Simulated preparation of supported porous catalyst and evaluation of its reaction-transport properties

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Abstract
In this contribution, mathematical model for the description of solvent evaporation and noble metal crystallization in a porous medium is presented. The methodology is based on the volume-of-fluid method and the aim is validation of the model by comparing the numerical simulation results with analytical solutions for evaporation from a single pore and for particle growth and Ostwald ripening of two freely suspended particles in a saturated solution.

Keywords: crystallization, drying, catalyst, volume-of-fluid method

1. Introduction
The preparation process of a supported metal porous catalyst can be formally divided into three stages: (i) impregnation of the metals or their precursors into the porous structure, where nucleation and crystallization take place; (ii) drying of liquid solution from the porous structure and (iii) after drying, reduction and calcination of the catalyst [1]. Mathematical modeling of such processes based on continuum-level equations can predict the resulting properties of porous catalysts on the macroscopic scale (level of entire particle), c.f. e.g. [2]. The aim of this contribution is to present a methodology based on the volume-of-fluid method which describes crystallization and drying processes on the nano-scale level, where the heterogeneous porous structure and spatial arrangement of individual crystallites are explicitly described and typical pore radii are in the order of 10 nm (e.g., in catalytic converters used in automobile industry [3]). The methodology presented here follows from our previous work which dealt with the characterization and prediction of porous structure [4]–[7] and modeling of reaction and transport inside the porous medium [8]–[11] and thus forms a new segment to the virtual platform for porous media simulations.

2. Studied system
The catalytic washcoat used in automobile converters is a bimodal porous structure with deposited noble metal crystallites acting as active catalytic sites, Fig. (1a). Simulation of crystallization and drying can be carried out in the porous medium representing the supporting material, reconstructed, e.g., by a particle packing method [6]. The digital porous medium is represented by a volume phase function [4]. At the beginning of our simulation the pores are filled with a liquid solution of the active metals. Nucleation centers are randomly generated on the surface of the solid phase and then liquid evaporation and crystallization are simulated. Final situation in
the system is depicted in Fig. (1b). Afterwards the influence of process conditions on the final noble metal distribution can be studied \textit{in silico}.

At this moment the following assumptions are considered:

1. mass transport in the liquid phase is governed by Fick’s diffusion;
2. migration caused by electrical charge is not considered;
3. capillary flow is not taken into account;
4. vapor pressure in the bulk is constant during drying;
5. isothermal conditions apply over the studied system;
6. absence of adsorption/desorption effects.

![SEM picture of meso-porous structure of Pt/γ-Al₂O₃ (white pores, grey γ-alumina, and black Pt); b) 3D reconstructed structure with dispersed Pt particles (blue) (Fig. 1)](image)

3. Model

3.1 Transport of dissolved species

Spatially 3D diffusion is described by mass balances in the form of the following partial differential equations for individual components \( i = 1..I \):

\[
\frac{\partial c_i}{\partial t} = \nabla \left( D_i \nabla c_i \right)
\]

(1)

Here \( c_i = c_i(x) \) is the local concentration of component \( i \), and \( D_i = D_i(x) \) is the local value of its diffusion coefficient. Diffusion in liquid can be described by Wilke-Chang equation [12]. Eq. (1) is solved only in liquid phase. Different types of initial and boundary conditions can be defined in the studied section of porous catalyst to account for different modes of crystallization and drying. In this paper the following set of initial and boundary conditions is used:

\[
c_i(x)|_{t=0} = c_{i}^{\text{init}}, \forall x: 0 < f_i(x) \leq 1
\]

(2)

\[
\frac{\partial c_i}{\partial x} \bigg|_{x=x_0,x_1} = 0, \frac{\partial c_i}{\partial y} \bigg|_{y=y_0,y_1} = 0, \frac{\partial c_i}{\partial z} \bigg|_{z=z_0,z_1} = 0
\]

(3)

\[
- D_i \nabla c_i = -c_i r_e \frac{M_w}{\rho_w}, \forall x: 0 < f_i(x) < 1, - D_i \nabla c_i = r_d, \forall x: 0 < f_s(x) < 1
\]

(4)

These boundary conditions correspond to a batch system with initial concentration \( c_{i}^{\text{init}} \) in time \( t = 0 \) s, where the rates of solvent evaporation \( r_e \) and deposition of noble metal (or precursor) crystallites \( r_d \) are computed only at the gas/liquid and noble solid/liquid interfaces, respectively.
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Eq. (1) is solved numerically within the spatially 3D section of porous catalyst. After equidistant spatial discretisation of the domain with a step \( h \), Eq. (1) can be rewritten as (shown only for \( x \) direction and subscript \( i \) is omitted for sake of brevity):

\[
\frac{c_i^{t+\Delta t} - c_i^t}{\Delta t} = \nabla \cdot \left( D_{<m-1,n,o>} \frac{c_{m-1,n,o} - c_{m,n,o}}{h^2} + D_{cm+1,m,n,o} \frac{c_{m+1,n,o} - c_{m,n,o}}{h^2} \right)
\]

(5)

Here \( \Delta t \) is time step, the subscripts \( m, n, o \) are discretisation indices of the spatial coordinates \( x, y, z \), respectively. The \( D_{<m-1,m,n,o>} \) denotes mean diffusion coefficient of the component between two adjacent volume elements with the coordinates \((m-1, n, o)\) and \((m, n, o)\):

\[
D_{<m-1,m,n,o>} = \frac{2D_{cm-1,m,n,o} D_{m,n,o}}{D_{cm-1,m,n,o} + D_{m,n,o}}
\]

(6)

The resulting set of equations is then solved iteratively by the Successive over-relaxation Gauss-Seidel method [13].

3.2 Solvent evaporation

The rate of liquid evaporation \( r_v(x) \) into its vapor surrounding during drying is computed from Hertz-Knudsen equation [14]:

\[
r_v = \left( p^*(x) - p_r \right) \varepsilon \left( \frac{M}{2\pi R^2 T} \right)^{1/2}
\]

(7)

Here \( \varepsilon \) is evaporation coefficient defined as the experimental rate of evaporation divided by the theoretical maximum rate for the same conditions and \( p^*(x) \) is the equilibrium vapour pressure above the curved interface in a surface point \( (x) \) computed from the Kelvin equation:

\[
p^*(x) = p_r \exp \left[ \frac{\kappa_l(x) V_1^{M} \gamma_1}{R^2 T} \right]
\]

(8)

The local curvature of the liquid-vapour interface \( \kappa_l(x) \) is evaluated from Eq. (14). The shift of the liquid-vapour interface \( l_i \) is then changed according to the following equation:

\[
\frac{dl_i}{dt} = \frac{r_c M_1}{\rho_i}
\]

(9)

3.3 Formation of crystallites

The rate of crystal growth \( r_d \) per unit surface area \( A \) is considered as a pseudo \( m \)-th order reaction \( A \rightarrow B \) where the order of reaction can be different for deposition and dissolution. The rate is computed from:

\[
r_d = k \left( c(x) - c^*(x) \right)^m
\]

(10)

Here \( k \) is the crystallisation/dissolution rate constant obtained from the Arrhenius relation. The rate of crystallization \( r_d \) depends on the local concentration of liquid solution \( c(x) \) above the solid-liquid interface and on the equilibrium concentration \( c^*(x) \) which is evaluated from the Ostwald-Freundlich equation, Eq. (11). As it can be seen Ostwald-Freundlich equation is analogous to the Kelvin equation, Eq. (8).
\[ c^*(x) = c_0 \exp \left[ \frac{\kappa_i(x) V_i^M p_s}{R^2 T} \right] \]  

(11)

The local curvature of the solid-liquid interface \( \kappa_i(x) \) is evaluated from Eq. (14). Then the shift of the solid-liquid interface \( l_s \) is computed from the following equation:

\[ \frac{dl_s}{dt} = \frac{\rho_s M_s}{\rho_s} \]  

(12)

### 3.4 Local interface curvature

The local curvature, \( \kappa(x) \), required for calculating \( p^*(x) \) and \( c^*(x) \) appearing in Eq. (8) and Eq. (11), is evaluated numerically [15] from the phase function of \( i \)-th phase \( f_i \) in every iteration (where \( i \) is liquid or solid phase). First, the unit normal vectors, oriented from the \( i \)-th phase outwards, are constructed at all interface points of phase \( i \):

\[ n_i(x) = -\frac{\nabla f_i(x)}{\| \nabla f_i(x) \|}, \forall x : 0 < f_i(x) < 1 \]  

(13)

Here \( f_i(x) \) is the "mollified" phase function, obtained from \( f_i \) by the application of the 1-6-1 smoothing kernel. Once the interface normal vectors are known, the radius of curvature at point \( (x) \) can be calculated from:

\[ \kappa_i(x) = -\nabla n_i(x), \forall x : 0 < f_i(x) < 1 \]  

(14)

The second-order, symmetric finite difference approximations of the partial derivatives have been used in Eq. (13) and Eq. (14), e.g.,

\[ \frac{\partial f_i}{\partial x} \approx \left( f_i^{i+1} - f_i^{i-1} \right) / 2h \]  

(15)

In a triple phase point s-l-g the normal vector of the liquid is obtained from \( n_L n_s = \cos \theta \), where \( n_s \) is computed from Eq. (13) and \( \theta \) is the contact angle.

### 4. Validation of the model

In this section the validation of the presented methodology for liquid drying and solids deposition modeling is shown. The numerical simulation results will be compared with results obtained from analytical solution in simple geometries, namely evaporation from a cylindrical pore and dissolution/deposition (Ostwald ripening) of two spherical particles.

An example of a volume-of-fluid numerical simulation of evaporation from a single cylindrical pore is shown in Fig (2a). The simulation starts from a completely filled pore and a curved meniscus gradually forms during evaporation as a consequence of Eqs. (5) and (6). The height of the meniscus \( H \) for varying equilibrium contact angle \( \theta \) between the liquid and the solid is depicted in Fig. (2b). Results from numerical simulation are compared with analytical calculation of the meniscus height calculated according to:

\[ H_{\text{anal}} = \text{abs} \left(\frac{R}{\cos \theta} (1 - \sin \theta)\right) \]  

(16)

The simulation verifies that the liquid is able to "adapt" to a new condition and thus creates the correct shape of meniscus. In a general porous medium the local meniscus results from the local shape, size and wettability of a pore during evaporation. It can be seen in Fig. (2b) there is quantitative agreement between the height of meniscus \( H \) obtained from numerical simulation and that obtained analytically over most contact
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angles. However, for contact angles below approximately 30 deg a deviation is observed, most likely caused by a discretisation error when evaluating interface curvature near the three-phase contact line.

Fig. 2. a) Example of liquid meniscus (blue) in a 3D reconstructed cylindrical pore with $r=20$ vox; b) height of meniscus in dependence on contact angle $\theta$.

The crystallization/dissolution module was separately validated by simulating Ostwald coarsening. The simulation was carried out in a batch system (boundary condition Eq. (3)) for two spherical particles of different initial size ($r_1=16$ vox and $r_2=8$ vox), as shown in Fig. (3a). Results obtained from the volume-of-fluid simulation are compared with a model based on material balances with a presumption of spherical shape and an ideal mixing of the batch according to equations:

$$\frac{dn_1}{dt} = A_1 k (c_L - c_1^*)^m; \quad \frac{dn_2}{dt} = A_2 k (c_L - c_2^*)^m$$  

$$\nu \frac{dc_1}{dt} = -[A_1 k (c_L - c_1^*)^m + A_2 k (c_L - c_2^*)^m]$$  

The subscript 1 refers to the initially larger particle and 2 to the smaller one. The quantity of the solid in each particle is $n$ [mol], $A$ is the particle surface area and $V$ the volume of the liquid batch. Equilibrium concentrations $c_1^*$ and $c_2^*$ are evaluated from Eq. (11) where $\kappa_s = 2/R_s$, and $R_s$ is the radius of each particle. It can be seen in Fig. (3b) that the small particle dissolves while the bigger one grows – the bigger particle is energetically more stable than the smaller one. The agreement between numerical simulations and analytical solution is quantitative in this case.

Fig. 3. a) Example of two spherical particles of active metal, reconstructed in 3D; b) simulation of Ostwald coarsening during the crystallization - dependence of particle radius on time.

An example of the evaporation and metal particles deposition in a general porous medium is depicted in Fig. (4). The porous medium filled with a liquid solution of the active metal is shown in Fig. (4a). Nucleation centers are randomly generated on the surface of the solid phase and then the evaporation and crystallization are simulated dynamically. The final distribution of metal particles after the evaporation is shown in
Fig. (4b). It can be seen that a couple of larger particles developed while several smaller particles dissolved.

Fig. 4. Example of evaporation and crystallization in a general porous medium with the discretization the 60x60x60 voxels and space step $h = 0.25$ nm

5. Conclusions

Novel models were presented for description of liquid evaporation and crystallization of particles in a general 3D porous medium. These processes are strongly relevant to practical application during the preparation of porous supported catalysts (impregnation of active metals dissolved in a liquid, followed by drying of the solvent). These models extend an existing range of tools for the 3D simulations of transformation, reaction and transport in porous media [4]–[11]. The model was validated separately for evaporation of liquid from a cylindrical pore and for crystallization of two spherical particles of different size. An application of the model in a general porous medium was also demonstrated. The following research will be aimed on a parametric study of catalyst preparation and description of unknown parameters from experiments as well as comparison of simulation results with measurements.

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