Electronic supplementary information

An atomic layer deposition diffusion–reaction model for porous media with different particle geometries

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Table S1, Example calculations for the shape factor s with spherical, cylindrical and slab particle.

R = Particle radius
h = Cylindrical particle height
s = shape factor

a) Sphere

$A = 4\pi R^2$

$V = (4/3)\pi R^3$

R	Area (A)	Volume (V)	A/V	a=A/V*R	$s = a$-1
1	13	4	3,0	3	2
2	50	34	1,5	3	2
3	113	113	1,0	3	2
4	201	268	0,8	3	2
5	314	524	0,6	3	2

b) Cylinder

$A = 2(\pi R^2)+2\pi hR$

$V = \pi hR^2$

h	R	Area (A)	Volume (V)	A/V	a=A/V*R	$n = h/R$	a=2(n+1)/n	s=2(n+1)/n-1	$s = a$-1
4	2	75	50	1,5	3,000	2	3	2	2
10	2	151	126	1,2	2,400	5	2,4	1,4	1,4
100	2	1282	1257	1,0	2,040	50	2,04	1,04	1,04
1000	2	12592	12566	1,0	2,004	500	2,004	1,004	1,004

c) Slab

$A = 2(xy+xR+yR)$

$V = xyR$

x (depth)	y (width)	R	Area (A)	Volume (V)	A/V	a=A/V*R*0.5	$s = a$-1
10	10	1	240	100	2,4	1,2	0,2
100	100	1	20400	10000	2,04	1,02	0,02
1000	1000	1	2004000	1000000	2,004	1,002	0,002

Table S2, Varied porous material physical properties with varying particle radius, specific surface area, pore diameter, pore volume and Knudsen number. Bold text presents the baseline parameters.

R Particle radius (um)	A_O Specific surface area (m^2/g)	d_{pore} Pore diameter (nm)	V_P Pore volume (cm3/g)	$\bar{S}$ A_O/V_P (m^{-1})	Knudsen number
100, 200, 300	100	45.0	0.550	1.82×10^8	155
100, 200, 300	125	40.0	0.560	2.23×10^8	175
100, 200, 300	150	30.0	0.570	2.63×10^8	233
100, 200, 300	175	25.0	0.580	3.02×10^8	279
100, 200, 300	**200**	**20.0**	**0.600**	$\mathbf{3.33 \times 10^8}$	349
100, 200, 300	225	19.0	0.610	3.69×10^8	368
100, 200, 300	250	18.0	0.615	4.07×10^8	388
100, 200, 300	275	17.0	0.620	4.44×10^8	411
100, 200, 300	300	16.0	0.625	4.80×10^8	436
100, 200, 300	325	15.0	0.630	5.16×10^8	466
100, 200, 300	350	14.0	0.635	5.51×10^8	499
100, 200, 300	375	13.0	0.640	5.86×10^8	537
100, 200, 300	400	12.0	0.645	6.20×10^8	582
100, 200, 300	425	11.0	0.650	6.54×10^8	635
100, 200, 300	450	10.0	0.655	6.87×10^8	698
100, 200, 300	475	9.0	0.660	7.20×10^8	776
100, 200, 300	500	8.5	0.670	7.46×10^8	822
100, 200, 300	525	8.0	0.675	7.78×10^8	873
100, 200, 300	550	7.5	0.677	8.13×10^8	931
100, 200, 300	575	7.0	0.678	8.48×10^8	998
100, 200, 300	600	6.5	0.680	8.83×10^8	1074
100, 200, 300	625	6.4	0.681	9.18×10^8	1091
100, 200, 300	650	6.3	0.683	9.52×10^8	1109
100, 200, 300	675	6.1	0.684	9.87×10^8	1145
100, 200, 300	700	6.0	0.686	1.02×10^9	1164
100, 200, 300	725	5.9	0.687	1.06×10^9	1184
100, 200, 300	750	5.7	0.689	1.09×10^9	1225
100, 200, 300	775	5.5	0.690	1.12×10^9	1270
100, 200, 300	800	5.2	0.691	1.16×10^9	1343
100, 200, 300	825	5.0	0.693	1.19×10^9	1397
100, 200, 300	850	4.8	0.694	1.22×10^9	1455
100, 200, 300	875	4.5	0.696	1.26×10^9	1552
100, 200, 300	900	4.2	0.697	1.29×10^9	1663
100, 200, 300	925	4.0	0.699	1.32×10^9	1746
100, 200, 300	950	3.8	0.700	1.36×10^9	1838
100, 200, 300	975	3.6	0.702	1.39×10^9	1940
100, 200, 300	1000	3.4	0.703	1.42×10^9	2054

Knudsen number (*Kn*)

The Knudsen number (Kn) in the Equation S1 is determined as the mean free path (λ) divided by the pore diameter (d_{pore}) [1]:

Equation S1

$$Kn = \frac{The\ mean\ free\ path, \lambda\ (m)}{Pore\ diameter, d_{pore}\ (m)}$$

The mean free path ($\lambda_{0,A}$) of the reactant molecule is given in the Equation S2 [2]:

Equation S2

$$\lambda_{0,\mathrm{A}} = \frac{k_\mathrm{B} T}{\sqrt{2} p_\mathrm{A} \sigma_{\mathrm{A,A}} + \sqrt{1 + \frac{m_\mathrm{A}}{m_\mathrm{B}}}\, p_\mathrm{I} \sigma_{\mathrm{A,I}}}$$

Where k_B is the Boltzmann constant (m^2 kg s^{-2} K^{-1}), T is temperature (K), p_A is the reactant partial pressure (Pa), p_I is the inert carrier gas partial pressure (Pa), $\sigma_{A,A}$ is the collision cross-section of the reactant molecule, $\sigma_{A,I}$ is the collision cross-section between the reactant and inert carrier gas molecule, m_A is reactant molar mass (kg mol^{-1}) and m_B is the molar mass of the inert carrier gas (kg mol^{-1}).

The collision cross-section of the reactant molecule ($\sigma_{A,A}$) is given in the Equation S3 and the collision cross-section between reactant molecule and inert carrier gas molecule ($\sigma_{A,I}$) is presented in the Equation S4 [3]:

Equation S3

$$\sigma_{A,A} = \pi {d_A}^2$$

Equation S4

$$\sigma_{A,I} = \pi \left(\frac{d_A}{2} + \frac{d_I}{2} \right)^2$$

Where d_A is the reactant molecule diameter and d_I is the inert carrier gas molecule diameter.

Table S3, Knudsen number and the mean free path calculation (above) and an example of Kn value calculation (below) with 45 nm pore diameter and relevant parameters for the ALD process in our modelling work.

Knudsen number calculation example

KB [m^2 kg/ (s^2 K)]	1,38065E-23	The Boltzmann constant
pA [Pa]	100	Reactant partial pressure
pI [Pa]	500	Inert carrier gas (N2) partial pressure
d_A [m]	6E-10	Reactant molecule diameter
d_I [m]	3,74E-10	Inert carrier gas (N2) molecular diameter
T [K]	423,15	ALD process temperature
rA [m]	3E-10	Reactant molecule radius
rI [m]	1,87E-10	Inert carrier gas (N2) molecular diameter
σ A,A	2,83E-19	The collision cross-section between two reactant molecules
σ A,I	7,45E-19	The collision cross-section between the reactant and inert carrier gas molecule
MA [kg/mol]	0,1	Molar mass of reactant
MI [kg/mol]	0,028	Molar mass of inert carrier gas
Mean free path [m]	6,98E-06	
Mean free path [nm]	6984	
Pore diameter [nm]	45	
Pore diameter [m]	4,50E-08	
Knudsen number (Kn)	155	

Table S4, The effect of selecting volumetric reactant number density (m^{-3}) or partial pressure (Pa) in a diffusion–reaction model as a function of temperature. Reactant partial pressure, volumetric reactant number density, ALD process temperature and achieved coating penetration depth ($r_{\vartheta=1/2}$).

	Reactant A partial pressure (Pa)	Volumetric reactant number density (m^{-3})	ALD process Temperature (K)	Penetration depth (µm)*
Fixed Partial pressure	100	1,94E+22	373	142
	100	1,71E+22	423	136
	100	1,53E+22	473	131
	100	1,38E+22	523	127
	100	1,26E+22	573	124
	150	2,91E+22	373	188
	150	2,57E+22	423	179
	150	2,30E+22	473	172
	150	2,08E+22	523	167
	150	1,90E+22	573	161
	200	3,88E+22	373	245
	200	3,42E+22	423	229
	200	3,06E+22	473	217
	200	2,77E+22	523	207
	200	2,53E+22	573	200
Fixed volumetric reactant number density	100	1,94E+22	373	142
	113,5	1,94E+22	423	148
	126,5	1,94E+22	473	153
	140	1,94E+22	523	159
	153,5	1,94E+22	573	164
	88	1,71E+22	373	131
	100	1,71E+22	423	136
	111,5	1,71E+22	473	141
	123,5	1,71E+22	523	146
	135	1,71E+22	573	150
	79	1,53E+22	373	122
	89,5	1,53E+22	423	127
	100	1,53E+22	473	132
	110,5	1,53E+22	523	136
	121	1,53E+22	573	140

* Penetration depth for a spherical particle

Plotted values in Figure 8 marked with grey color

55 **References**

56 [1] M. Knudsen, Ann. Phys. 333 (1909) 75–130.

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