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## GENERATION OF TiO<sub>2</sub> NANOPARTICLES FOR FOLLOW-UP INHALATION EXPERIMENTS WITH LABORATORY ANIMALS

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### Abstract

A method of TiO<sub>2</sub> nanoparticle generation appropriate for follow-up long lasting inhalation experiments with laboratory animals was tested. Nanoparticles were synthesized in an externally heated tube reactor using titanium tetraisopropoxide as a precursor. Total 264 hours of particle generation in four experimental campaigns was performed with one batch of precursor without observable decrease of precursor volatility. Particle production was studied in wide range of experimental conditions such as reactor temperature, reactor flow rate and precursor vapor pressure by pyrolysis, using nitrogen as a carrier gas, and also in oxidizing atmosphere (10 vol. % of oxygen in the reaction mixture). Particle characteristics were investigated by scanning/transmission electron microscopy, energy dispersive spectroscopy, inductively coupled plasma – optical emission spectrometry, elemental and organic carbon analyzer, X-ray diffraction and X-ray photoelectron spectrometry. As a result, particle production with number concentration high above  $1.0 \times 10^7$  #/cm<sup>3</sup> and with primary particle size well below 50 nm can be easily achieved in most of investigated experimental conditions. Particles are free of elemental carbon, content of organic carbon is less than 10 weight %, detected crystalline phase is typically anatase, Ti is present in bonds Ti-O (TiO<sub>2</sub>) and total Ti concentration recalculated on TiO<sub>2</sub> is approximately 80 mass %.

**Keywords:** Externally heated tube reactor, MOCVD, Nanoparticle generation, TiO<sub>2</sub> nanoparticles, Titanium tetraisopropoxide

### 1. INTRODUCTION

Health issues of nanoparticles (NP's) are considered to be important. When inhaled they can deposit in the lungs and then potentially move to other organs such as the brain, the liver, the spleen, etc. Some materials could become toxic if they are inhaled in the form of nanoparticles. However, the studies of allocation of inhaled NP's are rather rare. Recently, an inhalation chamber for study of allocation of nanoparticles in organs of laboratory animals was constructed in the Institute of Analytical Chemistry AS CR [1] and some results of inhalation experiments have been already reported [2]. For these experiments a source of continual generation of nanoparticles in duration of several weeks and with appropriate number concentration ( $N_t$ ) and particle size distribution is necessary. Methods for long term generation of nanoparticles MnO<sub>x</sub> [3] and Pb/PbO<sub>x</sub> [4] have been presented recently. The aim of this study was to test the method for long term generation of TiO<sub>2</sub> NP's suitable for subsequent inhalation study.

Generation of titania NP's in the gas phase is investigated quite a long time. Most frequently TiO<sub>2</sub> NP's were prepared by gas-to-particle method, either in a flame [5] or in an externally heated tube reactor [6], [7] by oxidation [5] or hydrolysis [7] of TiCl<sub>4</sub>, or by pyrolysis [6], oxidation [8] or hydrolysis [9] of metal organic precursors. Less often titania NP's were prepared by spray pyrolysis (droplet-to-particle method) using solutions of metalorganic precursors [10]. After evaluating the appropriateness of the methods described above and on the basis of our earlier experience [11], we decided to test the generation of TiO<sub>2</sub> NP's by pyrolysis and oxidation of titanium tetraisopropoxide (TTIP). Oxidation was examined with the intention to decrease the experimental cost replacing the part of nitrogen with compressed air.

## 2. EXPERIMENTAL

NP's were synthesized in an externally heated tube flow reactor with i. d. 25 mm and the length of heated zone 1 m. Total length of the work tube made from impervious aluminous porcelain was 1.5 m. 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 [12]:

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

Nitrogen, used as a carrier gas, was cleaned in the deoxygenator packed with Cu catalyst R3-11 (BASF) and dried in two drying columns filled with molecular sieve Dusimo S5A and with magnesium perchlorate 99 % (Fluka). TTIP saturator consists of two chambers. In the first one, a stream of nitrogen was saturated by TTIP vapors and in the second one the saturated carrier gas was diluted by another stream of N<sub>2</sub> to prevent condensation of TTIP in the tubing between saturator outlet and reactor inlet. At the inlet section of the reactor the stream saturated by TTIP was further diluted by additional stream of pure nitrogen (pyrolysis) or by the mixture of nitrogen and air (oxidation). Flow rates of individual gas streams were controlled by electronic mass controllers (Aalborg CFCS), temperatures of the saturator and the reactor by a thermostat and by electronic controller (THP 94), respectively.

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*).

## 3. RESULTS

### 3.1 NP'S PRODUCTION

Besides preliminary experiments we performed with one batch of precursor four experimental campaigns in total duration of 264 hours. NP's production and their characteristics were studied in dependence on TTIP vapor pressure ( $P_{\text{TTIP}}$ , 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<sup>3</sup>/min) and oxygen concentration ( $c_{\text{O}_2}$ ; 0 or 10 vol. %). Experiments have shown that particle size distribution can be controlled by  $T_R$ ,  $P_{\text{TTIP}}$  and  $Q_R$ . Generally, with increasing  $T_R$  and  $Q_R$  the number concentration ( $N_t$ ) increases and the geometric mean diameter (GMD) decreases, while the influence of the precursor vapor pressure has the opposite direction. At low precursor concentration  $N_t$  is high, often higher than  $2.0 \times 10^7$  #/cm<sup>3</sup>, but the size distribution is on the left edge of the measuring range of SMPS. With increasing precursor concentration size distribution shifts to the right (mass concentration increases) but number concentration decreases. An example of the dependence of particle production in the form of  $N_t$  and GMD on experimental conditions is shown in Fig. 1.

Similarly as in our earlier research performed with glass reactor [11] a start-up period of particle generation was observed (cca first 100 scans in Fig. 1), during which particle generation is gradually developing. According to Komiyama *et al.* [13] or Kim and Park [14] this is caused by the catalytic effect of arising titania particles being gradually deposited on the reactor wall at the beginning of the experiment and accelerating decomposition process. According to this theory it is supposed that the process of TTIP decomposition

proceeds both by homogeneous reaction in the reactor volume and also by heterogeneous catalytic reaction on the surface of TiO<sub>2</sub> NP's deposited on the reactor wall.

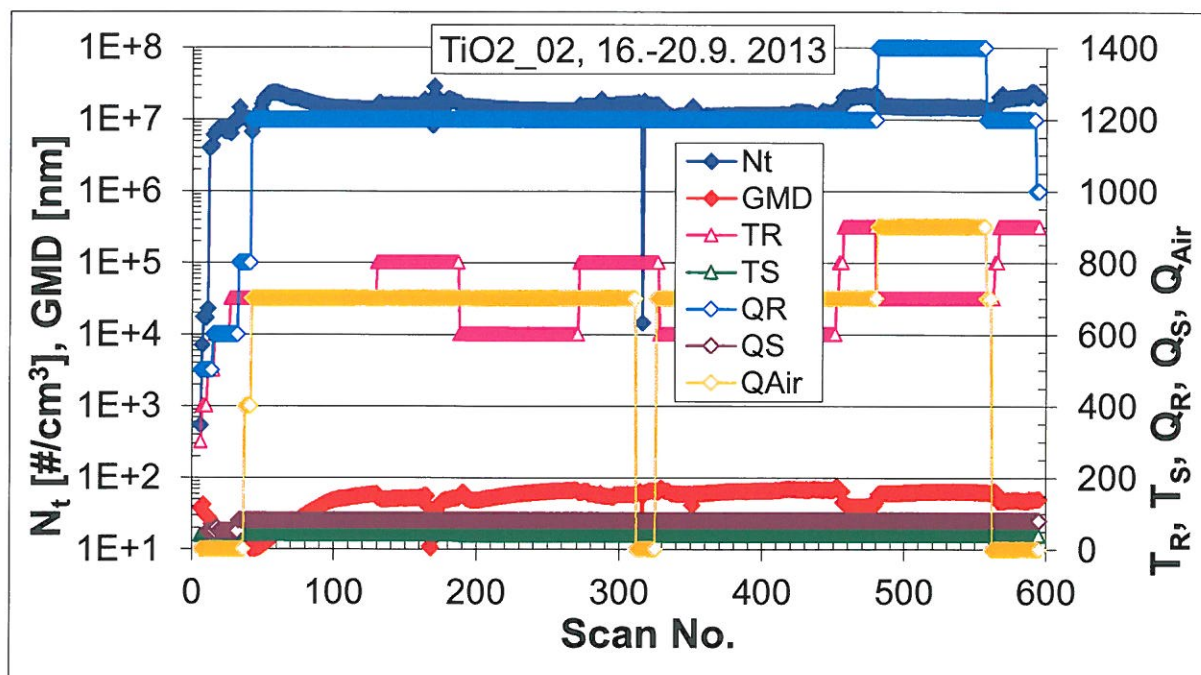


Fig. 1 Time dependence of  $N_t$  and GMD at given experimental conditions, one scan = 10 minutes.

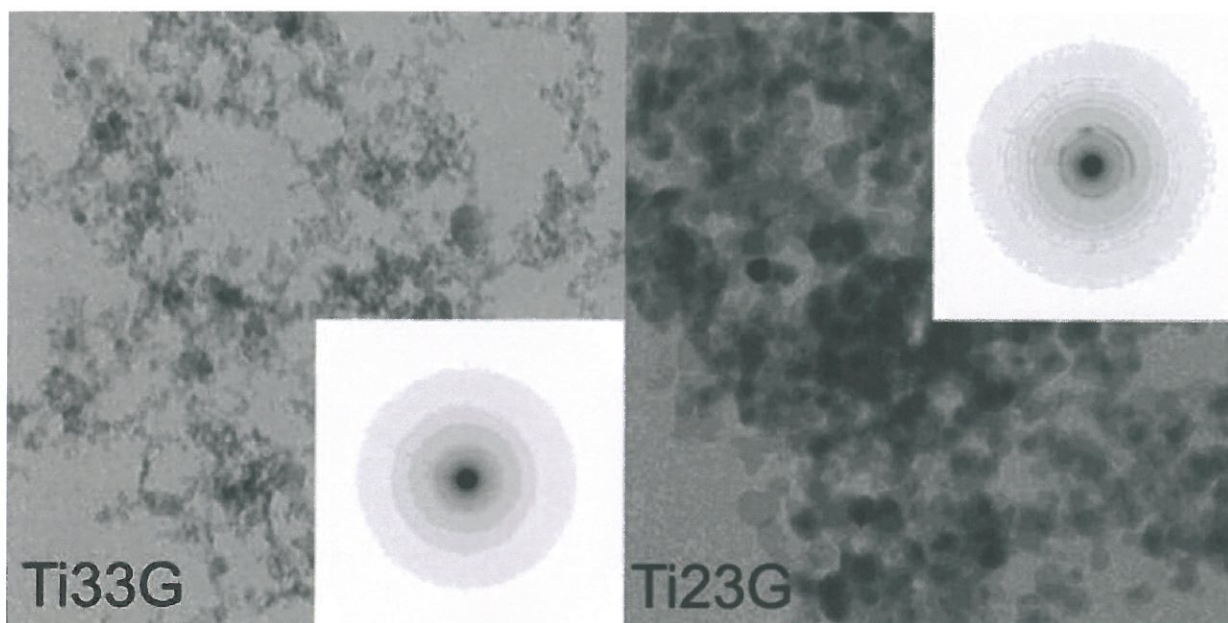
### 3.2 NP'S CHARACTERISTICS

Morphology of NP's was examined mainly by TEM from the samples deposited on TEM grids. NP's on TEM images are typically agglomerated into clusters and chains. 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. NP's synthesized by pyrolysis seem to be slightly larger than those formed by oxidation, but the difference is very small. Some morphology as well as selected area electron diffraction (SAED) characteristics are summarized in Table 1. At lower  $T_R$  the NP's were more polydisperse, which can be seen in Fig. 2. Some particles synthesized at 900 °C are faceted. The difference between GMD detected by SMPS (Fig. 1) and typical size of primary particles detected by TEM (Fig. 2, Table 1) indicates that SMPS detects agglomerates of primary particles.

Table 1 Morphology and SAED characteristics of NP's from TEM images, <sup>a</sup> estimated values from TEM images

Sample	Description	max. size <sup>a</sup> [nm]	typical size <sup>a</sup> [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 <sub>2</sub>	25	10 - 12	10
Ti23G	900 °C, air	24 - 28	12 - 16	11
Ti25G	900 °C, N <sub>2</sub>	24 - 32	12 - 20	11

In contrast with our previous research in glass reactor [11], where particles with bimodal size distribution and with some portion of submicron sized particles were produced, in this case the synthesized NP's were monodisperse with quite a low dispersity, which can be seen in Fig. 2. The reason may consists in higher  $T_R$  and higher  $Q_R$  (lower residence time) applied in present study. However, decreasing GMD from 300 to 65 nm with increasing  $T_R$  from 300 to 700 °C was reported by Kirkbir and Komiyama [15]. On the other hand, Okuyama *et al.* [12] reported increasing GMD from 19 to 37 nm with increasing  $T_R$  from 400 to 600 °C. An opposite trend in the study of Kirkbir and Komiyama [15] can be explained by much longer residence time and much higher precursor concentration used in their study.

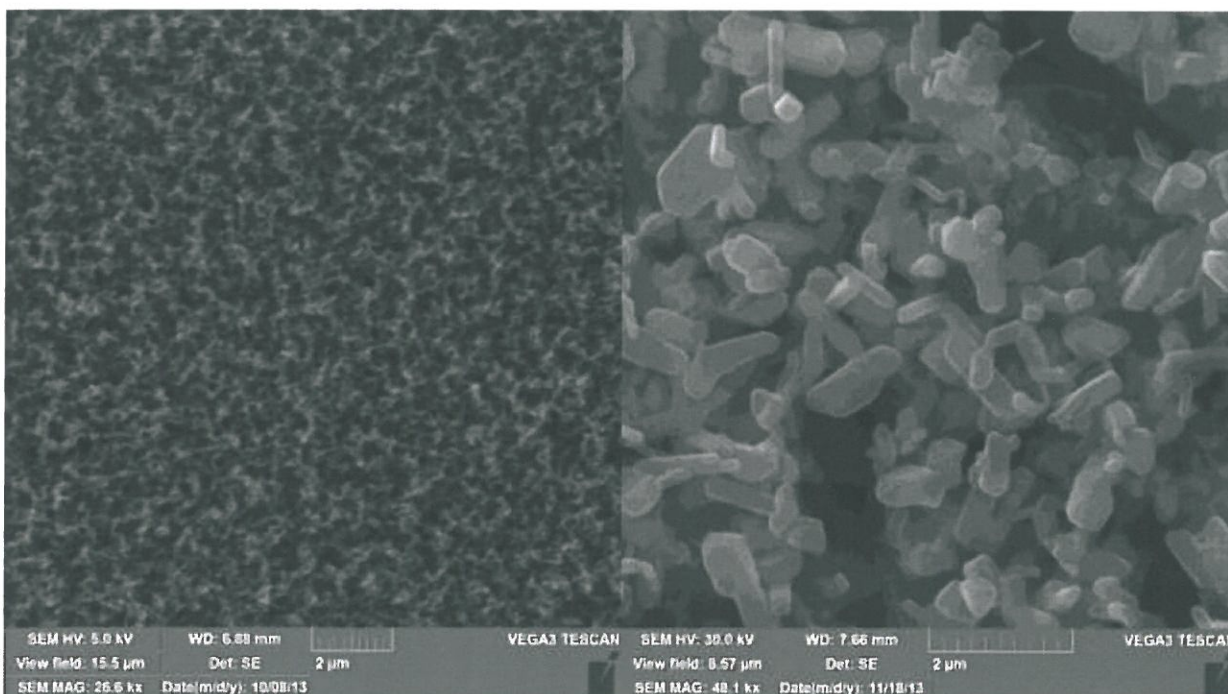


**Fig. 2** TEM images and electron diffraction patterns of the samples of NP's synthesized at 500 (Ti33G) and 900 °C (Ti23G), respectively. Size of both images is 343 x 343 nm.

EDS connected to TEM and/or SEM confirmed presence of Ti and O in the samples and also some other elements (C, Cu, Ag, Au) originating either from TEM grids or filters. Concentration of Ti in the samples on cellulose filters was analyzed by ICP-OES and the content of Ti recalculated on  $\text{TiO}_2$  was 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 [16]. All samples of NP's were free of EC and the content of OC was typically between 3 and 6 weight %, extreme values were 1.7 % on one side and 11 % on the other side. However, these values are somehow overestimated as the accuracy of this method is limited. Due to brittleness of quartz fiber filters some losses of filter's material occur when fixing them in the filter holder before sampling. As a result sample weight is underestimated and relative carbon content overestimated. Moreover, organic carbon is present in the atmosphere and it is adsorbed also on the filter surface. This was corrected by analysing the blank filter. However, during sampling not only NP's are deposited on the filter, but also gases from the precursor decomposition are adsorbed both on the filter and also on NP's surface, which further increases OC content detected by EC/OC analysis. 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 ( $\text{TiO}_2$ ) 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  $\text{O}^{1s}$  spectra to the right) and  $\text{CO}_2$ .

XRD analysis identified tetragonal anatase crystalline pattern (PDF ICDD 86-1156) in NP's and also cubic silver (87-0717) and cubic chlorargyrite ( $\text{AgCl}$ ; 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) were detected. In the samples synthesized by oxidation and pyrolysis no visible difference in crystalline patterns was detected. Sample Ti3F, synthesized at  $T_R=700$  °C by pyrolysis, underwent annealing at 800 °C in duration of two hours. Originally mostly amorphous  $TiO_2$  with some portion of anatase was converted (completely) to rutile. This demonstrates that residence time in the reactor is rather short to form well developed crystals and that substantial part of  $TiO_2$  remains amorphous. During annealing also morphology of NP's changed significantly; the shape of NP's changed from spherical to faceted particles and size of NP's increased from several tens nm in dia. to several hundred nm, see Fig. 3. Results obtained by XRD were confirmed by SAED. Number (and intensity) of visible rings is increasing with increasing  $T_R$ , see Table 1 and Fig. 2, and all of them belong to anatase electron diffraction pattern. However, at  $T_R=900$  °C there were also some visible dots of rutile electron diffraction pattern.



**Fig. 3** SEM images of the samples Ti4F,  $T_R=700$  °C,  $c_0=10$  vol. % (left) and Ti3F,  $T_R=700$  °C,  $c_0=0$ , after annealing, (right).

#### 4. CONCLUSIONS

A method of  $TiO_2$  NP's generation useable for long lasting inhalation experiments with laboratory animals was tested. NP's were synthesized by pyrolysis and oxidation of TTIP in an externally heated tube reactor. Using purified nitrogen as a carrier gas NP's production with  $N_t$  above  $1.0 \times 10^7$  #/cm<sup>3</sup> and with GMD less than 50 nm was performed for 264 hours in four experimental campaigns without noticeable decrease of NP's production. Production of NP's and their characteristics can be controlled by  $T_R$ ,  $Q_R$  and  $P_{TTIP}$ . Primary particle size increases with  $T_R$  and  $P_{TTIP}$ , and decreases with  $Q_R$ . Synthesized NP's contain approximately 80 weight % of  $TiO_2$ , they are free of EC and contain typically between 3 and 6 weight % of OC. X-ray and electron diffractions confirmed presence of tetragonal anatase crystalline phase in NP's.

Presented method of  $TiO_2$  NP's synthesis is suitable for long lasting inhalation experiments with laboratory animals. It is relatively easy to use,  $TiO_2$  NP's with sufficiently high number concentration, desired particle size distribution and with well-defined composition can be generated in wide range of experimental conditions. Number concentration and particle size distribution can be controlled as desired by experimental parameters  $T_R$ ,  $Q_R$  and  $P_{TTIP}$ .

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