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Design of Aerosol Coating Reactors: Precursor Injection

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Abstract

Particles are coated with thin shells to facilitate their processing and incorporation into liquid or solid matrixes without altering core particle properties (coloristic, magnetic, etc.). Here, computational fluid and particle dynamics are combined to investigate the geometry of an aerosol reactor for continuous coating of freshly-made titanium dioxide core nanoparticles with nanothin silica shells by injection of hexamethyldisiloxane (HMDSO) vapor downstream of TiO₂ particle formation. The focus is on the influence of HMDSO vapor jet number and direction in terms of azimuth and inclination jet angles on process temperature and coated particle characteristics (shell thickness and fraction of uncoated particles). Rapid and homogeneous mixing of core particle aerosol and coating precursor vapor facilitates synthesis of core-shell nanoparticles with uniform shell thickness and high coating efficiency (minimal uncoated core and free coating particles).

1. Introduction

At industrial scale, particles are made efficiently in the gas-phase (e.g. carbon black, fumed silica or pigmentary TiO₂) but coated and functionalized typically in the liquid-phase.^{1,2} Wet-chemistry processing routes, however, result in large volumes of undesirable liquid byproducts, require many process steps and costlier particle collection.³ So there is great interest to develop a continuous, gas-phase process to coat particles hermetically with a dense shell in a single step⁴ while they are still suspended (“on the fly”).

Aerosol co-oxidation of certain metal precursors leads “naturally” to core/shell particles like carbon-coated silica⁵, titania⁶ or copper⁷ and V₂O₅-coated titania.⁸ Vastly different properties of core and shell materials promote formation of V₂O₅ or C films (e.g. boiling point of V₂O₅ and TiO₂ or surface growth of C) on top of the core particles. Other materials, however, hardly form coating shells when co-oxidized e.g. C/Pt, where C is oxidized in the presence of Pt catalyst⁹, C/LiMn₂O₄ or C/LiFePO₄ requiring a second stage of coating.^{10,11} For SiO₂-coated TiO₂, for example, co-oxidation may form thin SiO₂ shells but only within a very narrow window of process conditions while typically segregated particles or very thick, matrix-like coatings are formed.^{12,13}

Although the advantages of aerosol processing of materials are well known¹⁴, the implementation of aerosol coating on industrial⁴ and even on laboratory¹² scale has been difficult. Particle and shell growth rates in the gas-phase are much faster than in liquid-phase making design and control of gas-phase coating quite challenging. A notable exception is the functionalization of fumed silica to convert it from hydrophilic to hydrophobic in fluidized beds.¹⁵ Silica coating on TiO₂ nanoparticles has been achieved in gas-phase with counter-flow diffusion flames¹², hot wall reactors¹⁶, atomic layer deposition¹⁷, or chemical vapor deposition¹⁸. Recently on a lab-scale spray flame reactor, continuous SiO₂ coating of flame-made TiO₂ nanoparticles (up to 30 g/h) has been achieved by sequentially injecting the SiO₂ coating precursor vapor downstream of TiO₂ core particle formation through a torus tube¹⁹, similar to a CFD-optimized flame quenching ring.²⁰ This reactor has been used to produce Fe₂O₃²¹, Ag²² or Fe₂O₃-Ag composite²³ nanoparticles hermetically coated with

thin SiO₂ shells. On the other hand, quantitative understanding of aerosol coating has been advanced with monodisperse²⁴, lognormal moment²⁵, Monte Carlo²⁶ or trimodal²⁷ coating particle dynamic models combined with computational fluid dynamics.²⁸

Using the latter²⁸ model, the effect of operation parameters of aerosol coating reactors¹⁹ (e.g. coating precursor concentration and mixing flow rate) was elucidated and found in good agreement with experimental data of the fraction of uncoated TiO₂ core particles. Furthermore the effect of these parameters on product characteristics that are difficult to measure (e.g. shell thickness distribution) was unraveled. For example, increasing either the coating weight fraction or the coating precursor jet flow rate broadens or narrows, respectively, the shell thickness distribution. More importantly, with such a fluid-particle dynamics model²⁸, the origin of uncoated particles was traced to incomplete mixing of core aerosol and coating precursor vapor.

Here, this model²⁸, is used to go beyond what has been investigated experimentally. So the focus shifts from the operation²⁸ to the design parameters of aerosol coating reactors and their effect on process temperature, spatial distribution and evolution of core-shell product particle characteristics (fraction of uncoated particles and shell thickness distribution).

2. Reactor and Simulation Conditions

2.1 Aerosol Coating Reactor and CFD

The aerosol coating reactor consists of a vertical quartz glass tube ($d_t = 4.5$ cm, $L = 50$ cm) and a torus tube ($d_t = 0.38$ cm) ring ($d_r = 4.5$ cm) with radially evenly distributed openings for coating precursor vapor jets ($d_j = 0.06$ cm) at its inner side.²⁹ Figure 1 shows a) axial and b) horizontal cross-sections of the reactor with the definition of inclination angle β (e.g. 20°) and azimuth angle α (e.g. 10°) of the 16 evenly distributed (every 22.5°) jets (open arrow) issuing the SiO₂ coating precursor (HMDSO) carried by N₂ into the core particle aerosol (filled arrow).

Standard simulation conditions correspond to the optimal reactor operation parameters:²⁸ TiO₂ core particles with diameter $d_p = 40$ nm are produced at 24 g/h and coated with SiO₂ shells having a weight fraction $WF = 20$ wt% in the final core-shell TiO₂-SiO₂ particles²⁸ (e.g. 6 g/h SiO₂ for 24 g/h TiO₂). The simulations with varying α or β have a total N₂ mixing flow rate of $Q = 15.8$ l/min ($T = 300$ K) issuing from 16 jets. The number of jets is investigated at constant N₂ mixing flow rate per jet $Q_{jet} = 0.99$ l/min.

Each simulation for α and β as well as number of HMDSO/N₂ jets requires a separate mesh. This has been generated by accounting for jet direction and taking advantage of the rotational periodicity (except the for the case of 1 jet) by periodic boundary conditions.²⁸ The gases have the properties of oxygen for the core particle aerosol ($T = 1900$ K) and nitrogen for the precursor vapor flow through the torus ring. Gravity ($g = 9.81$ m s⁻²) is included in the upstream direction. Turbulence is described by the Reynolds Stress Model since it gives more accurate results for confined swirling flows³⁰, that are expected here, than simpler³¹ (e.g. k- ϵ) turbulence models. The following particle dynamics model is connected with source terms for user defined scalars³² (UDS) to Ansys Fluent 12.1.4. All simulations are done in parallel on 8 cores on a desktop PC.²⁸

2.2 Particle Dynamics

The trimodal coating particle dynamics model²⁷ accounts for SiO₂ monomer generation, coagulation and sintering while terms for surface growth and gas volume variation are neglected.²⁸ Surface growth is ruled out as it resulted in bigger coating particles and rougher coating shells.²⁷

2.2.1 Coating Particles—The rate of change of coating precursor (HMDSO) concentration, C , is given by a first order reaction rate²⁷:

$$\frac{dC}{dt} = -k_g C \quad (1)$$

with $k_g = 4 \times 10^{17} \exp(-3.7 \times 10^5 / (8.314 \times T)) \text{ s}^{-1}$.³³

The rates of change of coating monomer number concentration, N_1 , and coating particle number, N_2 , surface area, A_2 , and volume, V_2 , concentration are²⁷:

$$\begin{aligned} \frac{dN_1}{dt} &= n_m k_g C - \frac{1}{2} \beta_{1,1} N_1^2 \frac{r}{r-1} - \beta_{1,2} N_1 N_2 - \beta_{1,c} N_1 N_c \\ \frac{dN_2}{dt} &= \frac{1}{2} \beta_{1,1} N_1^2 \frac{1}{r-1} - \frac{1}{2} \beta_{2,2} N_2^2 - \beta_{2,c} N_2 N_c \\ \frac{dA_2}{dt} &= \frac{1}{2} \beta_{1,1} N_1^2 a_1 \frac{r}{r-1} + \beta_{1,2} N_1 N_2 a_1 - \beta_{2,c} N_2 N_c a_2 - \frac{A_2 - N_2 a_{2f}}{\tau_2 (d_{p2})} \\ \frac{dV_2}{dt} &= \frac{1}{2} \beta_{1,1} N_1^2 v_1 \frac{r}{r-1} + \beta_{1,2} N_1 N_2 v_1 - \beta_{2,c} N_2 N_c v_2 \end{aligned} \quad (2)$$

where $n_m = 2$, for HMDSO producing two SiO_2 monomers per molecule, and τ_2 the characteristic sintering time for SiO_2 with $dp_{\min} = 1 \text{ nm}$.³⁴ A detailed discussion of each term of the above equations can be found in previous publications.^{27,28} The collision diameter of the coating particles is:³⁵

$$d_{c2} = d_{p2} n_{p2}^{\frac{1}{D_f}} = \frac{6V_2}{A_2} \left(\frac{A_2^3}{36\pi N_2 V_2^2} \right)^{\frac{1}{D_f}} \quad (3)$$

utilizing a constant fractal dimension³⁶ $D_f = 1.8$ and is used to calculate the collision frequency, $\beta_{i,j}$ with the Fuchs interpolation function.³⁷

2.2.2 Core particles—The rate of change of the number, N_c , surface area, A_c , and volume, V_c , concentration of core particles is given by:

$$\begin{aligned} \frac{dN_c}{dt} &= -\frac{1}{2} \beta_{c,c} N_c^2 \\ \frac{dA_c}{dt} &= -\frac{A_c - A_{c,fc}}{\tau_c} \\ \frac{dV_c}{dt} &= 0 \end{aligned} \quad (4)$$

Ideally, core primary particles have reached their final size (sintering has become negligible) before being coated.¹⁹ Therefore it would be sufficient to track only the number of core particle agglomerates while the total number of core primary particles and their size (surface area) remains practically constant. To confirm that this assumption is correct A_c was tracked by accounting for core particle sintering with characteristic sintering time³⁸, τ_c , and found to not change at the investigated conditions. With these concentrations the core primary particle diameter, d_{pc} , and number, n_{pc} , and their collision diameter, d_{cc} , is:³⁷

$$d_{pc} = \frac{6V_c}{A_c} \quad n_{pc} = \frac{A_c^3}{36\pi V_c^2} \quad d_{cc} = d_{pc} n_{pc}^{\frac{1}{D_{f,c}}} \quad (5)$$

with $D_{f,c} = 1.8$.

2.2.3 Coating Shells—The rates of change of rough coating shell surface area, A_r , volume, V_r , and smooth coating shell volume, V_s , concentrations are:²⁷

$$\begin{aligned}\frac{dA_r}{dt} &= \beta_{2,c} N_2 N_c a_2 - \frac{A_r}{\tau(d_{pr})} \\ \frac{dV_r}{dt} &= \beta_{2,c} N_2 N_c v_2 - \frac{V_r}{\tau(d_{pr})} \\ \frac{dV_s}{dt} &= \beta_{1,c} N_1 N_c v_1 + \frac{V_r}{\tau(d_{pr})}\end{aligned} \quad (6)$$

where d_{pr} is the primary particle diameter of the rough coating shells: $d_{pr} = 6 V_r / A_r$ ²⁴

2.2.4 Coating shell characteristics—Product particles are characterized by the equivalent shell thickness, δ , assuming uniform shells and the fraction of uncoated core particle surface area, F .²⁸ The shell thickness²⁷, δ , is the thickness of a spherical coating shell with constant density ($\rho_{SiO_2} = 2200 \text{ kg/m}^3$) and volume concentration $V_s + V_r$:

$$\delta = \frac{1}{2} \left(\sqrt[3]{\left(\frac{V_s + V_r}{N_c n_{pc}} + d_{pc}^3 \frac{\pi}{6} \right) \frac{6}{\pi}} - d_{pc} \right) \quad (7)$$

Core particles are coated hermetically if their δ exceeds a cut-off thickness, δ_{cut} , and partially coated or uncoated with $\delta < \delta_{cut}$, contributing proportionally²⁸ to F :

$$F = \frac{\int_0^{\delta_{cut}} \left(1 - \frac{(d_{pc} + 2\delta)^3 - d_{pc}^3}{(d_{pc} + 2\delta_{cut})^3 - d_{pc}^3} \right) A_c \frac{\dot{m}}{\rho} d\delta}{\int_0^{\infty} A_c \frac{\dot{m}}{\rho} d\delta} \quad (8)$$

where the term inside the brackets accounts for partially coated core particles proportional to the shell thickness.

Experimentally F has been obtained by measuring the acetone concentration from photocatalytic oxidation of isopropyl alcohol in suspensions of such particles.^{19,29} This reaction takes place on TiO_2 but not on SiO_2 so its rate is proportional to the (uncoated) TiO_2 surface area.³⁹ Here, δ_{cut} is set to 0.6 nm, corresponding to about 1.5 times the equivalent diameter of a single SiO_2 molecule⁴⁰, according to previous simulations²⁸ with the same model on varying reactor operation parameters and their agreement with several data points.^{28,29} The $\delta_{cut} = 0.6 \text{ nm}$ is consistent with wet-phase SiO_2 coating of TiO_2 nanoparticles: There 12⁴¹ to 20⁴² wt% of SiO_2 coating shells is sufficient to inhibit the photocatalytic oxidation of isopropyl alcohol on their rutile TiO_2 particles ($140 \text{ m}^2/\text{g}$). These weight fractions correspond to average coating thickness 0.4⁴¹ or 0.7⁴² nm bracketing the $\delta_{cut} = 0.6 \text{ nm}$ obtained before²⁸ and used here.

3. Results and Discussion

3.1 Azimuth angle of precursor vapor jets

Figure 2 shows the 3D-evolution of SiO_2 shell thickness (color-coded) on TiO_2 core particle flow streamlines by oxidation of HMDSO vapor issuing from 16 torus ring jets, each with inclination $\beta = 20^\circ$ and azimuth angle $\alpha =$ a) 0° (no swirl), b) 10° and c) 20° . Dark blue indicates uncoated TiO_2 particles. The red iso-surface corresponds to 1 % of the initial HMDSO concentration in the torus ring. The distance between beads on each streamline corresponds to a time interval of $\Delta t = 0.005 \text{ s}$.

For $\alpha = 0^\circ$ (Fig. 2a), all precursor vapor jets focus or aim at the reactor axis forming a (cone-like) stagnation point above the level of the torus ring. So some HMDSO vapor is

transported upstream coating TiO_2 particles before they have reached the torus ring level (please see green and yellow streamlines and beads just below the ring). It can also be seen that most streamlines flow parallel to the reactor axis without much mixing with the precursor vapor jets unless passing through them. The high axial velocities (large distance between beads) downstream of the stagnation point transport unreacted HMDSO far downstream along the reactor axis (red surface) but not much radially. This leads to well-coated particles along the axis (green and yellow streamlines inside the red surface) but partially (light blue) or completely uncoated (dark blue) ones towards the reactor wall.

Intermediate azimuth angles (Fig. 2b, $\alpha = 10^\circ$) mix better the core particle aerosol and HMDSO vapor jets by forming a swirl where the HMDSO vapor covers a large part of the reactor cross-section.²⁸ Some core particle streamlines however still pass in-between the HMDSO vapor jets of the torus ring and remain uncoated (dark blue) near the wall even though such streamlines swirl. Nevertheless, far more core particles are coated with SiO_2 than for $\alpha = 0^\circ$.

Larger azimuth angles (Fig. 2c, $\alpha = 20^\circ$) swirl even more the HMDSO vapor forming essentially a short “twister” before widening the swirl away from the reactor axis. The HMDSO vapor then stays close to the reactor wall while some core particles can pass uncoated through the center of the torus ring (dark blue streamlines). Clearly there should be an optimal azimuth angle of the precursor vapor jets for maximum contact between HMDSO and core particles (Fig. 2a-c).

Figure 3 shows temperature cross-sections along the reactor axis (Fig. 1a) for the conditions of Fig. 2. Cold HMDSO/ N_2 is injected from the torus ring (blue, $T = 300$ K) into the hot core particle aerosol (red, $T = 1900$ K) entering from the bottom. For $\alpha = 0^\circ$ (Fig. 2a) the stagnation point leads to flows in upstream and downstream direction decreasing markedly the reactor temperature above and even below the torus ring (green to light blue). Therefore the transport of HMDSO vapor far downstream (Fig. 2a, red cone) is caused, besides the increased axial velocities (Fig. 2a, longer distances between beads on streamlines closer to the reactor axis) also by the lower temperatures at the reactor axis that result in lower HMDSO oxidation rates (Fig. 3a). Further downstream (after 3 cm above the ring), the temperature decreases along the reactor wall also by heat losses. The upstream flow towards the highest temperatures results in some really large SiO_2 particles early in the coating process (Fig. SI.2b) leading to high coating efficiency early on in the process (Fig. SI.2a).

For $\alpha = 10^\circ$ there is no stagnation point²⁰ and upstream HMDSO flow. The improved mixing results in a homogeneous temperature distribution at about 3 cm above the torus ring (green) and significant fraction of core particles being coated as seen in Fig. 2b. For $\alpha = 20^\circ$ the temperature remains high (red) along the reactor axis by the widened swirl (Fig. 2c) preventing mixing of HMDSO/ N_2 gas and TiO_2 aerosol. As a result, the temperature decreases steeply at the reactor wall right after the ring where most of the HMDSO/ N_2 flow swirls because of the cold HMDSO/ N_2 jets pointing more towards the reactor wall than for $\alpha = 10^\circ$. This leads to lower HMDSO oxidation rates and decreases the coating efficiency to 86% from 98% for $\alpha = 10^\circ$ (Fig. 2b and SI.2a). The azimuth angle has a significant effect on the reaction temperature as a $0^\circ - 40^\circ$ variation results in a 200 – 300 K difference (Fig. SI. 1).

Figure 4 summarizes the above showing the fraction of uncoated core particle surface area, F_u , at the reactor exit as a function of α . The experimentally determined fraction of uncoated TiO_2 core particle surface at $\alpha = 10^\circ$ (circle)²⁹ is in good agreement with the present simulations as it has been already shown for the optimal operation parameters of this reactor.²⁸ The aerosol coating model²⁸ allows now to explore efficiently the influence of α

whereas an experimental study may require building a new torus ring for each α . A minimum of F of about 0.05 exists between $\alpha = 10^\circ$ and 15° . This is close to the optimal azimuth of 10° predicted by CFD for quenching open flame reactors.²⁰ Increasing α above 15° increases F drastically up to 0.45 for $\alpha = 40^\circ$ by the widened mixing swirl at the reactor axis. Decreasing α below 10° leads to unstable mixing conditions²⁰ and F up to 0.19.

Figure 5 shows the cumulative shell thickness distribution on the core particles, which is difficult to determine experimentally, for azimuth $\alpha = 0^\circ$ (solid line), 10° (dashed line), 20° (dash-dot line) and 40° (dash-double-dot line). Ideally these lines should be nearly vertical corresponding to an equal shell thickness on all core particles and therefore a high product particle quality. Increasing the azimuth to 20° and 40° and widening the swirl generated by the HMDSO/ N_2 jets results in increasingly bimodal shell thickness distribution of either nearly uncoated core particles originating from the reactor axis or relatively thick shells from the reactor wall region. In spite of this polydispersity, the large azimuth angles give the highest fraction of smooth shells (Fig. SI.2c) and smallest free coating particles (Fig. SI.2b). It should be noted that these distributions could deviate from experimental ones as at each streamline the average shell thickness is used for calculation and polydispersity of core particles is neglected.

3.2 Inclination angle of precursor vapor jets

Figure 6 shows the evolution of SiO_2 shell thickness on TiO_2 core particles across and along the reactor similar to Fig. 2 at the standard conditions but for inclination angle $\beta =$ a) -10° (pointing upstream) b) 10° and c) 30° where Fig. 2b shows $\beta = 20^\circ$. Decreasing β from 20° to 10° (Fig. 6b) creates a hollow HMDSO/ N_2 jet swirl around the reactor axis as in Fig. 2c and an increasing amount of core particles passes uncoated through the ring as indicated by the dark blue streamlines along the reactor axis. For jets with negative β (Fig. 6a), the HMDSO vapor (red cloud) remains closer to the torus ring level forming a stagnation disk. Nevertheless some core particles pass in-between the HMDSO/ N_2 jets uncoated. Increasing β from 20° (Fig. 2b) to 30° (Fig. 6c) leads to a swirl that swipes and contacts most of the core particle flow but again core particles are passing in-between the HMDSO vapor jets close to the reactor wall remain uncoated. The temperature evolution (Fig. SI.3) above the torus ring level are quantitatively the same 5cm above the torus ring for all β .

Figure 7 shows similar to Fig. 4 the fraction of uncoated particle surface area, F , for $\alpha = 10^\circ$ as function of β . The highest fraction of uncoated particles can be seen at $\beta = -10^\circ$ (upstream direction) of around 0.16 and the minimum around 0.02 at $\beta = 30^\circ$. For larger inclination angles the fraction of uncoated particles increases slightly to 0.04 at $\beta = 50^\circ$. Please note that the overall dependence of F on β seems to be smaller than on α . The experimental datum on the fraction of uncoated particles²⁹ (Fig. 4) was obtained with an inclination angle of $\beta = 20^\circ$ (circle). Also here, each experiment with another β would require an arduous modification of the coating reactor while the present aerosol coating reactor model²⁸ allows to screen such designs quite efficiently.

3.3 Number of precursor vapor jets

Figure 8 shows the evolution of SiO_2 shell thickness (similar to Fig. 2) for the number of HMDSO/ N_2 jets $n_{jet} =$ a) 1, b) 4, c) 8 and d) 16 with $\alpha = 10^\circ$ and $\beta = 20^\circ$. The flow rate per jet is $Q_{jet} = 0.99$ l/min while the total flow rate increases with n_{jet} corresponding to $Q = 15.8$ l/min for $n_{jet} = 16$ according to lab-scale experiments.²⁹ The total SiO_2 coating weight is always $WF = 20$ wt%, e.g. for $n_{jet} = 1$ the jet inlet HMDSO concentration is 16 times higher than that for a single jet with $n_{jet} = 16$. Two reactor cross-sections are shown at 4 and 7.5 cm. The color on the slices and the streamlines corresponds to the SiO_2 shell thickness.

For its simplicity in design and fabrication, single jet injection is applied commonly for mixing aerosols from a diffusion¹⁰ or spray⁴³ flame, water sprays⁴⁴ or to apply carbon⁹ coatings and even in-situ functionalization.⁴⁵ Typically, the jet direction, number and even flow rate have been hardly optimized since it would have required tedious modifications of the reactor. Flow rate and direction of the injection, however, are crucial for high quality mixing and to avoid jet impingement on the opposite reactor wall (too strong jet) or close to the jet inlet (too weak).

Figure 8a shows one single HMDSO/N₂ jet intercepting relatively few core aerosol streamlines. So the HMDSO and resulting SiO₂ particles cross the reactor in a quite narrow jet flow impinging on the tubular reactor wall opposite to the jet inlet. This is not ideal for aerosol reactors as it could lead to enhanced losses (deposition) of core and coating particles on the reactor wall. The few core particle streamlines that mix with the HMDSO jet obtain relatively thick coating shells of around 4 – 5 nm (orange to red) while many core particle aerosol streamlines flow around this jet without ever being coated (dark blue). The coating thickness distribution on the cross-section slices look like half-moon shapes formed by two vortices at their edges as commonly observed for jets into crossflows.⁴⁶

Figure 8b shows that 4 HMDSO jets introduce a symmetric, swirling motion downstream of the torus ring. Some of the SiO₂ coating particles are transported into the faster swirling region along the reactor axis resulting in thicker SiO₂ shells there (3 – 4 nm, orange) while part of the SiO₂ coating particles are crossing over the neighboring jet and are drawn into the slower swirling part closer to the reactor wall. Each slice shows four distinct spots of coating thickness (white arrows), originating from these SiO₂ particles, that are enlarging further downstream and rotating slowly around the reactor axis. That way coating shells are deposited on core particles across nearly the complete reactor cross-section.

The increased total flow rate of 8 precursor vapor jets (Fig. 8c) leads to a swirl that is rotationally more symmetric and focused closer to the reactor axis. The coating shells are distributed in homogeneous circles which remain rather closely confined around the reactor axis and open slowly farther downstream. The coating vapor and particles are absorbed into this stronger swirling region along the reactor axis forming thicker coating shells there (green to red) while most of core particles in the wall and axis region remain uncoated (dark blue). For 16 jets (Fig. 8d) the coating is distributed more evenly across the reactor cross-sections broadening these “circles” of coated particles on the slices at 4 and 7.5 cm above the torus ring. Please note that Fig. 8d is essentially the same to Fig. 2b as well as the dotted lines for 16 jets in Fig. SI.5 and the broken lines of Fig. SI.1.

For 1 and 2 jets the temperature increases to a maximum around 5 cm above the torus ring level close to where the jet crosses the reactor axis and decreases quite rapidly after impinging on the reactor wall (Fig. SI.5). More jets lead to more homogeneous temperatures across the reactor cross-section. This results in lower maximum T for higher jet numbers, caused by the increased flow of cold N₂, that cools the entire process (Fig. SI.5).

Figure 9 shows the fraction of uncoated core particle surface area, F , as function of n_{jet} and the conditions of Fig. 8. The F decreases with increasing number of precursor vapor jets from 1 to 4 by the improved and more symmetric mixing of core and coating aerosol from 0.3 to 0.05. Between 4 and 8 jets F increases again up to 0.35 as the jets start to focus the swirl closer to the reactor axis. For higher numbers of jets F decreases again to values between 0.03 and 0.06 for 12 to 32 precursor vapor jets because the mixing swirl starts to expand faster across the complete reactor cross-section. Please note that higher n_{jet} (or Q) could lead to too slow reaction rates and again an increasing F . The experimental data²⁹ (circle) shown also in Figs. 4 and 7 has been obtained for 16 precursor vapor jets. The

evolution of average coating efficiency, and the fraction of smooth coating show only a weak dependence on the number of jets (Fig. SI.6). The SiO₂ particle diameter and shell thickness, however, show quite some sensibility to n_{jet} . For example, thicker coating and finer, free coating particles are obtained at the highest n_{jet} .

While the azimuth and inclination angle simulations showed a clear minimum that would be relatively easy to interpret from experimental data, the non-linear behavior for varying number of precursor vapor jets seems to be more difficult. This shows the great advantage of this aerosol coating reactor model²⁸ that allows looking into the black box of the reactor and elucidating the sources for uncoated particles.

4. Conclusions

The influence of the geometry of an aerosol coating reactor has been investigated for SiO₂ coating of TiO₂ nanoparticles using a computational fluid and particle dynamics model focusing on direction and number of coating precursor vapor injection jets.

Increasing the azimuth or decreasing the inclination angle forms mixing swirls that are widened at the reactor axis and allow core particles to pass the coating zone without deposition of any coating shells. Decreasing the azimuth angle focuses the coating precursor vapor at stagnation points or disks where large parts of the coating precursor vapor are transported far downstream by the high axial velocity and low temperatures originating at the stagnation point or disk. The lowest fraction of uncoated particles was found for azimuth $\alpha = 12.5^\circ$ or inclination $\beta = 30^\circ$ which is close to the values found for quenching rings of open flames²⁰ and aerosol coating experiments¹⁹ ($\alpha = 10^\circ$, $\beta = 20^\circ$). Varying the number of mixing jets elucidated the changing shape of the mixing swirl and its influence on the fraction of uncoated core particle surface area.

The presented simulations show how to design and optimize the geometry of aerosol coating reactors for continuous gas-phase synthesis of coated nanoparticles, with minimal fraction of uncoated particles and maximum coating efficiency.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Footnotes

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Associated Content Supporting Information. Evolution of jet streamline and cross-section area-weighted temperature, coating efficiency and mixing-cup average of SiO₂ coating primary particle diameter, fraction of smooth shells and shell thickness as function of height above torus ring for varying number of jets and azimuth and inclination angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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6. Nomenclature

A_2	surface area concentration of coating particles	$[\text{m}^2 \text{ m}^{-3}]$
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A_c	surface area concentration of core particles	$[m^2 m^{-3}]$
$A_{c,fc}$	surface area concentration of fully coalesced core particles	$[m^2 m^{-3}]$
A_r	surface area concentration of rough coating shell	$[m^2 m^{-3}]$
a_1	surface area of coating monomer	$[m^2]$
a_2	surface area of coating particle	$[m^2]$
a_{2f}	surface area of fully-coalesced (spherical) coating particle	$[m^2]$
C	coating precursor vapor concentration	$[# m^{-3}]$
D_f	fractal dimension	$[-]$
d_{c2}	collision diameter of coating particle	$[m]$
d_{cc}	collision diameter of core particle	$[m]$
d_{p2}	primary particle diameter of coating particle	$[m]$
d_{pc}	primary particle diameter of core particle	$[m]$
d_{pr}	primary particle diameter of coating shell	$[m]$
F	fraction of smooth coating shells	$[%]$
k_g	gas phase oxidation rate constant	$[s^{-1}]$
$\dot{m}$	mass flux	$[kg s^{-1}]$
N_1	number concentration of coating monomers	$[# m^{-3}]$
N_2	number concentration of coating particles	$[# m^{-3}]$
N_c	number concentration of core particles	$[# m^{-3}]$
n_m	number of monomers per precursor molecule	$[-]$
n_{p2}	number of primary particles per coating particle	$[-]$
n_{pc}	number of core primary particles per core particle	$[-]$
r	volume ratio, $r = v_2/v_1$	$[-]$
V_2	volume concentration of coating particles	$[m^3 m^{-3}]$
V_c	volume concentration of core particles	$[m^3 m^{-3}]$
V_r	volume concentration of rough coating shells	$[m^3 m^{-3}]$
V_s	volume concentration of smooth coating shells	$[m^3 m^{-3}]$
v_1	volume of coating monomer	$[m^3]$
v_2	volume of coating particle	$[m^3]$
WF	weight fraction of coating material	$[%]$
6.1 Greek Letters		
α	precursor vapor jet azimuth angle	$[^\circ]$
β	precursor vapor jet inclination angle	$[^\circ]$
β_{ij}	collision frequency	$[m^3 s^{-1}]$
δ	total coating thickness	$[m]$
ρ	gas density	$[kg m^{-3}]$
τ_i	characteristic sintering time	$[s]$

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Figure 1. Axial (a) and horizontal (b) cross-sections of the coating reactor and its torus ring with 16 evenly distributed coating precursor vapor jet openings (every 22.5°) and enclosing quartz glass tube along with the definitions of jet inclination, β , and azimuth, α , angles.

Figure 2.

Three-dimensional evolution of SiO_2 shell thickness on TiO_2 core particles by oxidation of HMDSO vapor injected by 16 jets from the torus ring with azimuth angle $\alpha =$ a) 0° (no swirl), b) 10° and c) 20° . The color of the streamlines carrying TiO_2 particles corresponds to the coating thickness on these core particles where dark blue indicates uncoated TiO_2 . The distance between the beads on each streamline corresponds to a time interval of $\Delta t = 0.005$ s. The red iso-surfaces describe the areas where the HMDSO concentration has decreased to 1% of the initial one inside the torus ring.

Figure 3. Temperature on cross-sections along the reactor axis for azimuth angle $\alpha =$ a) 0° , b) 10° and c) 20° and inclination angle $\beta = 20^\circ$ (Fig. 2) where blue (below 1000 K) and red (1900 K) indicate cold and hot regions, respectively.

Figure 4. Fraction of uncoated core particle surface area, F , as function of HMDSO/N₂ jet azimuth angle, α , compared with experimental data²⁹ (circle) at $\alpha = 10^\circ$.

Figure 5. Cumulative mass distribution as function of SiO₂ shell thickness for azimuth $\alpha = 0^\circ$ (solid line), 10° (dashed line), 20° (dash-dot line) and 40° (dash-double-dot line).

Figure 6. Three-dimensional evolution of SiO_2 shell thickness for inclination angle $\beta =$ a) -10° (upstream), b) 10° and c) 30° while Fig. 2b shows $\beta = 20^\circ$ all for $\alpha = 10^\circ$ presented according to Fig. 2.

Figure 7.

Fraction of uncoated core particle surface area, F , as function of HMDSO/ N_2 jet inclination angle, β , compared with experimental data²⁹ (circle) at $\beta = 20^\circ$.

Figure 8.

Three-dimensional evolution of SiO_2 shell thickness on TiO_2 core particles for numbers of precursor vapor jets $n_{jet} =$ a) 1, b) 4, c) 8 and d) 16 with constant flow rate of $Q_{jet} = 0.99$ l/min per jet similar to Fig. 2. Color of streamlines and cross section slices at 4 and 7.5 cm above the mixing ring correspond to SiO_2 shell thickness where dark blue indicates uncoated TiO_2 .

Figure 9.

Fraction of uncoated particle surface area, F , as function of the number of HMDSO/ N_2 jets with constant N_2 flow rate per jet $Q_{jet} = 0.99$ l/min compared with experimental data²⁹ (circle) at 16 jets.