Mass-Mobility Characterization of Flame-made ZrO_2 Aerosols: the Primary Particle Diameter & Extent of Aggregation

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Aerosol particles are formed by natural and man-made processes, often resulting in fractal-like particle structures. These particles can be held together by either physical forces (van der Waals or electrostatic) resulting in agglomerates or chemical forces (sinter, ionic or covalent) resulting in aggregates. It should be noted here that these definitions have been used interchangeably in the literature: One's agglomerate might be an aggregate for another. The transport and optical properties of these structures are determined mainly by the composition, number, diameter and geometric arrangement of their constituent primary particles (Meakin, 1988). These properties may also affect the health impact of these particles (Scheckman and McMurry, 2011) as the potential toxicity of inhaled nanoparticles correlates better to their surface area than mass (Maynard and Kuempel, 2005). Thus real-time characterization of primary particle sizes and specific surface area of gas-borne nanoparticles is necessary for continuous monitoring of aerosol manufacturing and airborne pollutant particle concentrations. This far mostly ex-situ methods have been used to characterize such structures in terms of primary particle diameter and specific surface area by counting microscopic images, nitrogen adsorption, X-ray diffraction and light scattering.

Here, flame-made zirconia agglomerates or aggregates are characterized by DMA-APM measurements to obtain their mass, mobility diameter, mass-mobility exponent and prefactor. The precursor and oxygen flow rates as well as zirconium precursor concentrations are varied to generate fractal-like particles with different primary particle diameters, size distributions and degrees of aggregation (Mueller et al., 2004a; Mueller et al., 2004b). The average primary particle number, n_{va}, and surface area mean diameter, d_{va} (or specific surface area) are obtained from such data using a recent power law between agglomerate/aggregate volume, mobility and d_{va} (Eggersdorfer et al., 2012). These d_{va} data are compared to micrograph counting of primary particle diameters as well as nitrogen adsorption measurements and the effect of flame process parameters on product ZrO_2 particle characteristics is elucidated.

The mass-mobility determined primary particle diameter was in good agreement with primary particle diameters from counting TEM images and nitrogen adsorption measurements. In fact, the proximity of the DMA-APM primary particle diameter for aggregates to that determined by N_2 adsorption or TEM-image counting provided an indication to the extent of aggregation of these fractal-like particles.

The primary particle diameter varied between 5 and 25 nm and the mobility diameter from 30 - 400 nm depending on process conditions. These flame-made fractal-like particles rapidly obtain the self-preserving size distribution corresponding to their fractal dimension. Longer particle residence times at high temperatures and high precursor concentrations resulted in larger primary particles with increased degree of aggregation. The fractal-like zirconia particles have a mass-mobility exponent, $D_{fm} \approx 2.15$, and prefactor, $k_m \approx 1$, independent of investigated process conditions and corresponding primary particle diameter distributions. These values are consistent with fractal-like particles formed by cluster-cluster coagulation. In addition, increased particle concentration led progressively to more aggregated flame-made particles with increased primary particle polydispersity. At low particle concentrations, agglomerate particles were formed with little necking between primary particles.

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Primary Particle Diameter from Mass-Mobility Measurements

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Introduction

Real-time characterization of primary particle and agglomerate diameters is necessary for continuous monitoring of aerosol processes and airborne pollutant particle concentrations. This far, mostly ex-situ methods have been used to measure such structures. Here, the fractal-like particles are investigated by combining differential mobility analyzer (DMA) and aerosol particle mass (APM) analyzer measurements with a power-law (Eggersdorfer et al., 2012) for an example case of flame made zirconia nanoparticles. Measurement results were in agreement with conducted simulations interfacing fluid and particle dynamics.

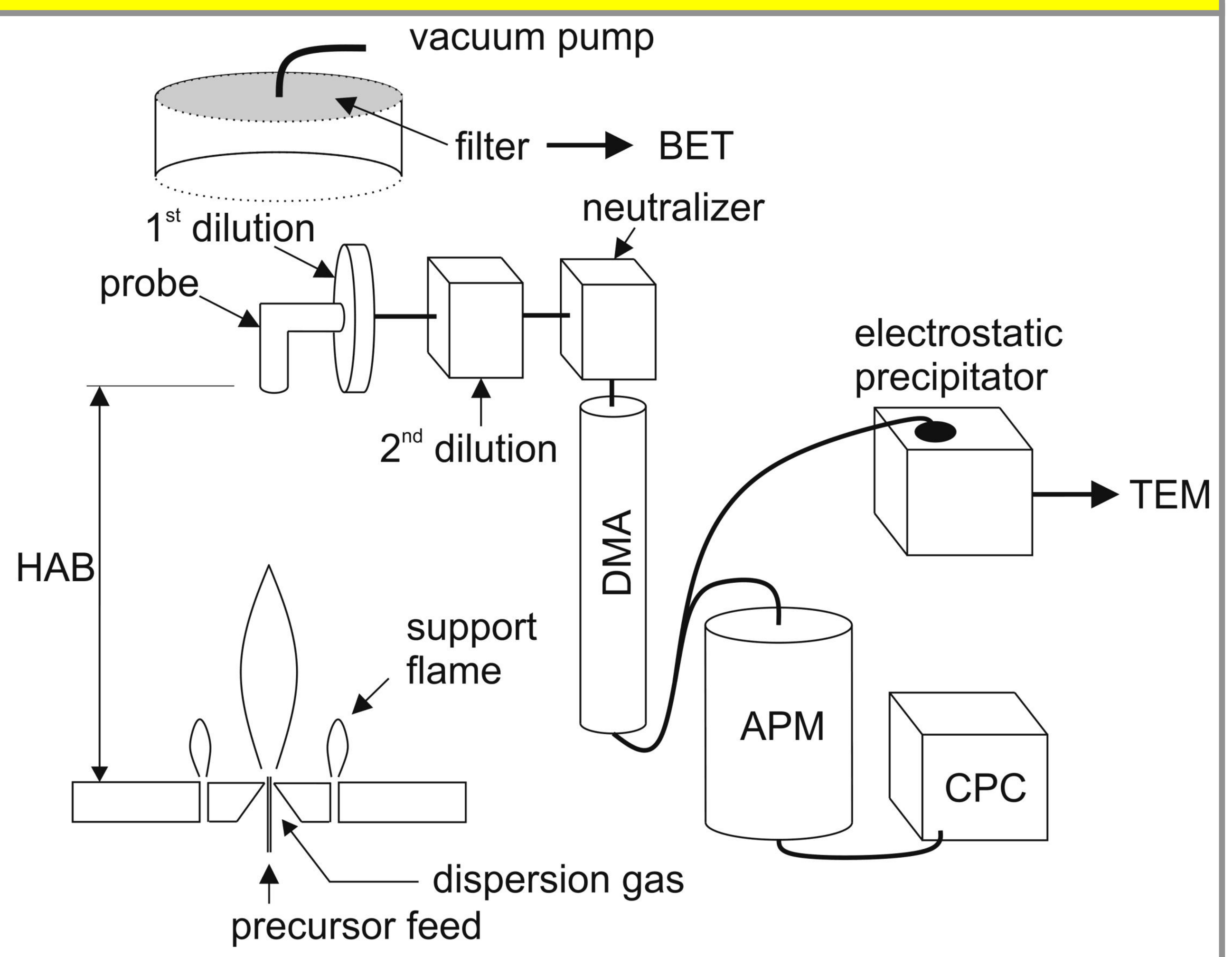

***Fig. 1.** Schematic of the experimental set-up.*

Primary Particle Growth

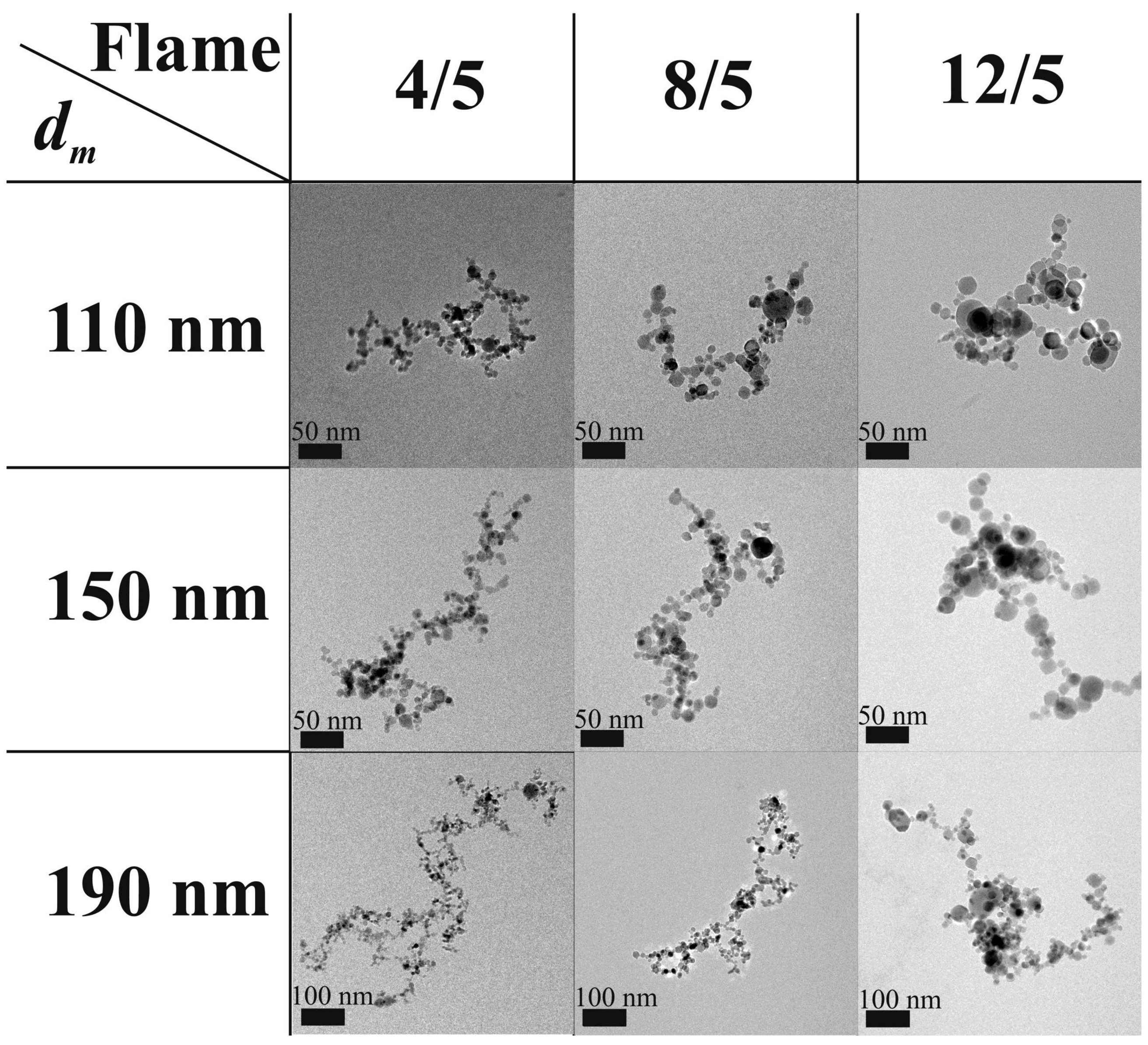

***Fig. 2.** TEM images of DMA size-selected agglomerates with mobility diameter 110, 150 and 190 nm generated with 4, 8 and 12 ml/min of 0.5 M Zr precursor (ZrEHA) and 5 l/min of dispersion O_2.*

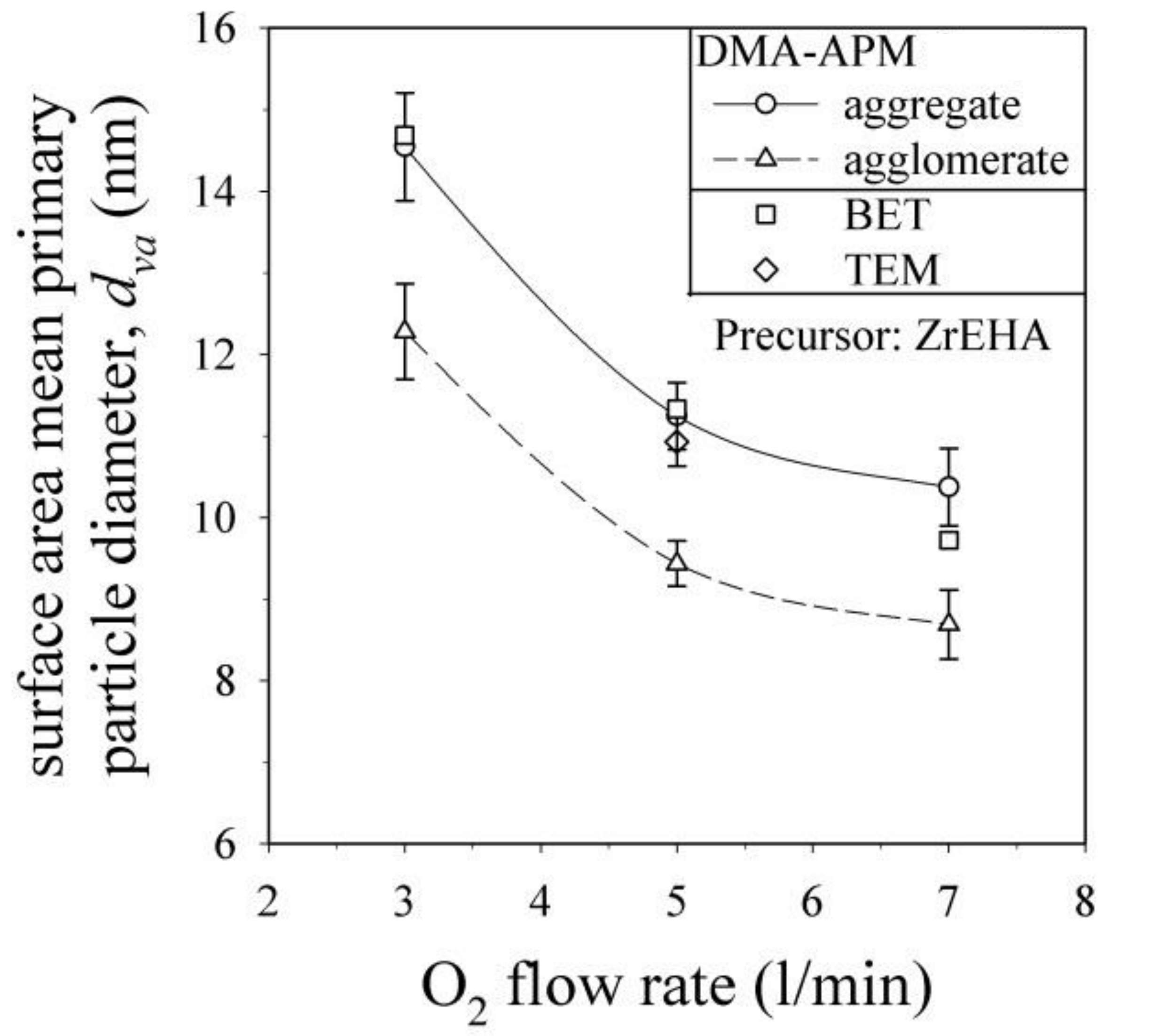

***Fig. 3.** Effect of O_2 flow rate on ZrO_2 primary particle diameter for 4 ml/min of 0.5 M Zr precursor (ZrEHA). The primary particle size obtained online during the DMA-APM measurement is in good agreement with the average diameter from nitrogen adsorption (BET) and counting TEM images.*

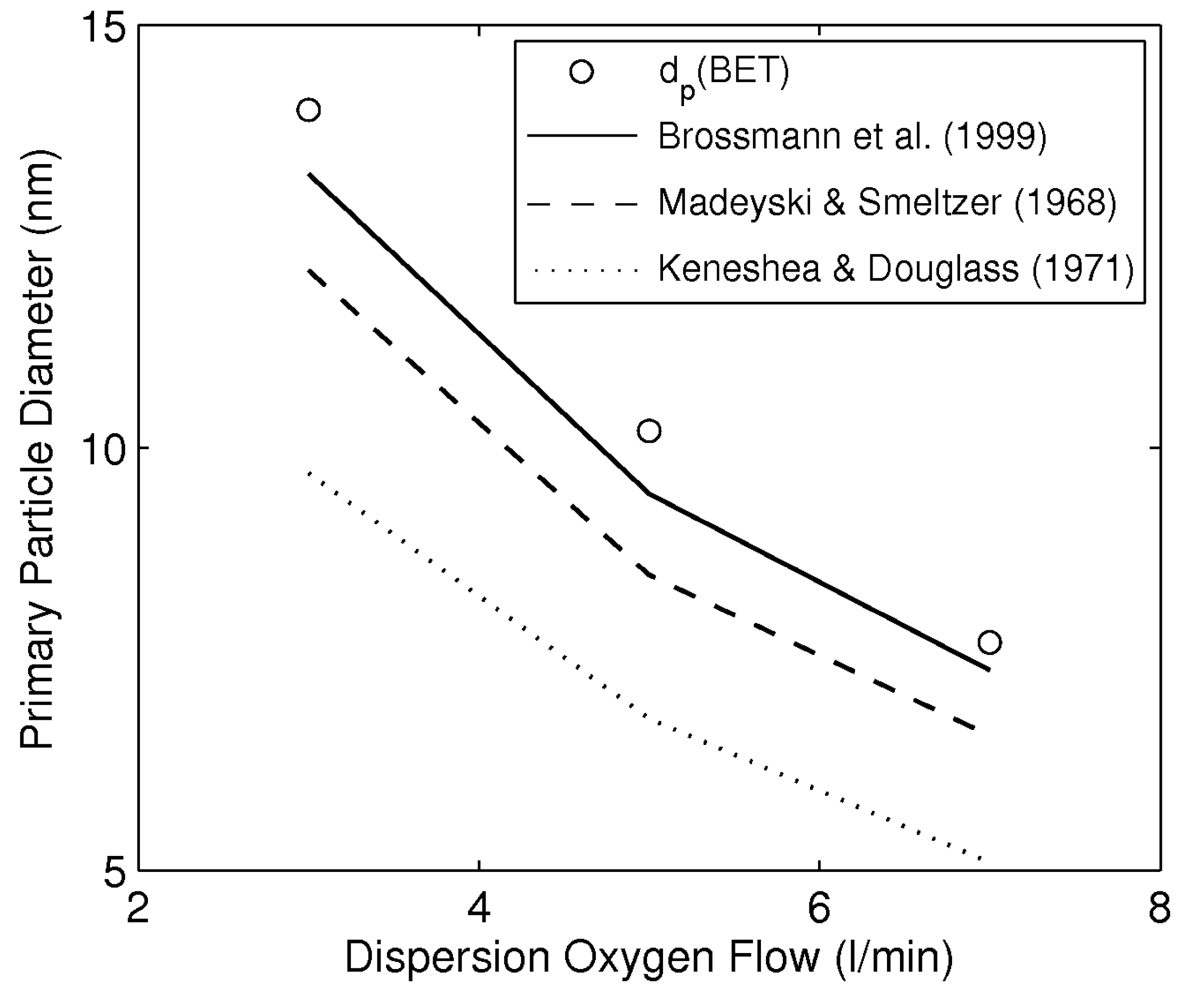

***Fig. 4.** Effect of sintering rate on the predicted particle diameters for 4 ml/min of 0.5 M Zr precursor (ZrProp). Grain boundary diffusivity of Brossmann et al. (1999) gave best agreement with experiments (circles).*

Agglomeration Dynamics

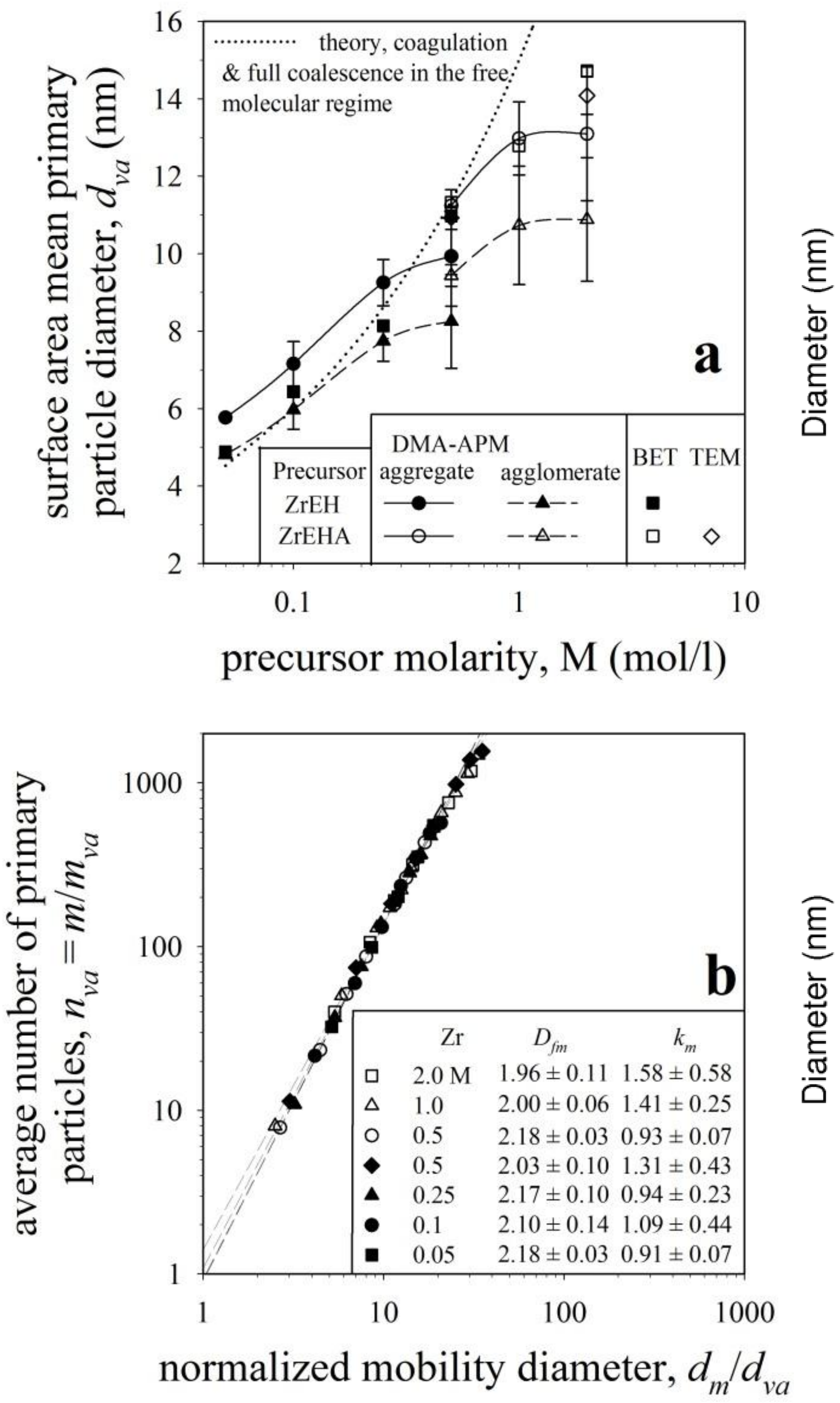

***Fig. 5.** Effect of precursor Zr concentration on a) primary particle diameter and b) mass-mobility exponent and prefactor at 4 ml/min precursor and 5 l/min O_2 flow rate. Increasing Zr concentration results in faster coagulation and larger particles. The d_{va} for agglomerates is closer to that from BET for Zr < 0.5 M while it is closer to that of aggregates for Zr ≥ 0.5 M.*

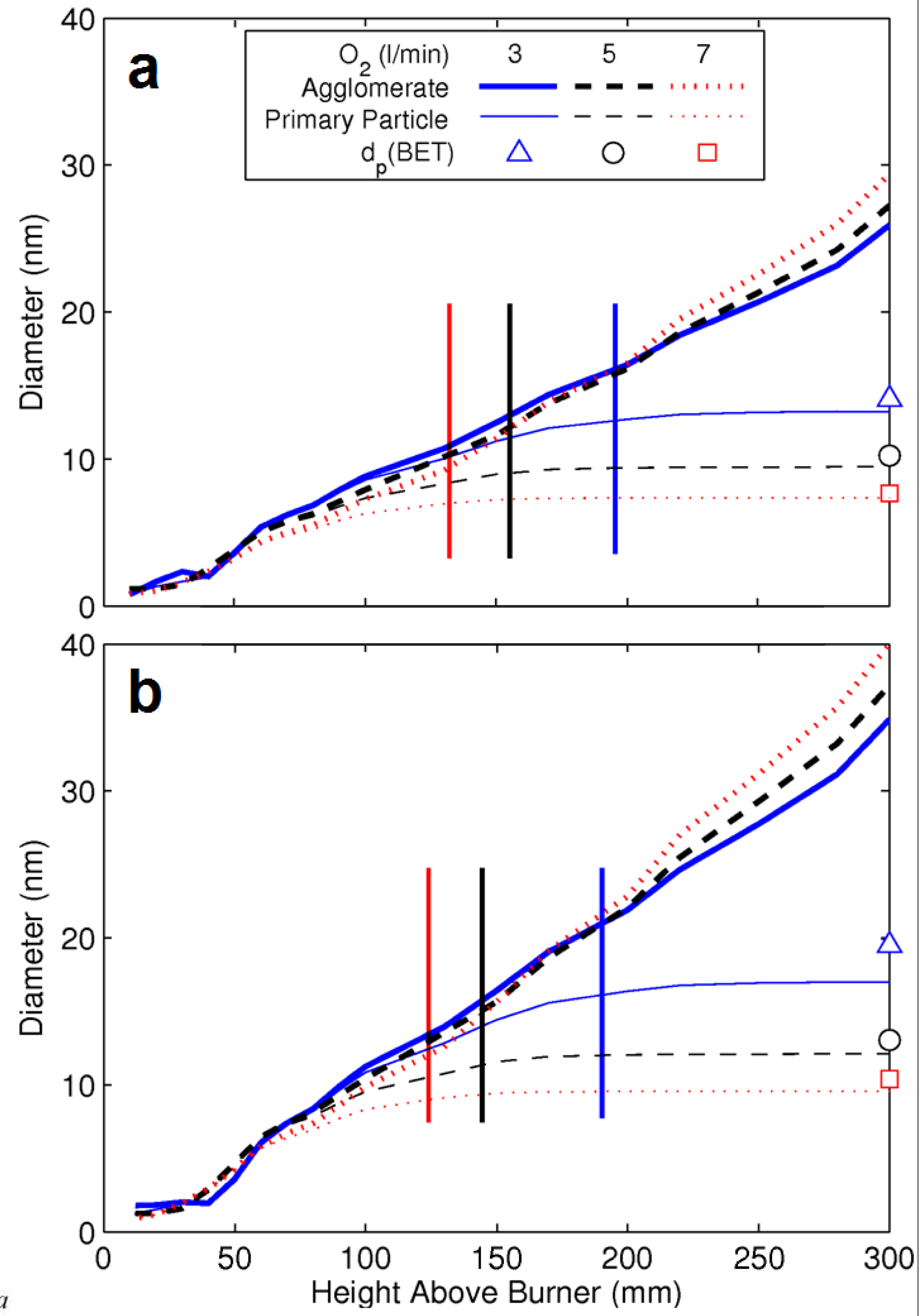

***Fig. 6.** Predicted evolution of primary particle and agglomerate collision diameters for 4 ml/min of a) 0.5 and b) 1 M Zr precursor (ZrProp). Initiation of soft-agglomerate formation is indicated with vertical lines. Simulations show an increase in the agglomerate size and degree of aggregation for increasing precursor concentration consistent with measurements.*

Conclusions

The DMA-APM determined primary particle diameters are in good agreement with counting TEM images and BET measurements. The fractal-like ZrO_2 particles have a mass-mobility exponent, D_{fm} ≈ 2.15, and prefactor, k_m ≈ 1, independent of investigated process conditions indicating fractal-like particles formed by cluster-cluster coagulation. Increased particle concentration leads to bigger and more aggregated particles both in experiments and simulations.

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