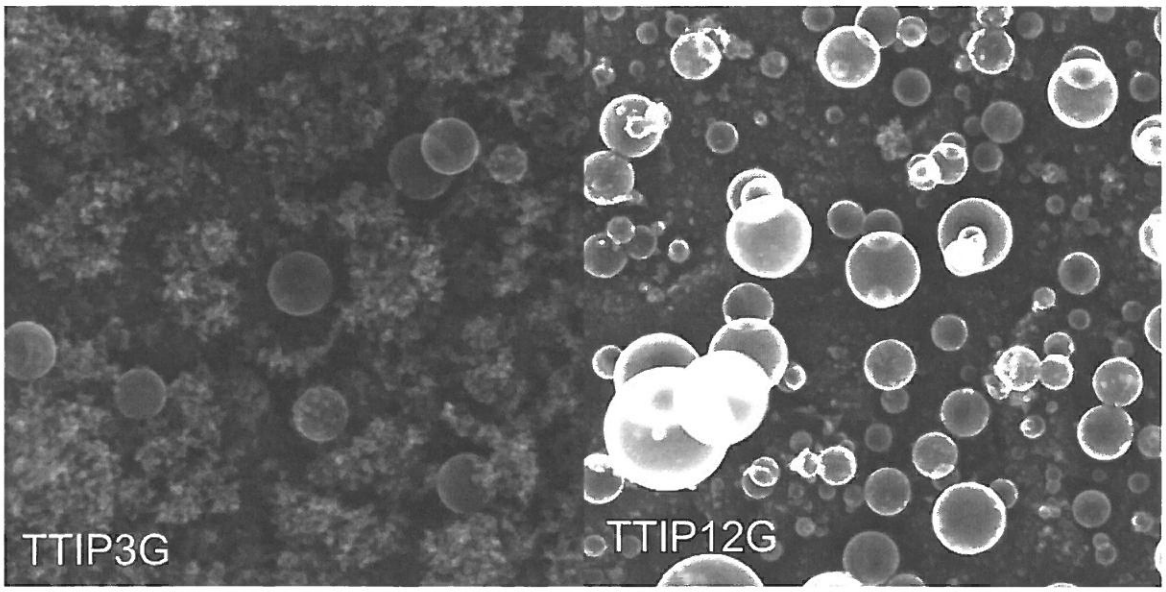

Fig. 3 SEM photos of the samples synthesized in glass reactor 3 at T_R=300 °C, P_{TTIP}=0.3 Pa (TTIP3G) and T_R=500 °C, P_{TTIP}=1.7 Pa (TTIP12G), respectively. Size of both images is 3.8x3.8 μm.

Moderate temperature glass reactor

NP's production occurred already at T_R below 300 °C and at P_{TTIP}=0.3 Pa. Above 350 °C, the number concentration of NP's decreased and instead of NP's a generation of submicron sized particles occurred. To increase the production of NP's it was necessary to increase the P_{TTIP} several times. However, the particle size distribution changed from

almost monomodal with GMD < 40 nm to bimodal with a lot of submicron sized particles, see Fig. 3. The maximum of particle production occurred at reactor flow rates 500 – 600 cm^3/min. It could be due to the deposition of NP's in the end section of the reactor and in the diluter by thermophoresis at higher flow rates.

EDS analysis confirmed presence of Ti and O in the particles. Dark field TEM images revealed that NP's synthesized by pyrolysis are mostly amorphous and crystalline nuclei are predominantly in submicron sized particles. Even though the SAED patterns are rather weak, they can be identified as a rutile electron diffraction pattern. Somehow different crystallinity was observed in the NP's prepared by oxidation. Dark field TEM image showed abundant occurrence of crystalline nuclei even in NP's. The SAED pattern differs from those in NP's synthesized by pyrolysis. However, the SAED pattern is rather weak and it is difficult to identify it correctly, but it looks like a combination of anatase and rutile electron diffraction patterns.

A comparison of the two reactors

In both reactors we observed an initial period necessary for development of full particle production. While in the glass reactor it usually did not exceed one hour, in the IAP reactor it took several times longer. Kirkbir and Komiyama (1987), who also reported formation of a great part of coarse particles in the quartz reactor in the temperature range from 300 to 700 °C, attributed this phenomenon to a competition of two simultaneous reaction mechanisms; heterogeneous reactions on the reaction wall catalyzed by the layer of TiO_2 deposit and the homogeneous reactions in the gas phase initiated by the intermediate products of heterogeneous reactions such as H_2O and free radicals from partial TTIP decomposition. However, a difference in the particle production and morphology in both reactors at the same T_R (500 °C) suggests that also material itself plays some role in initializing the process of TTIP decomposition and that heterogeneous reaction plays greater role in the glass reactor.

When a full rate of the particle production was achieved, several times higher N_t was generated in the IAP reactor and/because there were not generated any submicron sized particles. Also crystalline structures were different; mostly anatase in IAP reactor and predominantly rutile in the glass reactor. And finally, desired parameters of generated aerosol (N_t >1 x 10^7 #/cm^3, GMD<50 nm) for inhalation experiments could not be achieved in the glass reactor.

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REFERENCES

Cavalli F., Viana M., Yttri K.E., Genberg J., Putaud J.-P. Toward a standardized thermal-optical protocol for measuring atmospheric organic and elemental carbon: The EUSAAR protocol. *Atmospheric Measurement Techniques*, 2010, 3, 79-89, (2010).

Kirkbir F., Komiyama H. Formation and Growth Mechanism of Porous, Amorphous, and Fine Particles Prepared by Chemical Vapor Deposition. Titania from Titanium Tetraisopropoxide, *Can. J. Chem. Eng.* 65, 759-766, (1987).

Koivisto A. *et al.* Aerosol characterization and lung deposition of synthesized TiO_2 nanoparticles for murine inhalation studies, *J. Nanoparticle Res.* 13, 2949-2961, (2011).

Moravec P., Smolík J., Ondráček J., Večeřa Z., Mikuška P. Generation of Nanoparticles for Long Lasting Inhalation Experiments. *2nd QNano Integrating Conference*, Abstract Book, Prague, Czech Republic, 27 February - 01 March 2013a, p. 184 (7.12.).

Moravec P., Smolík J., Ondráček J., Vodička P., Fajgar R. Synthesis of lead and lead oxide nanoparticles for inhalation experiments. *Proc. of 14th Ann. Conf. of the Czech Aerosol Soc.*, Abstract Book, p. 19-22, Nový Smokovec, Slovakia, 23-25 October 2013b.

Moravec P., Smolík J., Levdansky V.V. Preparation of TiO_2 fine particles by thermal decomposition of titanium tetraisopropoxide vapor, *J. Mater. Sci. Letters*, 20, 2033-2037, (2001).

Moravec P., Schwarz J., Vodička P., Koštejn M. Generation of TiO_2 nanoparticles for follow-up inhalation experiments with laboratory animals, Nanocon 2014, 5.-7. 11. 2014, Brno, Czech Republic.

Okuyama K., Kousaka K., Tohge K., Yamamoto S., Wu J.J., Flagan R.C., Seinfeld J.H. Production of Metal Oxide Aerosol Particles by Thermal Decomposition of Metal Alkoxide Vapors. *AIChE J.*, 32, 2010-2019, (1986).

Nakaso K., Okuyama K., Shimada M, Pratsinis S.E., Effect of reaction temperature on CVD-made TiO_2 primary particle diameter, *Chem. Eng. Sci.*, 58, 3327-3335, (2003).

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.

Večeřa Z., Mikuška P., Moravec P., Smolík J., The first experience with new exposure system for the whole body inhalation experiments with small animals. Nanocon 2012, 23.-25.10.2012, Brno, Czech Republic.