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The effect of external electric fields during flame synthesis of titania

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Abstract

The evolution of nanoparticle growth inside electrically assisted flames is studied by thermophoretic sampling (TS) followed by transmission electron microscopy (TEM) and statistical evaluation of the counted images. Up to 11 g/h titania particles are produced by titanium tetraisopropoxide (TTIP) oxidation in a CH_4/O_2 premixed flame. An electric DC-field of 1.5 kV/cm is established across the flame with two plate electrodes. At each TS location, the flame temperature is measured by Fourier transform infrared (FTIR) spectroscopy while the product powder is analyzed with nitrogen adsorption (BET), X-ray diffraction (XRD), TEM and small-angle X-ray scattering (SAXS) that is used to estimate the extent of agglomeration. External electric fields decrease most dramatically the flame temperature downstream of the electric field controlling particle size, crystallinity and morphology and contribute to the formation of soft agglomerates. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Flame aerosol processing can be used for manufacture of high purity oxide particles, without the multiple steps and high liquid volumes associated with wet chemical processes [1]. Though additives, burner design and operation can be used for control of flame-made particle characteristics, external electric fields offer precision control of particle size, powder morphology and crystallinity [2].

Hardesty and Weinberg [3] showed that the primary particle diameter of silica was reduced by a factor of three when applying an electric field of 6 kV between two parallel plate electrodes in the direction of the flame gas flow. Katz and Hung [4], however, found an increase of the titania, silica, and germania particle size by a factor of 3 to 10 using light scattering techniques in a counterflow diffusion burner when electric fields were applied in co-flow also. Applying needle electrodes across diffusion flames, Vemury and Pratsinis [2] created highly focused electric fields that resulted in strong convection (ionic wind) across the flame, which entrained surrounding air and decreased the flame temperature that reduced primary particle size and crystallinity. In premixed flame aerosol reactors, Vemury and Pratsinis [5] and Vemury et al. [6] showed that increasing the electric field strength between needle or plate electrodes across the flame flow decreased the average primary particle diameter of product titania, silica or tin oxide powder. This was attributed to shorter particle residence times in the hot flame zone and reduced coagulation rates by electrostatic repulsion of charged particles. These studies were carried out for rather small powder production rates (1 to 4 g/h), but Kammler and Pratsinis [7] demonstrated that external electric fields can be used successfully also to precisely control the specific surface area of silica at production rates of up to 87 g/h. Katzer et al. [8] found that the number of primary particles per agglomerate did not change when applying an electric field by plate electrodes across a premixed flame making TiO₂ by TiCl₄ oxidation using a differential mobility analyzer (DMA). Furthermore, they found that the flame temperature measured in the absence of particles was decreased downstream of the plate electrodes. Kammler et al. [9] measured detailed temperature profiles of electrically assisted premixed flames in the presence of particles with non-intrusive FTIR emission/transmission spectroscopy [10]. They found that the flame temperature was not affected

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Fig. 1. Experimental set-up of the premixed aerosol reactor with electric fields for precision control of the particle characteristics. Flame temperatures are measured by FTIR at the same location where thermophoretic sampling is used to monitor the growth of particles.

close to the burner mouth, but further downstream it decreased significantly with increasing electric field strength.

Here, the latter study is extended to investigate, for the first time, particle growth *inside* these electrically assisted flames producing titania particles. This is accomplished by a thermophoretic sampler [11,12] equipped with ceramic isolators for use inside the electric field. The flame temperature is measured at the TS locations to follow precisely the temperature history of the growing particles. Measurements are carried out at a field strength of 1.5 kV/cm, where particle size and flame temperature are influenced by the field's presence while the flame is still rather stable [9].

2. Experimental

The experimental set-up (Fig. 1) consists of a honeycomb stabilized premixed burner (quartz glass, 25 mm inner

Table 1 Gas flow rates, fuel equivalence ratio (EQR), and Ti mol-fraction of the investigated flames

TiO ₂ (g/h)	Ar (l/min)	CH ₄ (l/min)	N ₂ (l/min)	O ₂ (l/min)	EQR ^a	Ti (mol fraction, %)
0.5	0.65	0.6	5.0	1.2	1.03	0.03
5.5	0.65	0.4	4.3	1.2	1.04	0.43
11	0.65	0.1	3.9	1.2	0.92	0.95

^a EQR is defined as the fuel/oxidizer ratio divided by the stoichiometric fuel/oxidizer ratio.

diameter) [9] with two plate electrodes at the side, a gas and precursor delivering system as well as a filter for product particle collection. An evaporator system (Bronkhorst) [13] using nitrogen (99.9995% Pangas, CH) as carrier



Fig. 2. Flame temperature profiles of TiO_2 particle-laden flames measured along the centerline by Fourier transform infrared (FTIR) spectroscopy for TiO_2 production rates of 0.5 (triangles), 5.5 (diamonds), and 11 g/h (circles) in the absence (open symbols) and presence of external electric fields (1.5 kV/cm, filled symbols).

gas is set at 150 °C to deliver the titanium tetraisopropoxide (TTIP, Aldrich, >97% but distilled over vacuum prior to use) to the flame. Oxygen, methane and argon (all 99.999% Pangas, CH; flow rates are summarized in Table 1) mixed with TTIP-laden nitrogen are delivered through heated tubes into the burner. The external electric field is created by two parallel plate electrodes (2.5 cm high, 3.8 cm wide and 0.4

cm thick [7]) that are 5 cm apart. One electrode is connected to a high voltage supply (negative polarity, 1.5 kV/cm, Glassmann High Voltage) and the other one is grounded [7]. A precision resistor ($\pm 0.1\%$, 25 ppm/K) is inserted between ground and that electrode to measure the current across the plates [2]. The potential drop across this resistor is measured with a voltage module (5B31, Analog Devices)



Fig. 3. TiO₂ particles collected by thermophoretic sampling at 0.5, 2.5, 5, 7.5, 10 cm HAB, and product powder (filter) in the absence (left hand side) and presence of external electric fields (1.5 kV/cm, right hand side) at 0.5 g/h TiO₂.

on a signal conditioning board (5B01, Analog Devices). The signal is recorded (10 samples/s) on a personal computer with a data acquisition board (PCI-Mio-16E-4, National Instruments).

The product powder is collected on glass fiber filters (Whatman GF/A) at 20 cm height above the burner (HAB). The BET specific surface area (SSA) of the

powder is determined by nitrogen adsorption (Tristar, Micromeritics Instruments) and the rutile content and crystal sizes are obtained by XRD (Bruker D8 advance diffractometer) using the fundamental parameter approach [14]. Small-angle X-ray scattering (SAXS) is measured under vacuum with a pinhole geometry SAXS camera (Molecular Metrology) with focussing optics along with a



Fig. 4. TiO₂ particles collected by thermophoretic sampling at 0.5, 2.5, 5, 7.5, 10 cm HAB, and product powder (filter) in the absence (left hand side) and presence of external electric fields (1.5 kV/cm, right hand side) at 5.5 g/h TiO₂.

2-d wire detector (Gabriel type design). The incident Xray beam is about 20 μ m wide at the sample. After correcting the data for detector sensitivity and background, the 2-d data are averaged, as all SAXS patterns are radially isotopic, and regressed using the unified equation for SAXS [15,16] to obtain the radius of gyration of the primary particles, $R_{\rm g1}$. This can be converted directly to the diameter of an equivalent sphere by $d_{ps}(SAXS) = 2(5/3)^{1/2}R_{g1}$ [17].

The flame temperature is measured by emission/transmission spectroscopy [10] using an FTIR spectrometer (Bomem, MB155S) operating in the range of 6500-500cm⁻¹ (1.5-20 µm) with 2 cm⁻¹ resolution. Two pairs of identical paraboloidal mirrors guide the IR beam (0.2 cm)



Fig. 5. TiO₂ particles collected by thermophoretic sampling at 0.5, 2.5, 5, 7.5, 10 cm HAB, and product powder (filter) in the absence (left hand side) and presence of external electric fields (1.5 kV/cm, right hand side) at 11 g/h TiO₂.

through the flame. The temperature at the flame centerline is described well by the line-of-sight measurements close to the burner (<1 cm HAB), while further downstream the line-of-sight measurements slightly underestimate the centerline flame temperature (up to 100 K) compared to tomographic reconstructed measurements [9].

2.1. Thermophoretic particle sampling

Samples for analyzing particle morphology and size distribution are collected by a thermophoretic sampler that rapidly moves a carbon coated copper TEM grid (200 mesh, Plano) to a precisely defined position in the flame [11]. The

TEM grid is hold between two stainless steel blades $(0.0125 \times 0.3 \times 3 \text{ cm})$ leaving however a 0.2-cm diameter hole at one side to expose the grid to the flame. This TEM grid-holder (that will be inserted in the electric field created by the plate electrodes) is mounted onto the end of a ceramic rod, which is connected to a double acting pneumatic cylinder (Bimba, EM-16050-UC, 1.6 cm diameter, 5 cm stroke) driven by a pneumatic 5/2 valve (SMC Pneumatic) using 5 bar absolute pressure. Only the grid-holder with the TEM grid travels through an isolated slotted shield [11] that protects the flame from disturbances caused by the rapid movement of the ceramic rod. The shield is placed with a distance of 0.5 cm to the burner edge, thus outside the



Fig. 6. Evolution of the primary particle size distribution in the absence (open diamonds) and presence (filled diamonds) of external electric fields (1.5 kV/cm) with increasing HAB at 5.5 g/h TiO₂.

flame, following the experimental investigation of Dobbins and Megaridis [11] who studied the effect of different shield geometries in detail. A controller varies the residence time of the TEM grid inside the flame (typically 50 ms). The residence time of the TEM grid at the flame center as well its traveling time is recorded and calibrated with a highspeed digital camera (Kodak Ektapro, Model 4540) taking 2250 frames/s.

The transmission electron microscopy (TEM) micrographs are taken with a Zeiss electron microscope 912 Omega operated at 100 kV using a slow scan CCD camera and the ProScan software. TEM micrographs from the filter powder are prepared from the powder as-is, dipping the TEM grid into the product powder that results in a good particle coverage of the grid. For each flame location as well as the product powders, typically 500–1000 primary particles are counted with OPTIMAS 6.51 (Media Cybernetics) software and evaluated statistically [18].

3. Results

3.1. Flame characteristics

Applying 1.5 kV/cm across the flame reduces its height from 6.5, 8.5 and 8 cm to 3, 3.5 and 4 cm during production of 0.5, 5.5 and 11 g/h TiO₂, respectively [5]. Fig. 2 shows axial flame temperature profiles of these three TiO₂ particle-laden flames. For all flames, the temperature first increases, reaches a maximum at 0.5 to 1 cm HAB, and then decreases with increasing HAB at about 100 K/cm as air entrainment and radiation dilute and cool the flame. The methane flow rate is decreased when increasing the TiO₂ production rate to conserve the stoichiometry of the flame, keeping the fuel equivalence ratio (EQR) around unity. This resulted in relatively similar temperature profiles at all investigated TiO₂ production rates in the absence of electric fields. Upon applying the electric field, the temperature is not affected close to the burner [9], but shows a marked decrease [8] of about 200 K/cm [9] further downstream by the ensuing ionic wind between the plates.

3.2. Evolution of particle growth

A unique feature of this study is the unraveling of the effect of electric fields on particle characteristics by monitoring the evolution of particle morphology by thermophoretic sampling (TS) *inside* the electrically assisted flame. During TS, the flame current, measured between the electrodes, is reduced at most by 10% indicating that the field is not disturbed significantly by the presence of the sampling probe [19].

Figs. 3-5 show TEM pictures from TS at 0.5, 2.5, 5, 7.5 and 10 cm HAB along the flame axis, as well as TEM pictures of the filter powder for 0.5 g/h (Fig. 3), 5.5 (Fig.

4), and 11 g/h TiO₂ (Fig. 5). On the left-hand side of Figs. 3-5, the evolution of titania growth in the flame is shown in the absence of electric fields, while on the right-hand side of Figs. 3-5 the electric field is present. The particle size increases with increasing HAB for all production rates [12]. At 0.5 cm HAB small primary particles are observed that are partly agglomerated with or without electric fields. In the absence of electric fields for 5.5 and 11 g/h TiO_2 (Figs. 4 and 5), the particles are significantly larger than those made at 0.5 g/h TiO₂ (Fig. 3) at all HAB and on the filter. The increase in particle concentration (Table 1) increases the particle collision frequency and, thus, coagulation rate and particle size, consistent with Pratsinis et al. [20]. Further downstream (2.5 cm HAB), however, only larger single particles are observed that increase in size with increasing HAB in agreement with Arabi-Katbi et al. [12]. For 0.5 g/h TiO₂ (Fig. 3) there is no significant change on particle size or the degree of agglomeration when applying the electric field. For 5.5 and 11 g/h TiO_2 in the presence of electric fields, however, agglomerates $(1-5 \ \mu m)$ along with widely spread single particles are observed at HAB = 5 cm (above the electrodes) and also at 7.5 and 10 cm HAB (Figs. 4 and 5).

Fig. 6 shows the evolution of the primary particle size distribution (PPSD) obtained from the TEM picture (Fig. 4) evaluation in the absence (open diamonds) and presence (filled diamonds) of external electric fields with increasing HAB. The PPSDs are shifted to larger sizes with increasing HAB in the absence of electric fields for



Fig. 7. Evolution of the TEM counted Sauter mean primary particle diameter with height above the burner (HAB) for TiO_2 production rates of 0.5 (triangles), 5.5 (diamonds), and 11 g/h (circles) in the absence (open symbols) and presence of external electric fields (1.5 kV/cm, filled symbols).



Fig. 8. Evolution of the primary particle geometric standard deviation $\sigma_{\rm g}$ with height above the burner (HAB) for TiO₂ production rates of 0.5 (triangles), 5.5 (diamonds), and 11 g/h (circles) in the absence (open symbols) and presence of external electric fields (1.5 kV/cm, filled symbols).

all production rates. For 0.5 and 2.5 cm HAB (inside the electric field), the PPSDs in the presence and in the absence of the electric field do not differ significantly. However, further downstream at 5 cm HAB, the size distribution of particles made in the presence of electric fields is shifted to smaller values than that of particles made in the absence of fields (Fig. 6). With increasing HAB, this difference seems to increase and is present even for particles collected on the filter. Similar pictures are also obtained for TiO₂ production rates of 3.1 g/h [9] and 11 g/h. It should be noted that at low TiO₂ production rates (0.5 g/h) the PPSD in the presence of the electric

Table 2

Particle size for TiO_2 produced at 0.5, 3.1, 5.5 and 11 g/h in the presence and absence of 1.5 kV/cm at cross-flow with the flame

TiO ₂ (g/h)	EF (kV/cm)	$\frac{\text{BET}}{d_{\text{p}}(\text{BET})}$ (nm)	XRD				TEM						SAXS
			d _p (XRD) (nm)	Rutile (wt.%)	d _{p (A)} (nm)	d _{p (R)} (nm)	$\overline{d_{1,0}}$ (nm)	d _g (nm)	$\sigma_{ m g}$	d _{3,2} (nm)	σ _{3,2} (nm)	<i>d</i> _{6,0} (nm)	$\overline{d_{\rm ps}}$ (nm)
0.5	0	19	20	9	21	10	16	15	1.47	21	6	22	23
0.5	1.5	16	17	11	18	10	14	13	1.51	18	6	19	20
3.1 ^a	0	43		8			35	32	1.59	49	16	50	50
3.1 ^a	1.5	35		11			29	27	1.60	39	13	40	38
5.5	0	48	46	8	47	31	44	38	1.73	63	22	63	62
5.5	1.5	39	38	11	39	28	31	27	1.72	46	16	47	46
11	0	54	55	22	56	50	35	29	1.89	71	26	69	65
11	1.5	44	50	48	45	56	32	26	1.87	54	20	52	53

Comparison of the BET average primary particle diameter $[d_p(BET)]$, the mass weighted average primary particle diameter obtained by XRD $[d_p(XRD)]$ along with the rutile content of the powders, the crystal size for the anatase $[d_p(A)]$ and rutile $[d_p(R)]$ particles, and the count mean particle diameter by TEM $[d_{1,0}]$, the geometric primary particle diameter $[d_g]$, the geometric standard deviation $[\sigma_g]$, the Sauter mean particle diameter $[d_{3,2}]$, its standard deviation $[\sigma_{3,2}]$, the diameter of the sixth moment $[d_{6,0}]$ all by TEM [18], and the average primary particle diameter of an equivalent sphere obtained by SAXS $[d_{ps}]$.

^a From Ref. [9].

field was slightly larger just above the electrodes but it became smaller than that in the absence of fields again on the filter.

Fig. 7 depicts the evolution of the corresponding Sauter mean primary particle diameter, $d_{3,2}$, with HAB for 0.5 (triangles), 5.5 (diamonds), and 11 g/h (circles) TiO₂ in the absence (open symbols) and presence (filled symbols) of electric fields. In the absence of electric fields, the average primary particle diameter increases steadily with increasing HAB for all TiO₂ production rates [12,21]. However, in the presence of the electric field, the Sauter mean primary particle diameter is similar to that measured in the absence of the electric field for HAB \leq 2.5 cm but downstream at locations above the electrodes (\geq 5 cm HAB), it remains almost constant or even decreases slightly (for 11 g/h TiO₂).

Fig. 8 shows how the geometric standard deviation σ_g (which describes the width of the primary particle size distribution) varies with HAB for TiO₂ production rates of 0.5 (triangles), 5.5 (diamonds), and 11 g/h (circles). In the absence of electric fields (open symbols), the σ_g increases steadily from 1.26 to 1.39 for 0.5 g/h TiO₂, from 1.38 to 1.45 for 5.5 g/h TiO₂, and for 11 g/h TiO₂ from 1.46 to 1.50 as HAB increases from 0.5 to 10 cm. The presence of the electric field increases the σ_g by 5–10%, except at 5 cm HAB, where a much larger σ_g is observed for all investigated production rates. At the filter, σ_g is 1.47, 1.73, and 1.89 for 0.5, 5.5 and 11 g/h TiO₂, respectively, in the absence of the electric field.

3.3. Product powder characteristics

Table 2 summarizes the characterization of the product powder made at 0.5, 5.5, and 11 g/h TiO₂ production rate (shown in the lowest rows of Figs. 3–5) using nitrogen adsorption (BET), X-ray diffraction (XRD), TEM analysis, and SAXS. The d_p (BET) is within $\pm 6\%$ of the d_p (XRD) indicating that most of the titania particles are single crystals



Fig. 9. Rutile content of TiO_2 powders made at different production rates in the absence (open symbols) and the presence of external electric fields (1.5 kV/cm, filled symbols).

at all conditions. For all powders the geometric mean d_{g} is the smallest, followed by the count mean diameter $d_{1,0}$, while $d_{p}(BET)$ is between $d_{1,0}$ and the Sauter mean diameter, $d_{3,2}$. This is typical for unimodal (self-preserving) particle size distributions [18]. The $d_{ps}(SAXS)$ is close to the $d_{6,0}$, consistent with the dependence of light scattering to particle diameter [18]. Only one length scale was found by SAXS for particles made in the absence of electric fields. Applying 1.5 kV/cm decreases the primary particle diameter by about 20% for all investigated TiO₂ production rates which is consistent with Vemury et al. [6] and Kammler et al. [21]. This decrease is measured with all applied techniques (TEM, BET, XRD, and SAXS, Table 2). The rutile content is increased slightly in the presence of the electric field at low particle concentrations and increased substantially from 22 to 48 wt.% at the highest one (Fig. 9).

4. Discussion

The applied electric field attracts oppositely charged ions and shortens the flame height significantly [22,23]. Following the particle growth with HAB (Figs. 6 and 7), it is shown that the primary particle diameter first—close to the burner—is not affected by the electric field but just above it the particle growth is slowed down when the flame is cooled faster (~ 200 K/cm, Fig. 2) by the presence of the electric field. This virtually stops the primary particle growth as sintering was slowed down. This decrease of the primary particle diameter (notably at 7.5 cm HAB and 11 g/ h TiO₂) comes along with the presence of large agglomerates with significantly broader PPSDs (Figs. 4–6 at 5–10 cm HAB). The relative decrease of the average product particle diameter is always about 20% for 0.5, 5.5, and 11 g/ h TiO₂ (Table 2) when applying 1.5 kV/cm consistent with Vemury et al. [6], and our previous work [9]. Increasing the electric field strength further amplifies the reduction of the average primary particle diameter [6,9]. Particles collected on the filter have been formed along different streamlines and therefore have experienced different temperature histories. This can explain that the primary particle diameter at the filter is smaller than that of particles collected at the flame centerline at 7.5 and 10 cm HAB as observed for the experiments with 11 g/h TiO₂ (Fig. 7).

The electric field separates the flame charges forming homopolar clouds of particles close to the electrodes [5,8,22]. These charged particles, however, mix further downstream by convection (HAB>2.55 cm, thus downstream of the electric field). The oppositely charged particles are attracted to each other, resulting in the formation of large agglomerates $(1-5 \ \mu m)$ (Figs. 4 and 5) as the average flame temperature is significantly lower in the presence of the electric field (Fig. 2). Additionally, agglomerates can be formed close to the edges of the electrically assisted flame, where the flame temperature is substantially lower than in the flame center, and complete coalescence is not reached anymore. Enhanced gas mixing by the recombination of the homopolar clouds formed by the electric field brings these agglomerates to the flame centerline. For low particle concentrations, this mixing may even enhance particle growth temporally as was shown at low production rates (Fig. 7).

The increase of the agglomerate diameter of aerosol particles by bipolar charging has been proposed to facilitate efficient particle collection [24]. Such an increase of the flame-made oxide particle diameter of 3-10 in the presence of an electric field was experimentally observed by Katz and Hung [4] using non-intrusive light scattering techniques. Considering that Katz and Hung [4] measured the diameter of agglomerates by dynamic light scattering, this is in good agreement to the current observations of enhanced agglomerate formation in the presence of the electric field. However, these agglomerates (Figs. 4 and 5) are most probably soft agglomerates as will be discussed in detail below.

The flame temperature at 5 cm HAB in the presence of the electric field is above 1120 K (Fig. 2), where complete coalescence of titania nanoparticles still can be observed [25]. Thus there is the possibility that part of these agglomerates will coalesce, which is also observed by TS. However, further downstream (at 10 cm HAB), these agglomerates cannot coalesce anymore. Considering that the flame temperature in the absence of the electric field, however, is still above 1120 K at 10 cm HAB (Fig. 2), explains why no agglomerate formation is observed under these conditions (Figs. 3-5) in agreement with Arabi-Katbi et al. [12]. As the particle residence time is shorter than the characteristic coalescence time of titania [26] (Fig. 6) for 2350 K (onset temperature of steep cooling, Fig. 2), all powders were non-agglomerated consistent with the TEM pictures (Figs. 3–5).

In the TEM micrographs of the filter powders made at 5.5 and 11 g/h (Figs. 4 and 5), no evidence for neck formation or sintering bridges between particles is found even at higher magnifications (100k) that is typical for hard agglomerates. In the filter powders, single particles are observed next to the agglomerates as well, and this indicates further that non-agglomerated or only weakly agglomerated particles are produced. This observation is corroborated by small angle X-ray scattering (SAXS) analysis, in which only one characteristic scale is obtained from the unified SAXS equation [15,16] for the powders produced in the absence of electric fields. This strongly indicates the presence of nonagglomerated particles [17]. Similar results are obtained for powders made in the presence of electric fields, even though a small degree of agglomeration (2.2 primary particles per agglomerate) is measured by SAXS for 11 g/h TiO₂. Katzer et al. [8] found that the number of primary particles per agglomerate collected from the flame center above the electric field was virtually not changed, or that number was even slightly lower further downstream in the presence of the electric field, which is in agreement with the lowest TiO_2 production rate (0.5 g/h) investigated here. The Ti molfraction in the flame of Katzer et al. [8] was 1.8 times higher than that of the 0.5 g/h TiO_2 flame here. Katzer et al. [8] produced agglomerates as the maximum (adiabatic) flame temperature was significantly lower than in the present study where spherical particles are made (Figs. 3-5). However, as higher precursor concentrations were employed by Katzer et al. [8] that increased the particle collision rate and therefore the primary particle diameter, thus slightly larger particles (19.5 nm by BET) were made than here with the 0.5 g/h TiO₂ flame (18.8 nm by BET). Compared to the 5.5 g/h TiO₂ flame, the initial particle concentration might have been too low with the 0.5 g/h TiO_2 flame to form soft agglomerates in the presence of the electric field when the unipolar clouds of particles mix further downstream (above the electric field). However, even though the electric field might have resulted in enhanced agglomeration of the particles, they might have been broken apart again during the quenching/dilution step, when sampling and simultaneously freezing the aerosol before entering the DMA [8]. Therefore, an increase in the apparently soft agglomerate size with increasing electric field strength as observed by Katz and Hung [4] or in the present results for 5.5 and 11 g/ h TiO₂ might not be observed when using the DMA by Katzer et al. [8]. Vemury and Pratsinis [5] observed a decrease of the extent of agglomeration of silica particles collected on the filter and seen by TEM when applying a unipolar electric field between plate electrodes. The decrease of flame temperature in the presence of the electric field might have slowed down the primary particle and agglomerate growth, and therefore they observed smaller agglomerates. However, even though soft agglomerates might have been formed, they could have been easily

broken apart during the dispersion in liquids for TEM preparation. A small decrease of the silica agglomerate size with increasing electric field strength was observed by Hyeon-Lee et al. [17] with SAXS also. But again one must consider that SAXS only measures hard agglomerates, even though soft agglomerates might be present.

The high values for σ_g at 5 cm HAB (Fig. 8) can be understood by considering the presence of small and large particles (Figs. 4 and 5) at the flame centerline that are formed at the flame edge and drawn to the center by enhanced mixing from the ionic wind. These different modes of primary particles can be clearly observed in the PPSDs (Fig. 6). The increase in σ_{g} is observed even for the 0.5 g/h TiO₂ flame where no agglomerates are observed. Thus even at this low production rate gas mixing induced by the electric field plays an important role. At 7.5 cm HAB, the σ_{g} decreases again, as the flame temperature is still high enough for sintering of particles from these diverse collision histories narrowing the PPSD (Fig. 6), as the sintering rate of titania is inversely proportional to the particle diameter (sintering time, $t_{\rm s} \sim d_{\rm p}^4$) [26]. Further downstream, as mixing with other fluid streamlines takes place at lower temperatures (Fig. 2), the $\sigma_{\rm g}$ increases again explaining also why the self-preserving limit is exceeded at the filter at all times. This is most pronounced with increasing particle concentrations that resulted in larger particles whose growth stopped earlier at various streamlines and particles could not further coalesce upon collisions.

The slight increase in the rutile content in the presence of the electric field for the 0.5 and 5.5 g/h TiO_2 flames (9 and 8 to 11 wt.%, Fig. 9) is in agreement to Kammler et al. [9] $(3.1 \text{ g/h TiO}_2 \text{ in Fig. 9})$, who also made TiO₂ from TTIP. However, at the highest production rate, this increase is quite substantial (22 to 48 wt.% rutile, Fig. 9) pointing out the possibility that the electric fields may affect the powder crystallinity aside from its temperature history. This is quite different than the TiO₂ made by TiCl₄ oxidation at lower temperatures [6,8]. Both, Vemury et al. [6] and Katzer et al. [8] found that the electric field decreases the rutile content. A change in flame chemistry (TTIP-versus TiCl₄-combustion) might explain these differences though it should be considered also that the premixed flame in the two latter studies was operated with an inner flame cone, while here premixed flat flames are investigated.

5. Concluding remarks

In situ thermophoretic sampling (TS) was used in combination with Fourier transform infrared (FTIR) spectroscopy to follow the particle growth history in electrically assisted flame aerosol reactors. The presence of 1.5 kV/ cm across the flame nearly doubled the flame cooling rate by ensuing ionic wind essentially and reduced the product primary particle diameter by about 20%. The geometric standard deviation of the particles, σ_{g} , increased sharply right above the electric field, indicating that enhanced fluid motion (ionic wind) broadened the particle size and residence time distributions. Further downstream, coagulation and sintering reduced the σ_g again, before low temperatures and the mixing of particles arising from various streamlines widened the collected particle size distribution on the filter.

While for small particle concentrations (0.5 g/h TiO₂) the employed electric field did not change particle morphology, at higher TiO₂ production rates (5.5 and 11 g/h TiO₂) large (soft) agglomerates were temporarily formed consistent with literature and small angle X-ray scattering (SAXS) of the product powders. This indicates the importance of in situ sampling techniques such as TS without post-processing steps before analysis, such as dilution/quenching before entering a differential mobility analyzer [8] or preparation of TEM from the product powder when soft agglomerates are analyzed.

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