

The effect of structure by coagulation & sintering of fractal-like particles

E. Goudeli, M.L. Eggersdorfer, and S.E. Pratsinis

Particle Technology Laboratory, ETH Zürich, CH-8092 Zürich, Switzerland

Typically nanoparticle formation by coagulation results in fractal-like structures in atmospheric and industrial systems. Though the asymptotic form of such structures is described well with the so-called fractal dimension, D_f , by either diffusion-limited or ballistic cluster-cluster agglomeration, little is known for the evolution of D_f , from that of initially tiny spheres ($D_f = 3$) to that of large fractal-like aerosol particles ($D_f = 1.9-2.1$). In process design, typically, the evolution of D_f is neglected or simplified using a constant value. Notable exceptions are those of Xiong and Pratsinis (1993) and Artelt et al. (2003) who had interpolated D_f at an arbitrary rate or slope from that of fully coalesced particles to that of non-coalescing agglomerates.

Here, the effect of the rapidly evolving structure D_f of newly formed TiO_2 particles is explored on their primary particle and collision diameters over their process synthesis parameter space by interfacing molecular dynamics, mesoscale and continuum models. A monodisperse continuum model is employed accounting for simultaneous coagulation and sintering of TiO_2 particles under non-isothermal conditions over the process synthesis parameter space (Tsantilis and Pratsinis, 2004; Kruis et al., 1993). The evolution of the agglomerate collision diameter and morphology is explored assuming a varying D_f based on mesoscale simulations (Schmid et al. 2006; Eggersdorfer and Pratsinis, in preparation) as well as constant and arbitrarily varying D_f (Artelt et al. 2003) using the characteristic sintering time of rutile titania from molecular dynamics (Buesser et al., 2011).

Figure 1 shows the evolution of the mass fractal dimension D_f as a function of the dimensionless characteristic time τ defined as the ratio of the characteristic sintering time to the characteristic collision time, $\tau = \tau_s/\tau_c$. The models of Artelt et al. (2003) for $s=0.75$ (red line), 1.0 (pink line) and 1.5 (blue line), Eggersdorfer and Pratsinis (in preparation; green diamonds) and Schmid et al. (2006; blue squares) are compared. The model of Artelt et al. (2003) bridges the constant values of $D_f = 1.8$ and 3 for the limiting cases of $\tau_s \gg \tau_c$ and $\tau_s \ll \tau_c$, respectively and was empirically derived for the transition regime. The duration of the transition region depends on the employed D_f model, with the power law of Eggersdorfer and Pratsinis (in preparation) predicting a narrow, abrupt D_f change, Schmid et al. (2006) a slower transition to the constant asymptotic value and Artelt et al. (2003) model a smooth transition of variable, arbitrarily defined rate (depending on parameter s) from fully fused spheres to fractal-like aggregates.

The effect of process conditions, such as the maximum operation temperature, cooling rate and initial number concentration on the primary particle, hard- and soft-agglomerate diameters are investigated. Accounting for the evolution of D_f hardly affects the primary particle and agglomerate diameters even though it alters the transient evolution of the agglomerate collision diameter up to 25% during the hard-aggregate to soft-agglomerate transformation.

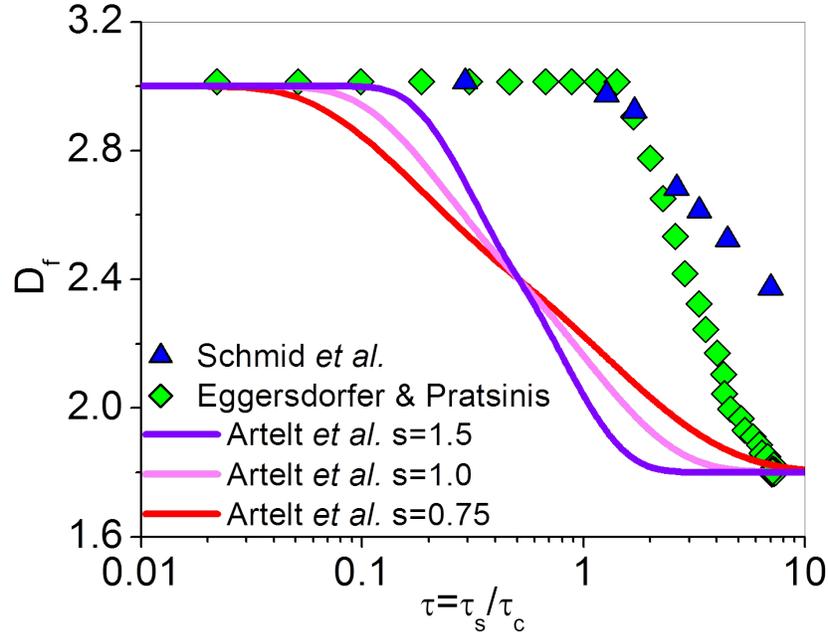


Figure 1. Evolution of mass fractal dimension as a function of the dimensionless characteristic time, defined as the ratio of characteristic sintering to characteristic collision time. The models of Artelt *et al.* (2003) for $s=0.75$ (red line), 1.0 (pink line) and 1.5 (blue line), Eggersdorfer & Pratsinis (in preparation; green diamonds) and Schmid *et al.* (2006; blue triangles) are shown. Artelt *et al.* (2003) assumed an empirical evolution of the fractal dimension, Schmid *et al.* (2006) determined the equilibrium fractal dimension at different constant characteristic times and Eggersdorfer & Pratsinis (in preparation) described the evolution of fractal dimension during particle growth of amorphous silica by coagulation and sintering accounting for the change in the characteristic time.

Figure 2 shows the primary (open circles) and hard-agglomerate (filled symbols) particle diameter of titania for three maximum flame temperatures ($T_{max} = 2000, 2200$ and 2400K) as a function of the cooling rate ($CR = 10^4, 10^5$ and 10^6 K/s) at precursor molar fraction $\phi = 0.01$ for the models of Eggersdorfer and Pratsinis (in preparation; green diamonds), Artelt *et al.* (2003) for $s = 1$ (pink squares) and Schmid *et al.* (2006; blue triangles) which are compared against the corresponding diameters using constant $D_f = 1.8$ (black circles). The evolution of D_f has a minor effect on the primary particle diameter, as also depicted in Figure 3, and hence only the d_{pH} for $D_f=1.8$ is shown here. Even though with increasing maximum operating temperature the hard-primary particle diameter increases and the hard-agglomerate diameter is not significantly affected, the increasing cooling rates cause both d_{pH} and d_{cH} to decrease. More specific, at high cooling rates low agglomerated (indiscernible difference between d_{cH} and d_{pH}) particles tend to form, a phenomenon that is more pronounced at higher maximum temperatures. Furthermore, the D_f models of Artelt *et al.* (2003) for $s = 1, s = 0.75$ and 1.5 (not shown here) and Eggersdorfer and Pratsinis (in preparation) predict hard-agglomerate diameters close to that of constant $D_f=1.8$ in contrast to Schmid *et al.* (2006) model that predicts a d_{cH} variation up to 25% for high precursor molar fractions, low maximum flame temperatures and low cooling rates. On the other hand, the hard-primary particle diameter is hardly affected by the evolution of fractal dimension (difference less than 4%), consistent with literature, regardless of the D_f model.

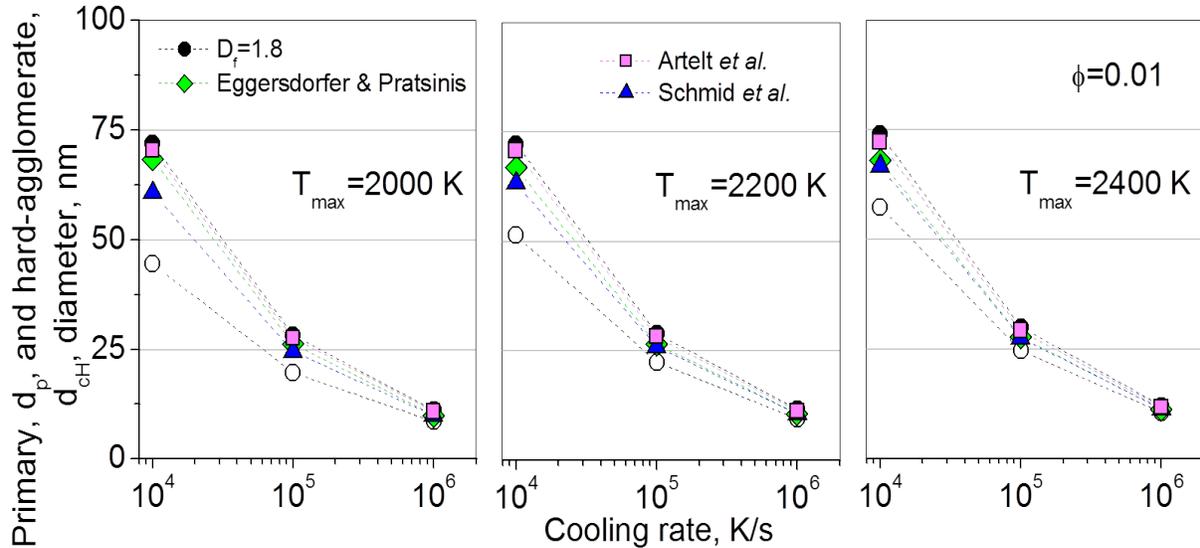


Figure 2. Primary particle diameter (open symbols) and hard agglomerate collision diameter (filled symbols) of titania particles as a function of the cooling rate for three maximum operating temperatures (2000, 2200 and 2400K) for initial precursor molar fraction $\phi=0.01$. The models of Eggersdorfer & Pratsinis (in preparation; green diamonds), Artelt et al. (2003) for $s=1$ (pink squares) and Schmid et al. (2006; blue triangles) are compared against the constant fractal dimension (black filled circles). The evolution of D_f has a minor effect on the primary particle diameter and hence only the d_{pH} of $D_f=1.8$ is shown here.

A similar analysis is performed for amorphous SiO_2 and the effect of two sintering rate descriptions on particle growth has been examined for the entire process parameter space. Generally, varying D_f practically does not affect the primary particle and hard-agglomerate diameter even though it affects the transient evolution of collision diameter for SiO_2 , as also predicted for TiO_2 . However, the sintering rate significantly affects both the transient and final primary particle and hard-agglomerate diameters that determine the final particle properties.

Artelt, C., Schmid, H.J. and Peukert, W. (2003) *J. Aerosol Sci.* **34**, 511-534

Buesser, B., Gröhn, A.J. and Pratsinis, S.E. (2011) *J. Phys. Chemistry C* **115**, 11030-11035

Eggersdorfer M.L., Pratsinis S.E. in preparation

Kruis, F. E., Kusters, K. A., Pratsinis, S.E. and Scarlett, B. (1993) *Aerosol Sci. Technol.* **19**, 514-526

Schmid, H-J., B. Al-Zaitone, C. Artelt and W. Peukert (2006) *Chem. Eng. Sci.* **61**, 293-305

Tsantilis, S. and Pratsinis S.E. (2004) *Langmuir* **20**, 5933-5939

Xiong, Y., and Pratsinis, S.E. (1993). *J. Aerosol Sci.* **24**, 283-300

E. Goudeli, M.L. Eggersdorfer, and S.E. Pratsinis
 Particle Technology Laboratory, ETH Zürich, CH-8092 Zürich, Switzerland
 goudeli@ptl.mavt.ethz.ch http://www.ptl.ethz.ch

Motivation

- Investigation of the effect of time-evolving fractal dimension, D_f on primary and hard-agglomerate diameters of TiO_2 and SiO_2 flame-made particles by interfacing continuum, mesoscale and molecular dynamics models.
- Identification of process conditions that affect agglomeration of TiO_2 and SiO_2 .

Aerosol Dynamics

Number Concentration, N : $\frac{dN}{dt} = -\frac{1}{2} \beta N^2 \rho_g$

Agglomerate Area Concentration, A : $\frac{dA}{dt} = -\frac{1}{\tau_s} (A - Na_s)$

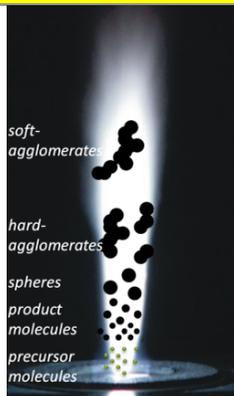
Agglomerate Volume Concentration, V : $\frac{dV}{dt} = 0$

Primary Particle Diameter d_p and Collision Diameter d_c

$$d_p = \frac{6V}{A}$$

$$d_c = d_p \left(\frac{A^3}{36\pi N V^2} \right)^{1/D_f}$$

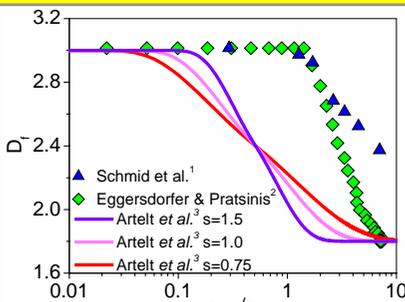
Flame Spray Pyrolysis



Spray flame producing nanoparticles: The precursor molecules react almost instantaneously, and particles are formed by condensation, sintering or coalescence and coagulation.

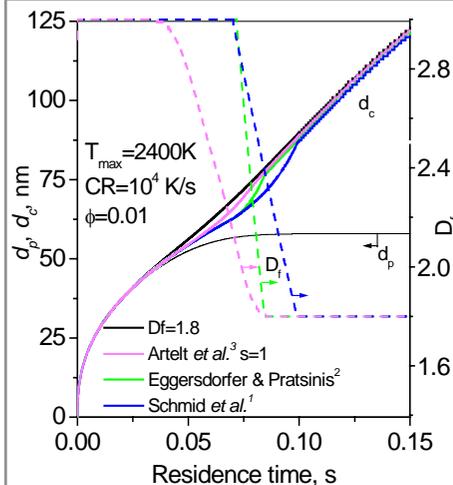
Hard-agglomerates are formed by sintering between particles. Soft-agglomerates are held together by physical forces and can be broken to their constituent parts more easily than hard-agglomerates.

Structure Evolution

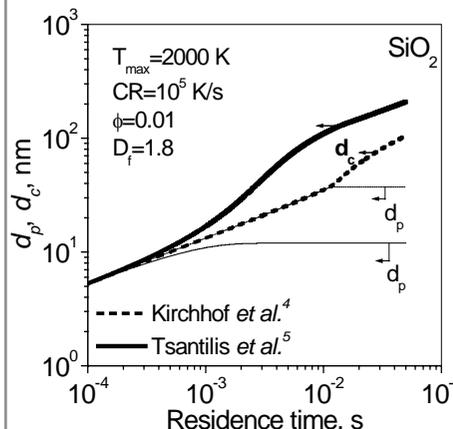


Evolution of D_f with the dimensionless characteristic time as predicted by mesoscale [1,2] and empirical [3] models.

Particle Growth

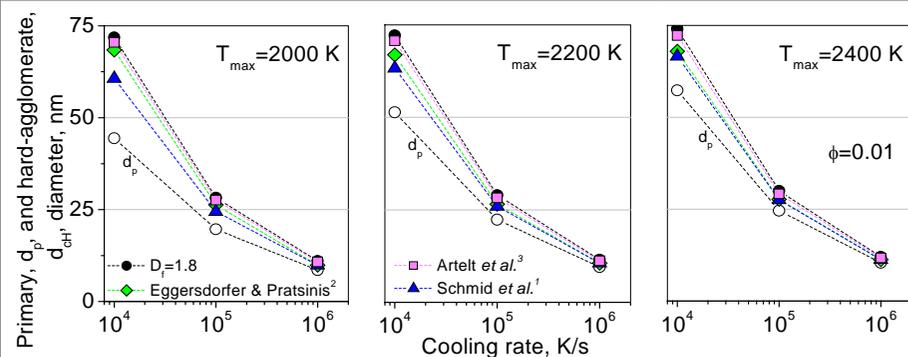


Evolution of TiO_2 d_p and d_c with varying and constant D_f .

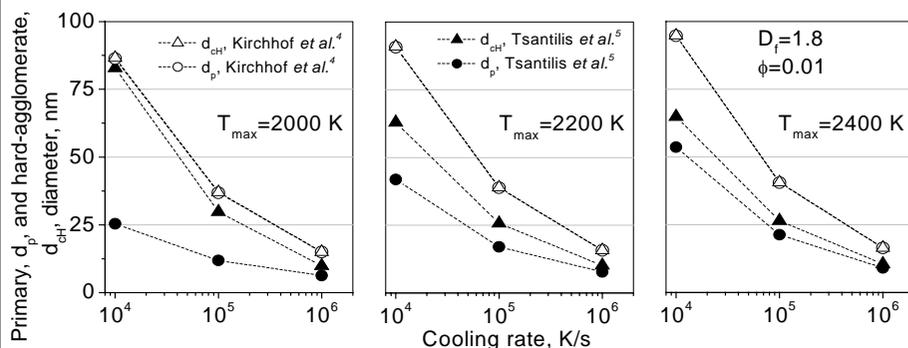


The evolution of SiO_2 d_p and d_c is sensitive to the characteristic sintering time.

Effect of Process Parameters on d_p and d_{ch}



Product diameters for various T_{max} and various D_f descriptions of TiO_2 .



Product diameters for various T_{max} and two sintering rates of SiO_2 .

Conclusions

- Varying D_f hardly affects d_p and d_{ch} even though it affects the transient evolution of d_c for both TiO_2 and SiO_2 .
- Particle growth depends on the characteristic sintering time. Over the process conditions no hard-aggregates of SiO_2 are formed accounting for Kirchhof et al. [4] sintering rate.
- The trend of the results is consistent with experimental data with d_p [6].

References

- [1] Schmid et al. (2006) *Chem. Eng. Sci.* **61**, 293.
- [2] Eggersdorfer & Pratsinis (in preparation).
- [3] Artelt et al. (2003) *J. Aerosol Sci.* **34**, 511.
- [4] Kirchhof et al. (2012) *J. Aerosol Sci.* **45**, 26.
- [5] Tsantilis et al. (2001) *Aerosol Sci. Tech.* **20**, 237.
- [6] Zhu & Pratsinis (1997) *AIChE J.* **43**, 2657