

## Integrated Multi-Scale Models for Microreactor Simulation and Design

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In this work we construct multi-scale models of continuous microreactors with Platinum (Pt) catalytic walls as an alternative to the conventional packed-bed configuration. The bulk (gaseous) phase is treated macroscopically using a reaction-diffusion model, while the catalytic activity is modelled at the micro/mesosopic level using kinetic Monte Carlo (kMC) simulations including effects such as adsorption, desorption surface reactions and surface diffusion. A number of kMC lattices depending on the discretisation of the computational domain are used to effectively represent the reactive surfaces. Time- and length-scales are coupled and results are compared to pure mean-field computations to validate the multi-scale approach.

### 1. Introduction

Microreactor systems are receiving increasing attention nowadays due to their enhanced operation characteristics such as increased mass and heat transfer capabilities, uniform flow, inherent safety and potential for high throughput through the construction of array configurations. They also ensure a smaller plant size, lower cost of production and more flexible response to market demand [1]. Catalytic microreactors can be designed following the “traditional” packed-bed configuration which is well-tested but suffers from pore-plugging which is enhanced at diminishing dimensions. Alternatively, a catalytic wall concept, following the design of deposition reactors used for the production of microelectronics and functional materials such as e.g. self-cleaning glasses can be adopted. Models for such reactors need to be able to describe both the bulk (gas-phase) and the catalytic (surface) phenomena taking place at different length- and time-scales. Traditional mean field (MF) models cannot always accurately capture such complex dynamics possibly resulting in lack of understanding of the interactions underpinning the system and consequently in sub-optimal designs. The aim of this work is to develop a multi-scale model for catalytic microreactors that uses a macroscopic MF approach for the bulk phase coupled with the microscopic kMC method to describe the surface dynamics. The well-known system of CO oxidation is used as a test case and comparisons with pure MF predictions are used to validate the multi-scale model.

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## 2. The multi-scale model

The multi-scale microreactor model consists of a MF model for the bulk phase coupled with a number kMC models that describe the catalytic surface. Alternatively the surface chemical reactions are modelled using a conventional MF model which is also coupled with the bulk phase macroscopic model for comparison purposes. A ternary gaseous system consisting of CO, O<sub>2</sub> and CO<sub>2</sub> is considered. A convection-diffusion model is used to describe the gas phase. The corresponding equation for mole fraction *i* (*i*=1,2) is given by:

$$c \cdot \left[ \frac{\partial X_i}{\partial t} + v_x \frac{\partial X_i}{\partial x} + v_y \frac{\partial X_i}{\partial y} \right] = c \cdot D_{i,\text{mix}} \cdot \left[ \frac{\partial^2 X_i}{\partial x^2} + \frac{\partial^2 X_i}{\partial y^2} \right] + r_i \quad (1.1)$$

where  $c$  [mol/m<sup>3</sup>] is the total concentration,  $D_{i,\text{mix}}$  [m<sup>2</sup>/s] is the diffusivity of the mixture,  $X_i$  [-] is mole fraction of the gas species *i* and  $v_x$  [m/s],  $v_y$  [m/s] are velocities in *x* and *y* directions.

Diffusivity is calculated using a mixture-average approximation (eq 1.2) and the binary diffusivity  $D_{ij}$  [cm<sup>2</sup>/s] with the Fuller approximation (Poling et al., 2001) (eq. 1.3)

$$D_{i,\text{mix}} = \frac{1 - Y_j}{\sum_{j=1}^n \frac{X_j}{D_{ij}}}, \quad (1.2) \quad D_{ij} = \frac{0.00143 \cdot T^{1.75}}{p \cdot M_{ij}^{0.5} \cdot \left[ (\sum_v)_i^{1/3} + (\sum_v)_j^{1/3} \right]^2}. \quad (1.3)$$

$Y_j$  [-] are the mass fractions of species *j*,  $T$  [K] is temperature,  $p$  [bar] the pressure of the binary mixture and  $(\sum_v)_i$  [-] is an atomic diffusion volume for each component (Poling et al., 2001).  $M_{ij} = 2 \cdot [1/M_i + 1/M_j]^{-1}$  [kg/kmol] is the binary molecular weight of species *i* and *j*. The total mass balance is given by:

$$\sum_{i=1}^3 X_i = 1 \quad (1.4)$$

The system of equations 1.2, 1.4 is solved using finite differences. The gas CO and O<sub>2</sub> diffuse through the microreactor's catalytic walls and react on a Pt catalyst to form intermediates and product CO<sub>2</sub>. The mechanism is shown in Table 1.

### 2.1. Surface mechanism MF Model

A mean field model for catalytic CO oxidation is described by the equations (1.5) and (1.6). The coverage of empty sites  $\theta_*$  is obtained from the conservation of all surface species (1.7)

$$\frac{\partial \theta_{\text{CO}^*}}{\partial t} = k_{a1} \cdot \frac{N_A}{c_T} \cdot c \cdot X_{\text{CO}} \cdot \theta_* - k_{d1} \cdot \theta_{\text{CO}^*} - k_{sr} \cdot \theta_{\text{CO}^*} \cdot \theta_{\text{O}^*} - k_{\text{diff}} \cdot \theta_{\text{CO}^*} \cdot \theta_* + k_{\text{diff}} \cdot \theta_{\text{CO}^*} \cdot \theta_* \quad (1.5)$$

$$\frac{\partial \theta_{O^*}}{\partial t} = 2 \cdot k_{a2} \cdot \frac{N_A}{c_T} \cdot c \cdot X_{O_2} \cdot \theta_*^2 - 2 \cdot k_{d2} \cdot \theta_{O^*}^2 - k_{sr} \cdot \theta_{CO^*} \cdot \theta_{O^*}, \quad (1.6)$$

$$\theta_{CO^*} + \theta_{O^*} + \theta_* = 1. \quad (1.7)$$

The corresponding rate constants for the above CO mechanism are

$$k_{a1} = s_{0,a1} \cdot \sqrt{\frac{1000 \cdot R \cdot T}{2\pi \cdot M_{CO}}}, \quad (1.8) \quad k_{d1} = A_{0,d1} \cdot \exp\left(\frac{-E_{a,d1}}{R \cdot T}\right), \quad (1.9)$$

$$k_{a2} = s_{0,a2} \cdot \sqrt{\frac{1000 \cdot R \cdot T}{2\pi \cdot M_{O_2}}}, \quad (1.10) \quad k_{d2} = A_{0,d2} \cdot \exp\left(\frac{-E_{a,d2}}{R \cdot T}\right), \quad (1.11)$$

$$k_{sr} = A_{0,sr} \cdot \exp\left(\frac{-E_{a,sr}}{R \cdot T}\right), \quad (1.12) \quad k_{diff} = A_{0,diff} \cdot \exp\left(\frac{-E_{a,diff}}{R \cdot T}\right), \quad (1.13)$$

Table 1 CO oxidation surface mechanism

Surface Reactions	CO Model
Unimolecular adsorption	$CO + * \xrightarrow{k_{a1}} CO^*$
Unimolecular desorption	$CO^* \xrightarrow{k_{d1}} CO + *$
Dissociative adsorption	$O_2 + 2 * \xrightarrow{k_{a2}} 2O^*$
Associative desorption	$2O^* \xrightarrow{k_{d2}} O_2 + 2 *$
Bimolecular surface reaction	$CO^* + O^* \xrightarrow{k_{sr}} CO_2 + 2 *$
Surface diffusion	$CO^* + * \xrightarrow{k_{diff}} * + CO^*$

where  $R$  [J/(mol·K)] is the ideal gas constant,  $M_{CO}$  [kg/kmol] and  $M_{O_2}$  [kg/kmol] are molecular weights of CO and  $O_2$ ,  $s_{0,i}$  [-] is the sticking coefficient,  $A_{0,i}$  [l/s] the pre-exponential factor and  $E_{a,i}$  [J/mol] is the activation energy. A two-dimensional microchannel is schematically shown in Figure 1. Here only the south boundary wall is assumed to be catalytic. The corresponding MF boundary conditions (BCs) are shown in Table 2. BC 4 depicts the non-zero diffusive flux [mol/(m<sup>2</sup>·s)] at the catalytic surface given by:

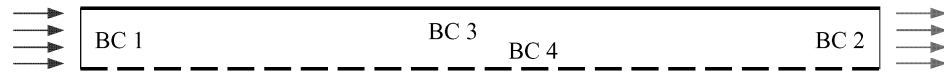


Figure 1 A mean field microreactor model with boundary conditions.

$$-c \cdot D_{CO,mix} \cdot \frac{\partial X_{CO}}{\partial y} = -k_{a1} \cdot c \cdot X_{CO} \cdot \theta_* + k_{d1} \cdot \frac{c_T}{N_A} \cdot \theta_{CO^*}, \quad (1.14)$$

$$-c \cdot D_{O_2,mix} \cdot \frac{\partial X_{O_2}}{\partial y} = -2 \cdot k_{a2} \cdot c \cdot X_{O_2} \cdot \theta_* + 2 \cdot k_{d2} \cdot \frac{c_T}{N_A} \cdot \theta_*, \quad (1.15)$$

$$-c \cdot D_{\text{CO}_2, \text{mix}} \cdot \frac{\partial X_{\text{CO}_2}}{\partial y} = k_{\text{sr}} \cdot \frac{c_{\text{T}}}{N_{\text{A}}} \cdot \theta_{\text{CO}^*} \cdot \theta_{\text{O}^*}. \quad (1.16)$$

Table 2 Initial and boundary conditions of a microreactor

Line	Initial and Boundary Conditions
BC 1	$v_{x, \text{CO}, \text{in}} = v_{x, \text{O}_2, \text{in}} \neq 0, v_{y, \text{CO}, \text{in}} = v_{y, \text{O}_2, \text{in}} = 0, X_{\text{CO}, \text{in}} \neq 0, X_{\text{O}_2, \text{in}} \neq 0$
BC 2	$\frac{\partial v_{x, \text{CO}, \text{out}}}{\partial x} = \frac{\partial v_{x, \text{O}_2, \text{out}}}{\partial x} = 0, v_{y, \text{CO}, \text{out}} = v_{y, \text{O}_2, \text{out}} = 0, \frac{\partial X_{\text{CO}, \text{out}}}{\partial x} = \frac{\partial X_{\text{O}_2, \text{out}}}{\partial x} = 0$
BC 3	$v_{x, \text{CO}, \text{n}} = v_{x, \text{O}_2, \text{n}} = 0, v_{y, \text{CO}, \text{n}} = v_{y, \text{O}_2, \text{n}} = 0, \frac{\partial X_{\text{CO}, \text{n}}}{\partial y} = \frac{\partial X_{\text{O}_2, \text{n}}}{\partial y} = 0$
BC 4	$v_{x, \text{CO}, \text{s}} = v_{x, \text{O}_2, \text{s}} = 0, v_{y, \text{CO}, \text{s}} = v_{y, \text{O}_2, \text{s}} = 0, \frac{\partial X_{\text{CO}, \text{s}}}{\partial y}, \frac{\partial X_{\text{O}_2, \text{s}}}{\partial y} \neq 0$

## 2.2. Kinetic Monte Carlo (kMC) Model

We have used a series of kMC models describing surface reactions in two-dimensional nano-scale lattices to represent the microreactor catalytic surface. Modelling of each lattice is based on statistical probabilities. Expressions for the rate constants are

$$k_{a,1} = \frac{s_{0,a1} \cdot N_{\text{A}}}{C_{\text{T}} \cdot \sqrt{2 \cdot \pi \cdot M_{\text{CO}} \cdot R \cdot T}}, \quad (1.17) \quad k_{d,1} = A_{0,d1} \cdot \exp\left(\frac{-E_{a,d1}}{R \cdot T}\right), \quad (1.18)$$

$$k_{a,2} = \frac{s_{0,a2} \cdot N_{\text{A}}}{C_{\text{T}} \cdot \sqrt{2 \cdot \pi \cdot M_{\text{O}_2} \cdot R \cdot T}}, \quad (1.19) \quad k_{d,2} = A_{0,d2} \cdot \exp\left(\frac{-E_{a,d2}}{R \cdot T}\right), \quad (1.20)$$

$$k_{\text{sr}} = A_{0,\text{sr}} \cdot \exp\left(\frac{-E_{a,\text{sr}}}{R \cdot T}\right), \quad (1.21) \quad k_{\text{diff}} = A_{0,\text{diff}} \cdot \exp\left(\frac{-E_{a,\text{diff}}}{R \cdot T}\right), \quad (1.22)$$

where  $C_{\text{T}}$  [sites/m<sup>2</sup>] is the density of surface sites and  $N_{\text{A}}$  [molecules/mol] the Avogadro number. The probabilities  $P_{\text{CO}^*}[-]$ ,  $P_{\text{O}^*}[-]$  and  $P_{*}[-]$  for one site involving a single surface species  $\text{CO}^*$ ,  $\text{O}^*$  or  $*$  are

$$P_{\text{CO}^*} = \frac{\Omega_{\text{CO}^*}}{\Omega_{\text{T}}}, \quad (1.23) \quad P_{\text{O}^*} = \frac{\Omega_{\text{O}^*}}{\Omega_{\text{T}}}, \quad (1.24) \quad P_{*} = \frac{\Omega_{*}}{\Omega_{\text{T}}}, \quad (1.25)$$

where  $\Omega_{\text{CO}^*}[-]$ ,  $\Omega_{\text{O}^*}[-]$  and  $\Omega_{*}[-]$  are the number of surface (catalyst) sites occupied by  $\text{CO}^*$ ,  $\text{O}^*$  and  $*$ , respectively.  $\Omega_{\text{T}}[-]$  is the total number of catalyst (lattice) sites.  $P_{\text{O}^*/\text{CO}^*}[-]$  and  $P_{\text{CO}^*/\text{O}^*}[-]$  represent the two-site class conditional probability of choosing a site  $\text{O}^*$ , once a site  $\text{CO}^*$  has been picked and vice versa

$$P_{\text{O}^*/\text{CO}^*} = \frac{\sum_{i=1}^4 i \cdot (\Omega_{\text{CO}^*-\text{O}^*-i})}{4 \cdot \Omega_{\text{CO}^*}}, \quad (1.26) \quad P_{\text{CO}^*/\text{O}^*} = \frac{\sum_{i=1}^4 i \cdot (\Omega_{\text{O}^*-\text{CO}^*-i})}{4 \cdot \Omega_{\text{O}^*}}. \quad (1.27)$$

$\Omega_{\text{CO}^*-\text{O}^*-i}[-]$  denotes a size of class  $\text{CO}^*-\text{O}^*-i$  and means the number of sites of  $\text{CO}^*$  having  $i$  adjacent sites of  $\text{O}^*$  and similarly for  $\Omega_{\text{O}^*-\text{CO}^*-i}[-]$ . Transition probabilities  $\hat{\Gamma}_i[-]$  for each reaction are summarized in equations from (1.28) to (1.33). The total transition probability  $\hat{\Gamma}_{\text{tot}}[-]$  is the sum of all individual probabilities  $\hat{\Gamma}_i[-]$

$$\hat{\Gamma}_{a1} = k_{a1} \cdot p_{\text{tot}} \cdot X_{\text{CO}} \cdot P_*, \quad (1.28) \quad \hat{\Gamma}_{d1} = k_{d1} \cdot P_{\text{CO}^*}, \quad (1.29)$$

$$\hat{\Gamma}_{a2} = k_{a2} \cdot p_{\text{tot}} \cdot X_{\text{O}_2} \cdot P_* \cdot P_{*/}, \quad (1.30) \quad \hat{\Gamma}_{d1} = k_{d1} \cdot P_{\text{CO}^*} \cdot P_{\text{CO}^*/\text{CO}^*}, \quad (1.31)$$

$$\hat{\Gamma}_{\text{sr}} = k_{\text{sr}} (P_{\text{CO}^*} \cdot P_{\text{O}^*/\text{CO}^*} + P_{\text{O}^*} \cdot P_{\text{CO}^*/\text{O}^*}) \quad (1.32) \quad \hat{\Gamma}_{\text{diff}} = k_{\text{diff}} (P_{\text{CO}^*} \cdot P_{*/\text{CO}^*} + P_* \cdot P_{\text{CO}^*/*}) \quad (1.33)$$

$$\hat{\Gamma}_{\text{tot}} = \sum_{i=1}^{n_r} \hat{\Gamma}_i, \quad (1.34)$$

where  $n_r[-]$  is the total number of events on a lattice. In the next step, the reaction with the highest transition probability to occur is chosen through random numbers  $R_1$  and  $R_2$  in conjunction with the equation (1.35). The final step in a loop over a lattice is to calculate average time  $\Delta t[\text{s}]$  during one kMC event with the equation (1.36)

$$\sum_{k=1}^{i-1} \hat{\Gamma}_k \langle R_1 \cdot \hat{\Gamma}_{\text{tot}} \rangle \langle \sum_{k=1}^i \hat{\Gamma}_k \rangle, \quad (1.35) \quad \Delta t = \frac{1}{\Omega_T \cdot \hat{\Gamma}_{\text{tot}}} \cdot \log\left(\frac{1}{R_2}\right). \quad (1.36)$$

The multi-scale model using an array of kMC lattices, to represent the Pt catalytic south boundary, is depicted in Figure 2.

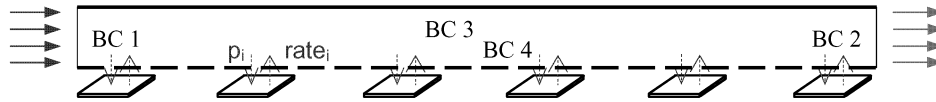


Figure 2 A kinetic Monte Carlo microreactor model with catalysts lattices.

kMC lattices are coupled to the gas-phase through partial pressures and reaction rates. kMC simulations yield surface coverages and the corresponding adsorbed and desorbed gas particles, which are used to compute the corresponding macroscopic rates needed by BC4, which essentially provides the length-scale coupling in the model:

$$-c \cdot D_{i,\text{mix}} \cdot \frac{\partial X_i}{\partial y} = -\text{net\_rate}_i \quad i = 1, \dots, 3, \quad (1.37)$$

All kMC lattices run for a reporting horizon using MPI parallelization. The MF gas-phase model is then executed for the same time horizon and this iteration is repeated until the final chosen time.

### 3. Results and Discussion

MF and the multi-scale simulations for microreactor CO oxidation were performed for 0.1 bar and 1.01295 bar at 700 K. The two-dimensional micro-channel was 9 mm x 1 mm. Initial surface coverage in both models was set to zero. The initial gas-phase

composition was  $X_{CO}=0.2$ ,  $X_{O_2}=0.8$ , while the inlet BC was set to  $X_{CO}=0.1$ ,  $X_{O_2}=0.9$ . 32 kMC lattices were used to represent the catalytic surface. A timestep of 0.01 was used and results are shown at 0.01 s and 0.2 s (Fig 3). Surface coverages were found to exhibit similar trends for both models at the different operating conditions. However, quantitative differences can be observed. At 0.1 bar and 0.2 s, where the system has nearly reached steady state the lattices are almost fully covered with  $O^*$ , which is not the case for 1.01295 bar, where both  $CO^*$  and  $O^*$  are present on the surface. It should be noted that at this high pressure the system is not yet near steady state at 0.2 s. The gaseous mole fractions on the catalytic surface predicted by both models are very close. Overall, the multi-scale model can provide accurate predictions of the system complex behaviour and has the potential to provide a better understanding of the surface reaction mechanism. Furthermore it can significantly contribute to the improvement of microreactor design.

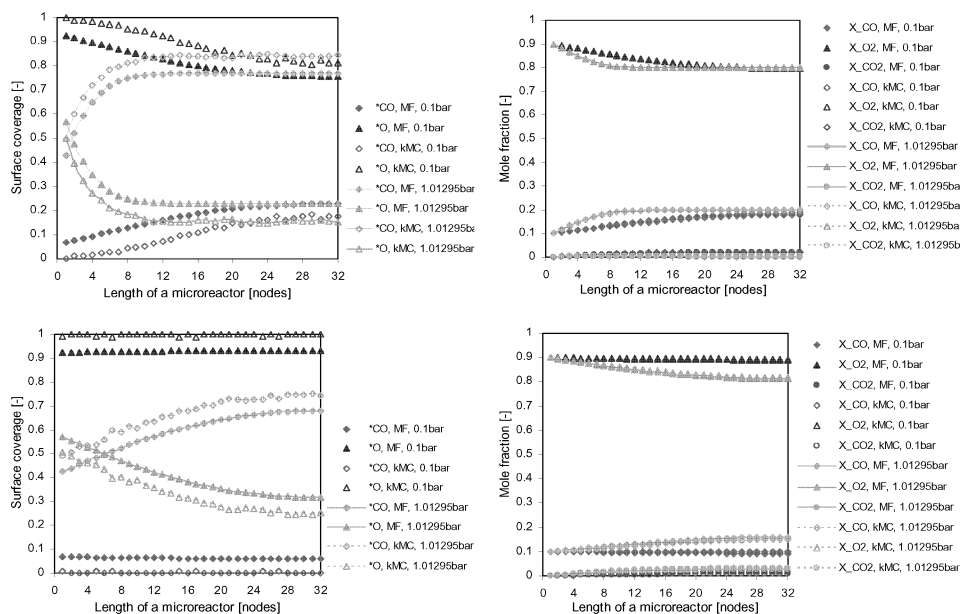


Figure 3 Comparison of surface coverages and gaseous mole fractions at the catalytic surface for the MF (filled symbols) and the multi-scale model (open symbols). Top graphs  $t=0.01$ s, Bottom graphs  $t=0.2$  s.

## References

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