



Modeling the precursor utilization in atomic layer deposition on nanostructured materials in fluidized bed reactors



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HIGHLIGHTS

- We model atomic layer deposition in fluidized beds on nanostructured materials.
- We assess the impact of the precursor transport on the precursor utilization.
- Fast ALD kinetics enable complete precursor uptake at high surface conversion.
- We study the effect of the nanoparticle agglomeration on the process dynamics.
- We propose the optimal reactor height depending on operating conditions.

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ABSTRACT

We present a multiscale dynamic model as a means of understanding and optimizing the precursor utilization during atomic layer deposition (ALD) on nanoparticles and micron-sized nano-porous particles in fluidized bed reactors. We used as case study the deposition of alumina using trimethylaluminum and water on both, titania nanoparticles and micron-sized nano-porous γ -alumina particles under low (~ 1 mbar) and atmospheric pressure. In doing so, we assess the effect of the precursor transport, from the inlet of the reactor to the particles active surface, on the precursor utilization efficiency. Our results show that, at proper operating conditions, fast ALD reaction kinetics enables the saturation of the particles surface area with hardly any loss of precursors. Finally, simple scaling rules for the optimization of the precursor utilization are proposed.

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1. Introduction

Atomic layer deposition (ALD) carried out in fluidized bed reactors (FBRs) is a promising technique for coating and decorating nanostructured materials such as nanoparticles and micron-sized nano-porous particles [1–4]. Such technology boasts the potential for attaining production schemes relevant to the industrial scale, thanks to the inherent scalability of FBRs, while retaining the capability of ALD to tune surfaces at the nanoscale [2–7]. In a foreseeable future, such potential could boost the application of nanostructured materials in fields such as the production of improved catalysts and enhanced materials for fuel cells and batteries. [1–3,5,8–12]. However, the economic and environmental feasibility of the scale-up of such process strongly depends on the efficiency with which the ALD precursors are used, as they represent

a major operating cost and may be harmful for the environment [6].

ALD is a technology derived from chemical vapor deposition that enables the deposition of conformal and pinhole-free films on both flat and high aspect-ratio substrates with a precision down to the atomic level [5,13]. In ALD the film thickness is controlled in a digital fashion by dividing the deposition process into cycles. Each cycle consists of a sequence of precursor exposures interposed by purging or evacuation steps. During a precursor exposure, a certain amount of material, usually a submonolayer, is deposited via self-saturating surface reactions. The purging steps are crucial to the thickness control, as they prevent the undesired material deposition arising from gas-phase reactions between two subsequent precursors and reaction by-products. The number of precursors used in each cycle and thus the number of exposures depends on the material to be deposited. Most ALD systems are binary and thus each cycle comprises of two precursor exposures referred to as half-reactions and two purging steps [5,13,14]. Although such technique has been mostly applied in the semiconductor industry

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to the coating of flat substrates, the sequential steps of ALD can be readily applied to the coating of particle-substrates in FBRs. In fact, ALD cycles can be performed in a FBR by properly modulating the composition of the fluidizing gas used for suspending the particle-substrate in a fluid-like state [6,11].

Gas fluidization of micron-sized particles has already been successfully employed in several industrial fields such as chemical synthesis, drying and coating technology [15]. Therefore, the expertise developed for such particles can be readily applied to ALD on micron-sized nano-porous particles. On the other hand, gas fluidization of nanopowders is a relatively new field, mostly limited to the lab-scale. Nevertheless, it is proving to be one of the best available technology for dispersing and processing large quantities of nanoparticles [7,16]. Notwithstanding the small size of the primary particles, nanopowders can indeed be fluidized as they form micron-sized highly porous agglomerates [7,17,18]. Upon fluidization a dynamic equilibrium between breaking and cohesive forces determines the properties of the nanoparticle agglomerates and thus their fluidization behavior [19,17]. Despite the tendency of nanoparticles to agglomerate during fluidization, several experimental studies have proven that the coating of individual nanoparticles via ALD in FBRs is indeed possible [1,5,11]. Finally, even if more research has to be devoted to its implementation in an industrial scale, ALD in FBRs is a technologically viable route for tailoring the surface of bulk quantities of nanoparticles and nano-porous micron-sized particles.

A comprehensive assessment of the economic and environmental feasibility of ALD in FBRs in an industrial scale is not yet available. Nevertheless, residual gas analysis (RGA) via in situ mass spectrometry has shown that the use of FBRs, at low pressures, enables high precursor utilization efficiency at relatively high surface conversion over a broad spectrum of particle-substrates and ALD chemistries [6]. This intrinsic high efficiency has been ascribed to the fact that the high degree of mixing, achievable in fluidized beds, coupled with the high surface area given by the particles, reduces the probability that a precursor molecule will not react with an active site before exiting the reactor [1,6,8]. Nevertheless, a thorough dynamic analysis of the governing processes that play a role in determining the precursor utilization efficiency has not yet been carried out.

The objective of this work is to characterize the dynamics of ALD on nanoparticles and micron-sized nano-porous particles in FBRs. To that end, we develop a multiscale reactor model capable of capturing the interplay between the typically fast ALD reaction kinetics and the transport of the precursor, from the inlet of the reactor to the particles active surface. In doing so, we investigate the influence of pressure, reactor height, average bubble size and internal structure of both nanoparticle agglomerates and micron-sized nano-porous particles on the precursor utilization efficiency. In particular, we will study the process at both reduced and atmospheric pressure. Both processes have their own advantages and drawbacks [6,11]. Working at atmospheric pressure is more attractive from a scale-up standpoint, whereas operating at reduced pressure might result in a more efficient process and a better product quality. Therefore, this study is also meant to further clarify the differences between the two approaches in terms of precursor utilization efficiency. Therefore, this study is also meant to further clarify the differences between the two approaches in terms of precursor utilization efficiency.

The trimethylaluminum (TMA) and water (H₂O) ALD process has been chosen as the base for the case study as it is the most studied and employed ALD system [5,13,14]. Degussa P-25 Titania (TiO₂) nanoparticles and Sasol puralox micron-sized nano-porous γ -alumina (γ -Al₂O₃) particles were selected as the particle substrate as they are among the most used supports for heterogeneous catalysis, and because they both exhibit bubbling fluidization behavior. The latter enables the study of the effect of the quality

of the gas–solid contact from a worst-case scenario perspective, as opposed to particle-substrates that exhibit homogeneous fluidization.

Notation

C_i	concentration of the <i>i</i> th precursor (mol m ⁻³)
$C_{i,b}$	concentration of the <i>i</i> th chemical species in the bubbles (mol m ⁻³)
$C_{i,em}$	concentration of the <i>i</i> th chemical species in the emulsion (mol m ⁻³)
$C_{i,in}$	inlet concentration of the <i>i</i> th chemical species (mol m ⁻³)
$C_{i,out}$	outlet concentration of the <i>i</i> th chemical species (mol m ⁻³)
$C_{i,p}$	concentration of the <i>i</i> th chemical species in the particles (mol m ⁻³)
$C_{i,s}$	concentration of the <i>i</i> th chemical species at the outer surface of the nanoparticle agglomerates (mol m ⁻³)
D_i	diffusion coefficient of the <i>i</i> th chemical species (m ² s ⁻¹)
$D_{f,j}$	fractal dimension of the <i>j</i> th level of the multi-level fractal structure of nanoparticle agglomerates (-)
$D_{i,K}$	Knudsen diffusion coefficient of the <i>i</i> th (m ² s ⁻¹)
$D_{i,k}$	effective diffusion coefficient of the <i>i</i> th chemical species in the <i>k</i> th level (m ² s ⁻¹)
$D_{i,p}$	effective diffusion coefficient of the <i>i</i> th chemical species in the particles (m ² s ⁻¹)
H	reactor height [m]
H^*	required reactor height to obtain the desired efficiency (m)
H_0	initial reactor height (m)
J	molar flux (mol s ⁻¹ m ⁻²)
K_{be}	interphase mass transfer coefficient (s ⁻¹)
K_{ga}	emulsion-gas-to-agglomerates mass transfer coefficient (m s ⁻¹)
K_{gp}	emulsion gas to particles mass transfer coefficient (m s ⁻¹)
M_i	molecular mass of the <i>i</i> th chemical species (kg)
P	absolute pressure (Pa)
$P_{i,in}$	inlet partial pressure of the <i>i</i> th precursor (Pa)
R_p	average particle radius (m)
R_c	average radius of the complex agglomerates (m)
R_{sa}	average radius of the simple agglomerates (m)
S_p^{ext}	external particle surface area (m ²)
S_p^{tot}	total particle surface area (m ²)
S_{BET}	Brunauer–Emmett–Teller (BET) surface area (m ² kg ⁻¹)
T	temperature (K)
V	reactor volume (m ³)
V_p	particle volume (m ³)
d_j	average diameter of the <i>j</i> th level of the multi-level fractal structure of nanoparticle agglomerates (-)
d_p	particle diameter (m)
d_t	reactor diameter (m)
d_{ag}	average nanoparticles agglomerates diameter (m)
d_b	average bubble diameter (m)
f	nondimensional position of the reaction front (-)
$\tilde{g}_{i,k}$	linearized generation term with respect to the precursor concentration C_i at the <i>k</i> th level of the multi-level fractal structure of nanoparticle agglomerates (mol s ⁻¹)
g_i	generation term of the <i>i</i> th chemical species (mol s ⁻¹)
k_b	Boltzmann constant (m ² kg s ⁻² K ⁻¹)
k_j	prefactor of the scaling law of density of the <i>j</i> th level of the multi-level fractal structure of nanoparticle agglomerates (-)
l	molecules mean free path (m)
n_p	number of particles (-)
n_{max}	maximum number of precursor molecules that can be chemisorb per unit area of the particle surface (m ⁻²)
r	radial coordinate (m)
r_c	radial coordinate at the complex agglomerate scale (m)
r_{rf}	position of the reaction front (m)

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