Supporting Information

Parametric studies of steam methane reforming using a multiscale reactor model

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1. Correlation between volume fraction, area fraction and tortuosity

Consider an infinitesimal control volume dV^p in the pellet domain, containing N_P cylinder-like pores of length L_i, whose intersection with the control surface dA^p has cross sectional area $N_P \cdot S_P$. The volumetric and surface fractions then satisfy equations (S1), and (S2) below.

$$\varepsilon_{f,V}^{p} \triangleq \frac{S_P \left(\sum_{i=1}^{N_P} L_i \right)}{dV^p} \tag{S1}$$

$$\varepsilon_{f,A}^{p} \triangleq \frac{S_P \cdot N_P}{dA^p} \tag{S2}$$

Defining tortuosity as the ratio of the average path length that molecules need to travel over a path length of a cylinder like control volume yields:

$$\tau \triangleq \frac{\left(\sum_{i=1}^{N_P} L_i \Big/ N_P \right)}{\left(dV^p / dA^p \right)} \tag{S3}$$

Combining equations (S1), (S2), (S3) yields:

$$\tau = \frac{\varepsilon_{f,V}^{p}}{\varepsilon_{f,A}^{p}} \tag{S4}$$

2. Supplementary model equations

The constants and functions used to model the reforming reactions are presented in Tables S1 and S2.

Table S1: Rate coefficients and adsorption constants for related Arrhenius or Van't Hoff Equations

Rate coefficient or adsorption constant	**Pre-exponential factor**	**Units of pre-exponential factor**	**Activation energy or adsorption enthalpy (kJ/mol)**
k_1	4.225×10^{15}	$kmol.bar^{0.5}/(kg_{cat}.h)$	240.1
k_2	1.955×10^{6}	$kmol/(kg_{cat}.h.bar)$	67.13
k_3	1.020×10^{15}	$kmol.bar^{0.5}/(kg_{cat}.h)$	243.9
k_{CO}*	8.23×10^{-5}	bar^{-1}	−70.65*
k_{CH4}*	6.65×10^{-4}	bar^{-1}	−38.28*
k_{H2O}*	1.77×10^{5}	*dimensionless*	88.68*
k_{H2}*	6.12×10^{-9}	bar^{-1}	−82.90*

*Values corresponding to adsorption

Table S2: Reaction equilibrium constants

Equilibrium constant	Function of T(K)	Units of equilibrium constants
$\boldsymbol{K_1}$	Eq.(S5)	bar^2
$\boldsymbol{K_2}$	Eq.(S6)	*dimensionless*
$\boldsymbol{K_3}$	Eq.(S7)	bar^2

$$K_1 = e^{\left[(26{,}830/T)+30.114\right]} \tag{S5}$$

$$K_2 = e^{\left[(4{,}400/T)\,-\,4.036\right]} \tag{S6}$$

$$K_3 = K_1 \cdot K_2 \tag{S7}$$

Table S3: Binary diffusion coefficient estimation

Binary mixture of non-polar gases A and B [3]

Binary diffusion coefficient:

$$D_{AB}^{\alpha} = \left(\frac{0.00266}{p \sigma_{AB}{}^{2} \Omega_{AB}^{\mathrm{D}}} \right) \sqrt{\frac{\left(T_f^{\alpha}\right)^3}{M_{AB}}} \tag{S8}$$

Reduced molecular mass:

$$M_{AB} = 2\left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{-1} \tag{S9}$$

Lennard-Jones dimension:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{S10}$$

Collision integral

$$\left\{ \Omega_{AB}^{\mathrm{D}} = \frac{1.06036}{\left(T_{AB}^{*}\right)^{0.1561}} + \frac{0.193}{\exp\left(0.47635 T_{AB}^{*}\right)} + \frac{1.03587}{\exp\left(1.52996 T_{AB}^{*}\right)} + \frac{1.76474}{\exp\left(3.89411 T_{AB}^{*}\right)} \right\} \tag{S11}$$

Reduced temperature:

$$T_{AB}^{*} = \frac{k_B T_f^{\alpha}}{\hat{\varepsilon}_{AB}} \tag{S12}$$

Lennard-Jones energy:

$$\hat{\varepsilon}_{AB} = \left(\hat{\varepsilon}_A \hat{\varepsilon}_B \right)^{1/2} \tag{S13}$$

Table S4: Binary diffusion coefficient estimation

Binary mixture of polar gases A and B [3]

Binary diffusion coefficient:

$$D_{AB}^{polar} = \left(\frac{0.00266}{p\left(\sigma_{AB}^{polar}\right)^2 \Omega_{AB}^{\mathrm{D},polar}} \right) \sqrt{\frac{\left(T_f^{a}\right)^3}{M_{AB}}} \tag{S14}$$

Lennard-Jones dimension:

$$\sigma_{AB}^{polar} = \left(\sigma_A^{polar}\sigma_B^{polar}\right)^{1/2} \tag{S15}$$

$$\sigma_k^{polar} = \left(\frac{1.585 V_k^b}{1+1.3\left(\delta_k^{polar}\right)^2} \right)^{1/3} \quad ; \quad k = A, B \tag{S16}$$

Collision integral

$$\Omega_{AB,polar}^{\mathrm{D}} = \Omega_{AB}^{\mathrm{D}} + \frac{0.19\left(\delta_{AB}^{*}\right)^2}{T_{AB}^{*}} \tag{S17}$$

Stockmayer potential:

$$\delta_{AB}^{*} = \left(\delta_A^{polar}\delta_B^{polar}\right)^{1/2} \tag{S18}$$

$$\delta_k^{polar} = \frac{1.94\times10^3 \left(\hat{\mu}_k\right)^2}{V_k^b T_k^b} \quad ; \quad k = A, B \tag{S19}$$

Reduced temperature:

$$T_{AB}^{*} = \frac{k_B T}{\hat{\varepsilon}_{AB}^{polar}} \tag{S20}$$

Lennard-Jones energy:

$$\frac{\hat{\varepsilon}_{AB}^{polar}}{k_B} = \left(\frac{\hat{\varepsilon}_A^{polar}}{k_B} \frac{\hat{\varepsilon}_B^{polar}}{k_B} \right)^{1/2} \tag{S21}$$

$$\frac{\hat{\varepsilon}_k^{polar}}{k_B} = 1.18\left[1+1.3\left(\delta_k^{polar}\right)^2\right] T_k^b \quad ; \quad k = A, B \tag{S22}$$

In the equations presented in Tables S2 and S3, pressure has units of *bar*, temperatures are in *K*, and the resulting binary diffusivities has units of cm^2/s. Units for the parameters not mentioned here are listed in the notation section of the manuscript.

Table S5: General model equations implemented in the simulations

Additional model equations		
Partial pressure of species i:	$p_i^p = c_i^p \tilde{R} T^p$	(S23)
Dalton's law:	$p^p = \sum_{i=1}^{\upsilon} p_i^p$	(S24)
Total molar concentration:	$c_{f,tot}^{\alpha} = \sum_{i=1}^{\upsilon} c_{f,i}^{\alpha}$	(S25)
Total mass concentration:	$\rho_f^p = \sum_{i=1}^{\upsilon} \rho_i^p$	(S26)
Molar fraction of species i:	$x_{f,i}^{\alpha} = c_{f,i}^{\alpha} \big/ c_{f,tot}^{\alpha}$	(S27)
Mass fraction of species i:	$w_i^p = \rho_i^p \big/ \rho_f^p$	(S28)
Mass fraction of species i:	$w_i^{\alpha} = \left(\rho_{f,i}^{\alpha} \big/ \rho_f^{\alpha} \right) = x_i^{\alpha} M_i \big/ M_{Mix}^{\alpha}$	(S29)
Molar mass of the mixture:	$M_{Mix}^{\alpha} = \sum_{i=1}^{\upsilon} \left(w_{f,i}^{\alpha} \big/ M_i \right)^{-1} = \sum_{i=1}^{\upsilon} \left(c_{f,i}^{\alpha} M_i \right)$	(S30)
Combined mass flux of species i:	$\overrightarrow{n_i^p} = \overrightarrow{j_i^p} + \rho_i^p \overrightarrow{v_f^p}$	(S31)
Diffusive flux relation:	$\overrightarrow{j_k^r} = -\sum_{\substack{i=1 \\ i \neq k}}^{\upsilon} \overrightarrow{j_i^r}$	(S32)
Effective binary diffusion coefficient:	$D_{ij}^{eff} = \varepsilon_{f,A}^p D_{ij}$	(S33)
Knudsen diffusion coefficient:[4,5]	$D_{iK} = \varepsilon_{f,A}^p \left(\frac{2\, d_{pore}^p}{3} \right) \sqrt{\frac{\tilde{R} T^p}{2\pi M_i}}$	(S34)
Knudsen diffusion coefficient:[6]	$B_O = \left[\varepsilon_{f,A}^p \left(d_{pore}^p \right)^2 \right] \Big/ 32$	(S35)
Volumetric fraction (two-phase system):	$\varepsilon_{f,V}^{\alpha} + \varepsilon_{s,V}^{\alpha} = 1$	(S36)
Surface fraction (two-phase system):	$\varepsilon_{f,V}^{\alpha} + \varepsilon_{s,V}^{\alpha} = 1$	(S37)

Table S6: Properties dependence

Property description	**Dependence in the simulation**	
	Pellet	**Reactor**
Fluid phase viscosity	$\mu_f^p = \mu_f^p\left(T^p, \{c_i^p\}\right)$	$\mu_f^r = \mu_f^r\left(T^r, \{c_i^r\}\right)$
Fluid phase conductivity	–	$k_f^r = k_f^r\left(T^r, p^r, \{c_i^r\}\right)$
Binary diffusion coefficients	$D_{ij}^p = D_{ij}^p\left(T^p, p^p\right)$	$D_{ij}^r = D_{ij}^r\left(T^r, p^r\right)$
Knudsen diffusivities	$D_{iK} = D_{iK}\left(T^p\right)$	–
Species i heat capacity	$C_{P,i}^p = C_{P,i}^p\left(T^p\right)$	$C_{P,i}^r = C_{P,i}^r\left(T^r\right)$
Species i molar enthalpy	$\tilde{h}_{f,i}^p = \tilde{h}_{f,i}^p\left(T^p\right)$	$\tilde{h}_{f,i}^r = \tilde{h}_{f,i}^r\left(T^r\right)$

References – Supporting Information

(1) Xu, J.; Froment, G. F. Methane Steam Reforming, Methanation and Water-Gas Shift: I. Intrinsic Kinetics. *AIChE J.* **1989**, *35* (1), 88–96.

(2) Pena Lopez, J. A.; Manousiouthakis, V. I. Natural Gas Based Hydrogen Production with Zero Carbon Dioxide Emissions. *Int. J. Hydrog. Energy* **2011**, *36* (20), 12853–12868.

(3) Poling, B. E.; Prausnitz, J. M.; O'connell, J. P.; others. *The Properties of Gases and Liquids*; Mcgraw-hill New York, 2001; Vol. 5.

(4) Mason, E. A.; Malinauskas, A. P. *Gas Transport in Porous Media: The Dusty-Gas Model*; Elsevier Science Ltd, 1983; Vol. 17.

(5) Jakobsen, H. A. *Chemical Reactor Modeling*; Springer International Publishing: Cham, 2014.

(6) Solsvik, J.; Jakobsen, H. A. Modeling of Multicomponent Mass Diffusion in Porous Spherical Pellets: Application to Steam Methane Reforming and Methanol Synthesis. *Chem. Eng. Sci.* **2011**, *66* (9), 1986–2000.