Modeling reaction-diffusion processes within catalyst washcoats:

II. Macroscale processes informed by microscale simulations

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Abstract

This paper first develops a two-dimensional Thiele-type cylindrical-pore model that predicts catalytic washcoat performance, albeit for idealized cylindrical pores. The primary purpose for the cylindrical-pore model is to serve as a basis of comparison with three-dimensional models of catalytic performance in actual geometrically complex washcoat pores that are tomographically reconstructed from focused-ion-beam-scanning-electron-microscopy (FIB-SEM) measurements. In both models, the reaction-diffusion processes are characterized by a Damköhler number that is based on a pore diffusion coefficient and a single first-order reaction rate. Performance metrics include effective product flux from the pores, pore effectiveness, and reaction depth within the pore. In all cases, the models are generalized by casting the conservation

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equations and performance metrics as dimensionless variables. The paper then derives expression to upscale individual pore performance to full-scale washcoats. The new understanding that emerges from these studies provides qualitative and quantitative insight that can assist the design and fabrication of improved washcoat microstructures.

Keywords: Catalyst washcoat, Mass-transport limitations, Damköhler number, Thiele modulus, Effectiveness factor

1. Introduction

The objective of this paper is to develop and apply geometrically simple models that can be used to assist the qualitative and quantitative interpretation of three-dimensional models that predict performance in geometrically complex pore microstructures that are reconstructed from an actual catalyst washcoat. A companion paper [1] develops and models microscale performance based upon focused-ion-beam–scanning-electron-microscope (FIB-SEM) reconstructions of an actual Rh- γ -Al₂O₃ partial-oxidation catalyst washcoat. The geometrically simple cylindrical-pore model and the geometrically complex three-dimensional reconstructed-pore model both characterize the reaction-diffusion processes in terms of a Damköhler number that relates an irreversible first-order reaction and a pore diffusion coefficient. Both models report performance metrics in terms of dimensionless effective product flux emerging from the pore opening, the pore effectiveness, and the depth of reaction. The paper reports analysis and interpretation, as well as new insights, that are based upon direct comparison between the two models.

[Figure 1 about here.]

18 Figure 1 illustrates the multi-scale nature of a typical catalytic monolith.
19 The individual channel dimensions are typically on the order of a millimeter
20 and the monolith is typically a few centimeters long. The thin catalyst wash-
21 coat, which covers the monolith walls, is typically a few tens of microns thick.
22 When modeling at the monolith macroscale and the individual channel scale,
23 because of great scale disparity, microstructural details of the washcoat must
24 be approximated. The simplest approach, which is widely practiced, is simply
25 to assign an empirical factor by which the effective catalyst area is a multiple
26 of the channel wall area [2, 3]. Of course, the multiplicative factor should
27 be informed by measurements, such as BET surface area or chemisorption
28 characteristics. The present paper seeks to improve the empiricism that is
29 inherent in upscaling by incorporating knowledge from models that consider
30 the actual catalyst microstructure.

31 As illustrated in the upper balloons of Fig. 1, alternative notional repre-
32 sentations of the catalyst microstructure can be developed. One approach
33 is to represent the microstructure as assemblies of packed spheres, which
34 can be characterized by packing structure, particle diameter, pore diameter,
35 porosity, and tortuosity. Such representation has appeal because model-
36 ing approaches are well established. For packed spheres, Kozney–Carman
37 relationships can be used to model the effective porous-media properties.
38 Dusty-Gas models have been developed and applied successfully to repre-
39 sent reactive porous-media in applications such as fuel-cell electrodes [4, 5].
40 However, such success depends upon the underlying microstructures being
41 adequately represented by homogeneous porous media.

42 The right-hand balloon in Fig. 1 illustrates a different idealized notion of
43 the washcoat layer. In this case, cylindrical holes penetrate into the washcoat
44 layer. Considering Fig. 3 from the companion paper [1], penetrating holes
45 may provide a better idealization than isotropic porous media. Such hole
46 structures can be modeled using approaches based on the Thiele modulus [6,
47 7].

48 As discussed in the companion paper [1], Fig. 3 shows an actual re-
49 constructed catalyst washcoat. The microstructure is clearly different from
50 packed spheres or regular cylindrical pores. It is largely solid, with a highly
51 textured top surface. A variety of features that resemble cracks, fissures, and
52 crevices penetrate into the washcoat. Five representative pore volumes are
53 extracted from the geometrically complex three-dimensional reconstruction.
54 Reaction-diffusion processes within each of these pore volumes are modeled,
55 with summary representations (e.g., net product flux, pore effectiveness, re-
56 action depth) being reported as functions of Damköhler number.

57 The present paper seeks to interpret the geometrically complex pores
58 in the context of equivalent cylindrical pores. To begin, an axisymmetric,
59 cylindrical, pore model that is motivated by the well known one-dimensional
60 Thiele analysis [6, 7] is developed. This two-dimensional pore model is struc-
61 tured and non-dimensionalized in ways that are analogous to the approach
62 in a companion paper that directly models actual geometrically complex
63 pores [1]. By casting the models in compatible forms, insight from the com-
64 plex microscale geometry can be used in the more traditional setting. The
65 overall performance metrics for the reconstructed pores are mapped to the
66 same performance metrics that emerge from the ideal cylindrical-pore model.

67 This process provides quantitative insight that assists understanding the re-
68 lationships between approximate macroscale models and actual washcoat mi-
69 crostructures. The objective is to seek generalizations that enable the actual
70 complex catalyst microstructures to be represented in terms of easier-to-use
71 dimensionless representations. The results from this study can be further
72 used to assist designing and improving washcoat morphologies (e.g., thick-
73 ness, porosity, surface/volume ratio) for targeted catalytic chemistries.

74 *1.1. Prior research*

75 Models based on Thiele modulus are well understood and widely prac-
76 ticed, but usually applied to pores within pelletized catalysts in packed beds.
77 However, there are alternative implementations of the Thiele modulus, lead-
78 ing to alternative representation of performance metrics such as pore effec-
79 tiveness [8–11]. Such models lump complex microscopic geometric influences
80 into empirical pore diffusion coefficients. Without direct knowledge of actual
81 pore microstructures, establishing and validating the needed empiricism is
82 difficult.

83 Reaction and transport processes within the porous catalysts proceed on
84 greatly disparate length scales (nano, micro and macro), depending on multi-
85 scale pore geometries and characteristics. One upscaling approach to bridge
86 these length scales is based upon evaluating pore diffusion coefficients within
87 porous media. However, because the effective transport depends on com-
88 plex microscale processes, finding general macroscale representations of pore
89 diffusion coefficients is difficult. Berson et al. [12] developed a procedure to
90 predict pore diffusion coefficients within computer-synthesized porous media.
91 Their studies showed that for discrete geometries, because the definition of

the characteristic length is difficult, it is not possible to accurately predict diffusivity for a wide range of porosities. Salejova et al. [13] studied the effect of microstructural properties to determine pore diffusion coefficients and permeabilities in porous media. The pore structures are computer generated based on the microscopic images. They presented that the contribution of nano-pores towards to the total diffusion flux is significant and can not be neglected, but they can be neglected for calculating the permeability. Zalc et al. [14] studied the diffusion processes within random porous structures. By using computer-generated random loosely packed spheres, they reported the effect of porosity on the determination of tortuosity, and hence the pore diffusion coefficient. Their simulations revealed that accurate determination of Knudsen diffusion length scale is crucial.

Using synthesized or reconstructed microscale geometries, a number of groups have developed three-dimensional models to study catalyst performance at the microscale [15–18]. However, generalization of the reaction-diffusion problems are difficult. Studies often focus on specific reaction kinetics for given operating conditions and a specific catalyst.

Novák et al. [18] studied diffusion within catalytic coatings for a digitally reconstructed, three-dimensional, porous layer for CO oxidation over a Pt- γ -Al₂O₃ catalyst. Their model represented the microscale and macroscale structures of the catalyst. Results showed that random-pore models cannot accurately predict effective diffusivities (25-45% lower compared to the three-dimensional model) for CO, and hence cannot predict experimental measurements. The differences were more pronounced at lower levels of macroporosity. Thus, accurate three-dimensional representations should include both

117 micro and macro pore structures. Pereira et al. [17] also studied the effect
118 of catalyst microstructures on CO oxidation rates in three-dimensional and
119 one-dimensional washcoat models. The catalysts were composed of nanoscale
120 to macroscale pores. These results showed that accurate effective diffusivities
121 are needed to accurately represent measured performance.

122 Koči et al. [15, 16] developed relationships between the catalyst’s particle
123 size and effectiveness factor for the CO oxidation reaction over Pt- γ -Al₂O₃
124 catalysts within a three-dimensional computer-generated porous structure.
125 Their model, which incorporated macroscale and mesoscale pores, predicted
126 concentration and temperature variations within the catalytic media. They
127 reported a correlation between process optimization and its relationship to
128 microstructural properties of the catalyst (e.g., porosity and particle size) at
129 a larger scale (e.g., monolith channel in a catalytic converter for automotive
130 exhaust gas after-treatment).

131 Naseri et al. [19] studied the effect of microscale characteristics on macroscale
132 methane reforming processes. They synthesized three-dimensional catalyst
133 microstructures with a particle-packing algorithm. The three-dimensional
134 simulations considered methane steam reforming at both reactor level (macroscale)
135 and the catalyst microstructure level (microscale). Their study emphasized
136 the significant effect of the catalyst intraparticle and interparticle porosity
137 as well as the particle size on the reaction effectiveness factor and methane
138 conversion. Results suggested optimal washcoat structures for methane re-
139 forming.

140 The present study is the first to make concrete connections between ideal
141 pore models (i.e., along the lines of the Thiele modulus) and reconstructed

142 pores from actual catalyst washcoats. This approach provides significant new
 143 insight and quantitative approaches for incorporating microscale knowledge
 144 into approximate models at the macroscale.

145 2. Cylindrical pore model

146 At the scale of a complete monolith or reactor, there is certainly no possi-
 147 bility for simulating the washcoat’s detailed pore-scale microstructure in its
 148 entirety. Thus, it is valuable to seek generalizations based on a lower-order
 149 model, but one that can be quantitatively informed by characteristics of the
 150 actual catalyst microstructures. The two-dimensional cylindrical-pore model
 151 developed here is an extension of widely used models based on the Thiele
 152 modulus [6, 7]. The extensions are motivated by the need to be directly
 153 comparable to the detailed reconstructed pore volume models.

154 2.1. Thiele modulus

155 The Thiele modulus Φ provides a dimensionless representation of a reaction-
 156 diffusion process within a bottomless cylindrical pore. Assuming a first-order
 157 catalytic reaction, the Thiele modulus may be defined as

$$\Phi = Z \sqrt{\frac{2k}{RD_{\text{pore}}}}. \quad (1)$$

158 In this definition, Z and R are the pore’s depth and radius, respectively. The
 159 rate constant for the single irreversible reaction (e.g., $A \rightarrow B$) is represented
 160 as k , and D_{pore} is an effective gas-phase diffusion coefficient. When Φ is large,
 161 internal diffusion limits the overall rate of reaction. When Φ is small, the
 162 surface reaction is the rate-limiting process [7].

163 With this definition of the Thiele modulus, the reactant composition pro-
 164 file within the pore can be evaluated by solving a well known and straightfor-
 165 ward ordinary differential equation. The pore effectiveness can be evaluated
 166 from the solution to the Thiele problem as [7]

$$\eta_T = \frac{\tanh \Phi}{\Phi}. \quad (2)$$

167 The Thiele pore effectiveness represents the catalytic activity of the pore
 168 relative to the catalytic activity if the reactant composition within the entire
 169 pore volume were the same as at the top pore opening. Of course, $\eta_T \leq 1$
 170 because the reaction-diffusion processes within the pore depletes the reactant
 171 concentration as a function of depth within the pore.

172 2.2. Two-dimensional cylindrical pore

173 The cylindrical pore model developed here departs from the Thiele ap-
 174 proach in two ways. First, the gas-phase diffusion problem is two dimen-
 175 sional, with axial and radial coordinates being the independent variables.
 176 Second, the catalytic bottom surface of the pore is included. As illustrated
 177 in Fig. 2, the pore geometry is characterized by its depth Z and radius R .
 178 The pore opening has an area of $A_p = \pi R^2$. The total top-surface area (pore
 179 opening plus catalytic surface surrounding the pore opening) is designated
 180 as A_o . The model solves the axisymmetric reaction-diffusion problem within
 181 the pore volume.

182 As was the case for the reconstructed pores [1] and the Thiele approach,
 183 the model considers only two generic gas-phase species. A first-order irre-
 184 versible reaction ($A \rightarrow B$, with rate constant k) proceeds at the gas-catalyst
 185 interfaces. The problem is assumed to be isothermal and isobaric.

186

[Figure 2 about here.]

187 In casting the cylindrical pore model in terms of dimensionless variables,
 188 the cylindrical coordinates and species concentration are scaled as

$$\hat{z} = \frac{z}{L}, \quad \hat{r} = \frac{r}{L}, \quad \hat{C}_A = \frac{C_A}{C_{A,\text{top}}}. \quad (3)$$

189 As with the reconstructed pore volume model, this results in Eq. 5 and Eq. 6
 190 from the companion paper representing the dimensionless species conserva-
 191 tion and gas-surface boundary condition, respectively. For the cylindrical
 192 pore, the characteristic length scale (Eq. 3) is equivalently written as

$$L = \frac{\pi R^2 Z}{2\pi RZ + \pi R^2} = \frac{RZ}{2Z + R} = \frac{Z}{2\alpha + 1}. \quad (4)$$

193 The definition of L is chosen such that the cylindrical-pore model is analogous
 194 to the length scale used in the more-complex reconstructed pore model.

195 Although the Damköhler number is the only parameter that appears ex-
 196 plicitly in the governing equations (Eqs. 5 - 6 from the companion paper [1])
 197 , the two-dimensional solutions also depend on the pore aspect ratio,

$$\alpha = \frac{Z}{R}. \quad (5)$$

198 The computational domain for solving Eq. 5 from the companion paper [1]
 199 is

$$0 \leq \hat{z} \leq (2\alpha + 1), \quad 0 \leq \hat{r} \leq \left(2 + \frac{1}{\alpha}\right). \quad (6)$$

200 The reason to consider the two-dimensional problem and use the partic-
 201 ular characteristic length scale (Eq. 3 from the companion paper [1]) is to
 202 assist in establishing relationships with the computational simulations using
 203 the actual geometric complexity of reconstructed microscale pore volumes.

204 As discussed previously, the characteristic length scale ($L = V_p/A_s$) can be
 205 extracted computationally from the reconstructed pore geometry.

206 Although the cylindrical-pore model and complex-pore model are best
 207 characterized with the Damköhler number, it is useful to consider the rela-
 208 tionship between the Thiele modulus (Eq. 1, applicable for a one-dimensional
 209 cylindrical pore model) and the more general Damköhler number. For the
 210 two-dimensional cylindrical pore, the relationship depends on the aspect ratio
 211 as

$$\Phi = \sqrt{2 \text{Da} \alpha (2\alpha + 1)}. \quad (7)$$

212 *2.3. Computational solution*

213 Equations 5 and 6 from the companion paper [1] represent a linear, el-
 214 liptic, boundary-value problem. In principle, within the context of an ax-
 215 isymmetric cylindrical pore, the problem is solvable analytically using sepa-
 216 ration of variables, leading to an infinite-series solution. The present study
 217 solves the problem computationally. Following finite-volume discretization
 218 on a uniform axisymmetric mesh network, the resulting linear system of alge-
 219 braic equations is easily and rapidly solved by an iterative conjugate-gradient
 220 method. The computational solution is programmed in Python. The prob-
 221 lem is solved for a large range of aspect ratios $10^{-2} \leq \alpha \leq 10^3$ and for five
 222 Damköhler numbers $10^{-5} \leq \text{Da} \leq 10^{-1}$.

223 *2.4. Performance Metrics*

224 Once the cylindrical-pore model is solved for a range of parameters, the
 225 solutions can be investigated to extract certain performance metrics. As dis-
 226 cussed in the companion paper, three performance metrics are used to charac-

227 terize the reaction-diffusion processes in actual reconstructed pore volumes.
 228 These are the effective pore flux Γ_p , the pore effectiveness η_p , and the pore
 229 depth by which 95% of the reaction has occurred $\hat{Z}_{95}$. The same metrics are
 230 used here to characterize the cylindrical pore volume. Considerable insight
 231 can be gained by comparing the performance metrics between the idealized
 232 and reconstructed models.

233 **3. Cylindrical and reconstructed pore performance**

234 The cylindrical-pore model is exercised over a wide range of pore as-
 235 pect ratios and Damköhler numbers to predict performance metrics. The
 236 cylindrical-pore simulation results are directly compared with results from
 237 the five reconstructed pores [1].

238 *3.1. Effective pore flux*

239 [Figure 3 about here.]

240 Figure 3 shows predicted effective pore flux Γ_p as a function of Damköhler
 241 number and pore aspect ratio α . At small aspect ratios, the pore resembles a
 242 shallow disk, which approaches flat-plate behavior. At large α , the effective
 243 pore flux depends greatly on the Damköhler number, and hence on the com-
 244 petition between reaction and diffusion processes. At low Da and high α the
 245 effective pore flux is large, meaning that the catalyst area is used effectively
 246 throughout the pore.

247 The symbols on Fig. 3 show results from the five reconstructed pore-
 248 volume simulations from the companion paper [1]. These simulations are
 249 based on specified Damköhler numbers, but with the geometrically complex

reconstructed pore microstructures. Each of the simulated results predicts the effective pore flux Γ_p . Thus, each result can be placed onto Fig. 3, on the line associated with the specified Da and the predicted Γ_p . However, doing so leads to a different aspect ratio α for each Damköhler number. Because reconstructed pore geometries are so geometrically complex, there is no unique definition for the aspect ratio. Nevertheless, even an approximate α has value in characterizing the pore performance and relating the performance to the much simpler cylindrical-pore model. In any case, the pore geometry is fixed and cannot change as a function of Damköhler number.

The reconstructed pore-volume symbols are placed onto Fig. 3 with effective aspect ratios (α) that are established for each of the five reconstructed pore volumes. The effective aspect ratio α_{eff} for a given pore is established by calculating the α that minimizes the root-mean-square distance between the effective pore flux predicted by the reconstructed pores $\Gamma_{p,r}$ and the respective $\Gamma_p(\alpha, \text{Da})$ curve, or

$$\min_{\alpha_{\text{eff}}} \left(\sqrt{\sum_{\text{Da}} |(\alpha_{\text{eff}}, \Gamma_{p,r}(\text{Da})) - \Gamma_p(\alpha, \text{Da})|^2} \right) . \quad (8)$$

The symbols that appear on Fig. 3 are placed according to α_{eff} and predicted $\Gamma_{p,r}$. Although the Damköhler number is not independently specified, the results show that the points fall very close to the appropriate cylindrical-pore Damköhler-number curves. At high and low Damköhler numbers the cylindrical-pore model and the reconstructed-pore models agree well. However, there is some discrepancy at intermediate Damköhler numbers. At low Damköhler numbers, where the process is not transport limited, and at high Damköhler numbers where very little of the pore is being utilized, the details

of the pore microstructure are essentially irrelevant. It is only at intermediate Damköhler numbers where the individual pore morphology plays a significant role. Nevertheless, overall agreement is good and the approach enables the assignment of effective aspect ratios for each of the microstructurally complex reconstructed pore volumes.

3.2. Pore effectiveness

[Figure 4 about here.]

Figure 5 shows predicted pore effectiveness η_p (Eq. 12 from the companion paper [1]) as a function of Damköhler number and pore aspect ratio α . A pore effectiveness of unity means that the maximum concentration of reactant is reaching all reactive surfaces within the pore. A pore effectiveness approaching zero indicates high diffusive resistance relative to the kinetic rate, limiting access to catalyst surfaces deep within the pore. At small aspect ratios, the pore effectiveness approaches flat-plate behavior (i.e., very shallow pore). However, at small aspect ratios and $Da = 10^{-1}$ the pore effectiveness doesn't approach unity. Strictly speaking, this is the case for all Da , but is much less apparent for lower Da . This is the result of the normalization used in Eq. 11 from the companion paper [1]. As α shrinks, the characteristic length L tends toward Z and the cylindrical-pore model resembles a flat plate catalytic surface with diffusion length Z . This solution will always underperform with respect to the normalization case $J_o = C_{A,top}k$ by varying degrees depending on the Damköhler number.

The symbols on Fig. 4 show the simulation results from the five reconstructed pores. These simulations specify a Damköhler number for the complex pore microstructure, and the three-dimensional simulations predict η_p .

298 As was done in placing reconstructed points on the Γ_p map (Fig. 3), an ef-
 299 fective aspect ratio is established for each of the reconstructed pores on the
 300 η_p map. As is the case in Fig. 3, the reconstructed pores that are fit with
 301 effective aspect ratios α lie close to the appropriate Da lines. However, com-
 302 paring Figs. 3 and 4, it is seen that the average aspect ratios as predicted
 303 from the pore effectiveness are slightly higher than are the average aspect
 304 ratios as predicted from the effective pore flux. Perhaps not surprisingly, it is
 305 difficult to uniquely establish an average aspect ratio for such geometrically
 306 complex pore microstructures.

307 Figures 3 and 4 both show strong dependence on the Damköhler number.
 308 At high Damköhler numbers, both Γ_p and η_p depend weakly on the aspect
 309 ratio. However, at low Damköhler numbers Γ_p depends strongly on the aspect
 310 ratio, while η_p depends weakly on α .

311 [Figure 5 about here.]

312 3.2.1. Pore effectiveness and Thiele approach

313 Figure 5 is a contour plot of pore effectiveness as predicted by the one-
 314 dimensional Thiele model η_T (Eq. 2) and by the two-dimensional cylindrical-
 315 pore model η_p (Eq. 12 from the companion paper [1]). Both the Thiele
 316 model and the cylindrical-pore model predict the same effectiveness at high
 317 α and low Damköhler number. However, the two models deviate somewhat
 318 at high Damköhler numbers and low α . This is because the cylindrical model
 319 includes a reactive pore bottom and two-dimensional diffusion effects, which
 320 are more apparent at low α and high Da.

321 The symbols on Fig. 5 represent simulation results for the five recon-
 322 structed pore volumes. In this case an average pore aspect ratio is not used.

323 Rather, the symbols are placed at specified values of Damköhler number
 324 and η_p as predicted from the three-dimensional models of the reconstructed
 325 pores. With the exception of Pore 5 at low Da, each pore shows very nearly
 326 a constant de-facto aspect ratio.

327 [Figure 6 about here.]

328 3.3. Depth of reaction

329 Figure 6 illustrates the predicted depth of reaction $\hat{Z}_{95}$ as a function of
 330 Damköhler number and pore aspect ratio α . The cylindrical-pore model pre-
 331 dictes that at low Damköhler numbers, where the reaction-diffusion problem
 332 is kinetically limited, most of the pore depth is effectively used, up to very
 333 large aspect ratios. At high Damköhler numbers, on the other hand, much
 334 of the pore depth is catalytically ineffective for a large range of aspect ratios.

335 The symbols on Fig. 6 represent results from the reconstructed pore vol-
 336 umes. The symbols are placed according to the specified Damköhler number
 337 and the predicted $\hat{Z}_{95}$. At low Damköhler numbers (with the exception of
 338 Pore 1) the reconstructed simulations show that the $\hat{Z}_{95}$ depths tend to reach
 339 asymptotic values that depend only weakly on the apparent aspect ratio α .
 340 At $Da = 10^{-1}$, none of the reconstructed pores used more than approximately
 341 30% of the pore depth, with the average being about 23%.

342 Based on depth-of-reaction results, the apparent aspect ratios vary greatly,
 343 with the apparent aspect ratios at low Damköhler numbers being much larger
 344 than those inferred from the analysis of Γ_p and η_p . These results indicate
 345 that the depth of reaction is highly dependent on unique pore morphology
 346 that is not fully captured in the idealized pore model.

347 3.4. *Effective pore flux characteristics*

348 [Figure 7 about here.]

349 Figure 7 is a contour map of predicted effective pore flux Γ_p as a function
 350 of the Damköhler number and aspect ratio α . For the cylindrical-pore model,
 351 this map shows the same information as in Fig. 3, but presented differently.
 352 At high Damköhler numbers and large aspect ratios α , the effective pore
 353 flux depends only on the Damköhler number. Conversely at low Damköhler
 354 numbers and small α , the effective pore flux depends only on the pore aspect
 355 ratio. This behavior suggests an optimum in terms of washcoat fabrication
 356 that follows the “knee” in the pore-flux contours.

357 For a given reaction-diffusion regime, a particular aspect ratio will tend
 358 to maximize the product species flux from washcoat pores, beyond which no
 359 gains in flux are obtainable. Based upon Eq. 7 and plotted on Fig. 7, the knee
 360 is approximately bounded by the Thiele modulus in range $0.5 \leq \Phi \leq 2.0$.
 361 The measure of effective pore flux as a fraction of the maximum effective
 362 pore flux at high α is designated as the maximum effective pore flux $\Gamma_{\max,p}$.

363 The fractional pore flux, relative to the maximum possible, may be rep-
 364 resented as a function of α and Da.

$$\Gamma_{\text{frac},p}(\text{Da}, \alpha) = \frac{\Gamma_p(\text{Da}, \alpha)}{\Gamma_p(\text{Da}, \alpha \rightarrow \infty)}. \quad (9)$$

365 Due to the asymptotic nature of the effective pore flux at high α , a cut-
 366 off value of $\Gamma_{\text{frac},p} = 95\%$ can be used to define the knee. At $\Gamma_{\text{frac},p} =$
 367 95% the corresponding Thiele modulus is $\Phi_{\text{opt}} \approx 1.832$ or $\eta_{T,\text{opt}} \approx 51.862\%$.
 368 The optimal aspect ratio α_{opt} associated with this cut-off parameter can be

369 approximated as

$$\alpha_{\text{opt}} = -\frac{1}{4} + \sqrt{\frac{1}{16} + \frac{\Phi_{\text{opt}}}{4\text{Da}}}. \quad (10)$$

370 This optimum knee in the effective pore flux plot can also suggest an optimum
 371 pore depth. If the average effective pore radius $\bar{R}$ for a washcoat can be
 372 approximated, then Eq. 10 can be used to evaluate the optimal washcoat
 373 thickness based on pore diffusion and kinetic rate as

$$Z_{\text{opt}} = \sqrt{\frac{D_{\text{pore}}\bar{R}}{2k}\Phi_{\text{opt}}}. \quad (11)$$

374 These optimum variables specify the limit above which no further gains in
 375 effective pore flux can be achieved by increasing pore aspect ratios for a given
 376 reaction-diffusion regime (i.e., Damköhler number).

377 The symbols on Fig. 7 show the simulation results from the five recon-
 378 structed pore volumes. In this case (unlike in Fig. 3) an effective aspect
 379 ratio is not used. Instead, the simulated results are shown at the specified
 380 Damköhler number and predicted effective pore flux.

381 At high Damköhler numbers, Pore 1 is operating at a Thiele modulus of
 382 approximately $\Phi \approx 1.73$ which corresponds to an effectiveness as predicted
 383 by the Thiele approach of $\eta_{\text{T}} = 54.16\%$ and maximum pore flux effectiveness
 384 of $\Gamma_{\text{max,p}} = 94.0\%$. At the other end of the scale, Pore 5 has a Thiele
 385 modulus of approximately $\Phi \approx 0.662$ with a effectiveness $\eta_{\text{T}} = 87.6\%$ and
 386 maximum pore flux effectiveness of $\Gamma_{\text{max,p}} = 58.0\%$. At high Damköhler
 387 numbers, the effective pore fluxes for Pore 2 are slightly above the maximum
 388 predicted values for the cylindrical-pore model (cf., Fig. 3). Consequently
 389 three effective pore fluxes for Pore 2 cannot be directly mapped onto the
 390 appropriate contour and therefore do not appear on Fig. 7.

391 The symbols on Fig. 7 appear to indicate that effective aspect ratios do
 392 not accurately represent the pore morphologies at high Damköhler numbers.
 393 At high Damköhler numbers, the flux performance suggests effective aspect
 394 ratios in the range $1 \leq \alpha \leq 3$. Also, there appears to be a relationship be-
 395 tween the reconstructed pore performance at high Damköhler numbers and
 396 the contours of Thiele modulus. However, this may well be a computational
 397 artifact. As previously noted, for $\Phi \geq 1.832$ the pore-flux performance de-
 398 pends insensitively on α , meaning that any small deviations in normalized
 399 flux tend to produce large variations in effective α . Inasmuch as nearly all
 400 of the reconstructed pores performed slightly below the idealized pore model
 401 at high Damköhler (cf., Fig. 3) their points on the contour tend toward the
 402 knee. However, effective aspect ratios that fall below the knee are particularly
 403 insensitive to minor variations in Γ_p .

404 Because the Thiele modulus lumps reaction kinetics and pore morphol-
 405 ogy into a single parameter, it accurately predicts the pore effectiveness but
 406 not the maximum pore performance. This suggests that there is value in
 407 defining reaction-transport competition (Da) and pore morphology (α) as
 408 two independent parameters to characterize the maximum product flux from
 409 a pore. By separating the Thiele modulus into two independent paramet-
 410 ers, a non-linear relationship is found between the Damköhler number and
 411 aspect ratio in determining effective pore flux. For example, considering
 412 Fig. 7, at low Damköhler numbers the effective pore fluxes are largely inde-
 413 pendent of the Damköhler number and vary only between pore microstruc-
 414 tures. This is likely due to the transport limitations within the reconstructed
 415 pores being the dominant effect compared to the reaction limitations. At low

416 Damköhler numbers the microstructure controls pore performance and thus
 417 none of the actual pores reach a fractional pore-flux effectiveness greater than
 418 $\Gamma_{\text{frac,p}} \approx 20\%$.

419 3.5. *Effective aspect ratio α_{eff}*

420 [Figure 8 about here.]

421 There are inherent inaccuracies in characterizing complex pore morpholo-
 422 gies in terms of effective aspect ratios. The reconstructed pore volumes are
 423 tortuous and contain a range of narrow constrictions and choke points that
 424 cause complex mass-transport resistances. The cylindrical-pore model does
 425 not directly consider such complex morphologies, but instead subsumes them
 426 into an effective aspect ratio. Thus, simplifying pore morphology solely in
 427 terms of effective aspect ratios has varying degrees of success in predicting
 428 catalyst performance metrics.

429 Figure 8 illustrates the average de-facto aspect ratios for the reconstructed
 430 pores as predicted by each output parameter. The average aspect ratio $\bar{\alpha}$ is
 431 determined for each output parameter and Damköhler number by averaging
 432 the de-facto α values as predicted by the reconstructed pore simulations. Ad-
 433 ditionally, the variations in the de-facto aspect ratios between reconstructed
 434 pores is illustrated by the shaded regions, indicating the minimum and max-
 435 imum bounds of the de-facto pore aspect ratios for each performance metric.
 436 It should be noted that the shaded region does not quantify error bounds,
 437 only the observed range of de-facto α for the five reconstructed pore volumes
 438 that were simulated.

439 It is clear from Fig. 8 that the de-facto α predicted by pore effectiveness
 440 η_p is generally consistent for the full range of simulated Damköhler numbers.

441 This consistent behavior is not simply an effect of the averaging procedure,
 442 but is also consistent for each respective reconstructed pore (cf., Figs. 4 and
 443 5). This suggests η_p is a good performance metric for upscaling the pore
 444 results to a full washcoat.

445 Figure 8 suggests that the effective pore flux Γ_p is not well characterized
 446 by the effective aspect ratio for all Damköhler numbers. At low Damköhler
 447 numbers, $\bar{\alpha}$ based on Γ_p agrees well with the $\bar{\alpha}$ based on η_p , but the two mea-
 448 sures diverge at high Damköhler numbers. This divergence likely stems from
 449 computational sensitivities. Considering Fig. 3, the cylindrical-pore model
 450 predicts the effective pore flux reasonably accurately for the reconstructed
 451 pores. At high Damköhler numbers, however, the de-facto α is very sensi-
 452 tive to small variations in Γ_p (cf., Fig. 7). For example, at $Da = 10^{-1}$, the
 453 de-facto α as fit by the effective flux of the cylindrical pore model for Pore 1
 454 is 2.79 whereas α_{eff} as fit by Eq. 8 is 33.4. The factor of 12 difference be-
 455 tween these two α values represents a difference in predicted effective flux of
 456 approximately 9%. Thus, approximating $\bar{\alpha}$ based on Γ_p is not as well suited
 457 for upscaling as is predicting an effective $\bar{\alpha}$ based on η_p .

458 The $\bar{\alpha}$ based on $\hat{Z}_{95}$ shows a similar divergence as does $\bar{\alpha}$ based on Γ_p ,
 459 but at low Damköhler numbers. At high Damköhler numbers, where pore
 460 morphology is less important because so little of the pore is actually used, α
 461 as fit by $\hat{Z}_{95}$ and η_p agree well. At low Damköhler numbers pore morphology
 462 plays a significant role that is not captured in the idealized pore model.
 463 Thus, depth predictions for reconstructed pore volumes deviate from ideal
 464 predictions. Therefore $\bar{\alpha}$ based on $\hat{Z}_{95}$ has some predictive capabilities for
 465 estimating depth of reaction, especially for mid-to-high Damköhler numbers.

466 Nevertheless, $\bar{\alpha}$ based on $\hat{Z}_{95}$ does not provide a good basis for upscaling for
467 all Damköhler numbers, especially for low Damköhler numbers.

468 4. Upscaling to a full washcoat structure

469 A single-pore model, whether reconstructed or ideal, can only partially
470 capture the behavior of the full washcoat. To extrapolate to a complete
471 washcoat structure, effective parameters related to geometric area, washcoat
472 depth, pore area, pore density, and average pore radius must be approxi-
473 mated. Figure 9 illustrates only the top surface of the reconstructed catalyst
474 sample area. The surface is irregular and highly textured. Even with the
475 detailed geometry from the FIB-SEM reconstruction, unambiguous measures
476 of pore density and pore-opening area are at best difficult.

477 [Figure 9 about here.]

478 Table 1 tabulates the relevant surface areas and the average aspect ratios
479 of the pores that are extracted from the FIB-SEM reconstruction. These
480 statistics provide some relevant clues for upscaling.

481 [Table 1 about here.]

482 4.1. Average washcoat geometry

483 Of course, pore microstructures significantly increase catalytic surface
484 area within washcoat structures. However, depending on the reaction-diffusion
485 processes all the catalyst surface area may not be practically accessible. Thus,
486 developing approaches to design and fabricate optimal pore structures and
487 pore densities has practical value.

488 A parameter β is introduced to assist the study of pore densities

$$\beta = \frac{A_o}{A_p}. \quad (12)$$

489 In this definition A_p is the pore-opening area and A_o is the area of the pore
490 opening and the surrounding area (cf., Fig. 2).

491 Using data from Table 1, the reconstructed washcoat has a measured
492 pore density of $\beta = 26.53$. For the idealized pore model, the external surface
493 area A_o is equal to the geometric surface area A_{geo} . However, because of
494 the texture in the actual washcoat surface (cf., Figs. 3 from the companion
495 paper [1] and 9), the measured A_o for the reconstructed washcoat is approx-
496 imately twice the projected geometric area.

497 If the washcoat surface were assumed to be flat and populated by cylin-
498 drical pores plunging into the surface (cf., Fig. 1), the total catalytic surface
499 area A_c would be expressed as

$$A_c = A_o + N \times 2\pi \bar{R} \bar{Z}, \quad (13)$$

500 where N is the number of pores on the washcoat surface, $\bar{R}$ is the average
501 pore radius, and $\bar{Z}$ is the average depth of the washcoat (assumed to be a
502 good approximation of average pore depth Z). The pore volume is

$$V_p = N \times \pi \bar{R}^2 \bar{Z}. \quad (14)$$

503 Combining the above two equations, the average radius can be expressed as

$$\bar{R} = \frac{2V_p}{A_c - A_o}. \quad (15)$$

504 With an effective pore aspect ratio $\bar{\alpha}$ being expressed as

$$\bar{\alpha} = \bar{Z}/\bar{R}, \quad (16)$$

505 the average pore density can be expressed as

$$\overline{\beta} = \frac{2\overline{\alpha}}{A_c/A_o - 1}. \quad (17)$$

506 Although developing processes to fabricate washcoats with specific pore den-
 507 sities and pore radii may be difficult in practice, the foregoing relationships
 508 assist developing target specifications that are informed by model-based pre-
 509 dictions.

510 4.2. Average washcoat performance

511 Using the cylindrical-pore model, the total flux from the surface (pores
 512 and external surface) can be expressed as

$$J_{\text{tot}} = \frac{J_p A_p + (A_o - A_p) J_o}{A_o}. \quad (18)$$

513 As in the case of a single pore, the normalized flux for the entire washcoat
 514 Γ_{tot} is evaluated by normalizing with respect to external surface flux J_o as

$$\Gamma_{\text{tot}} = \frac{J_{\text{tot}}}{J_o} = 1 - \frac{1}{\overline{\beta}} + \Gamma_p \frac{1}{\overline{\beta}}. \quad (19)$$

515 The total effectiveness factor for the washcoat follows as

$$\eta_{\text{tot}} = \frac{J_{\text{tot}} A_o}{J_o A_c} = \frac{J_p A_p + (A_o - A_p) J_o}{J_o A_c} \quad (20)$$

516 Using Eqs. 12 and 13, and the fact that $A_o = N \times \overline{\beta} \pi \overline{R}^2$ the total pore
 517 effectiveness can be simplified further as

$$\eta_{\text{tot}} = \Gamma_{\text{tot}} \frac{\overline{\beta}}{\overline{\beta} + 2\overline{\alpha}}. \quad (21)$$

518 Using the relationships developed above, data from Table 1, and perfor-
 519 mance results from the simulated reconstructed pores, the performance of the

washcoat as a whole can be predicted. For example, assuming $\text{Da} = 10^{-3}$, the average effective pore flux for all five samples is $\Gamma_{\text{p,avg}} = 22.06$. Knowing $\bar{\beta}$, the average normalized flux for the washcoat is

$$\Gamma_{\text{tot}} \approx 1.79. \quad (22)$$

Using the effective pore aspect ratio $\bar{\alpha}$ for the five samples $\bar{\alpha}_{\text{avg}} = 28.378$, the total washcoat effectiveness is

$$\eta_{\text{tot}} \approx 0.57. \quad (23)$$

As the $\hat{Z}_{95}$ measures suggest, significant portions of the total catalytic area may not be accessible for reaction. For example, using the reconstructed area profiles (Table 1), the measure of actual catalytic area to geometric area $F_{\text{cat,geo}}$ for the reconstructed washcoat is

$$F_{\text{cat,geo}} = \frac{A_{\text{c}}}{A_{\text{geo}}} \approx 6.39. \quad (24)$$

Based on the idealized washcoat model, a relationship can be derived for a modified washcoat factor $F_{\text{cat,geo}}(\bar{\alpha}, \bar{\beta}, \text{Da})$, which is a function of the surface's physical characteristics and the reaction-diffusion regime. Using the definitions of A_{c} , A_{o} , and $\bar{\beta}$, the modified $F_{\text{cat,geo}}$ is expressed as

$$F_{\text{cat,geo}} = \frac{\bar{\beta} + 2\bar{\alpha}\hat{Z}_{95}}{\bar{\beta}}. \quad (25)$$

[Figure 10 about here.]

Figure 10 shows contour maps of $F_{\text{cat,geo}}$ as functions of $\bar{\alpha}$ and $\bar{\beta}$ for five Damköhler numbers. The strong Damköhler number dependence is apparent. For $\text{Da} = 10^{-1}$ and any realistic $\bar{\beta}$, the modified $F_{\text{cat,geo}}$ is unlikely to be above 2 or 3. Alternatively, at $\text{Da} = 10^{-5}$ double-digit $F_{\text{cat,geo}}$'s are achievable, although only at large α and high pore density.

539 5. Summary and conclusions

540 A microscale two-dimensional cylindrical-pore model is developed and
541 used to evaluate catalysis performance metrics, including effective pore flux,
542 pore effectiveness, and reaction depth. The pore itself is characterized by
543 an aspect ratio, while the first-order reaction-diffusion competition is char-
544 acterized by a Damköhler number. This model is a two-dimensional version
545 of the well-known analysis based on a Thiele modulus. The principle rea-
546 son to develop a cylindrical-pore model is to provide a basis for comparison
547 with three-dimensional models that predict the performance of geometrically
548 complex pore volumes that are reconstructed from actual washcoats using
549 FIB-SEM techniques [1].

550 Using the same quantitative performance metrics, predictions from the
551 ideal cylindrical-pore model and the three-dimensional reconstructed pore
552 model can be compared directly. The performance relationships presented
553 here are based on a first-order, irreversible reaction. As discussed briefly
554 in the companion paper [1], the general approach can be extended to more
555 complex, but still global, reaction kinetics. Although results should be quali-
556 tatively similar, the reaction pathways and rates will surely affect the results.
557 Nevertheless, even with simple chemistry, the results provide significant new
558 insight about the performance of actual catalyst washcoats. The geometri-
559 cally complex microstructures certainly do not appear as simple cylindrical
560 pores plunging into the washcoat. Nevertheless, there are interesting com-
561 mon features in the performance metrics. By identifying and analyzing such
562 commonalities and trends, the results suggest qualitative and quantitative
563 insights that advance the fundamental understanding of reaction-diffusion

564 processes within catalytic washcoat structures. Such understanding con-
565 tributes new insight that can assist the improved design and fabrication of
566 washcoat microstructures.

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Figure 1: Illustration of a rectangular-channel monolith, showing a range of scales for a washcoat catalyst. The two upper balloons illustrate alternative idealizations of the washcoat microstructure.

Figure 2: Illustration of a cylindrical pore plunging into a washcoat.

Figure 3: Effective pore flux Γ_p as a function of aspect ratio and Damköhler number for the cylindrical pore model (lines). The symbols represent simulated results from the three-dimensional reconstructed pore volumes.

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Figure 8: Average de-facto aspect ratios $\bar{\alpha}$ as functions of Damköhler number for the three performance metrics. The shaded regions show maxima and minima of the de-facto aspect ratios for the five pores for each performance metric.

Figure 9: Top surface of the reconstructed washcoat.

Figure 10: Contour maps of $F_{\text{cat,geo}}$ as functions of $\bar{\alpha}$ and $\bar{\beta}$ for five Damköhler numbers.

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Table 1: Reconstructed washcoat and sample pore volume statistics

Parameter	Value
Pore top surface area, A_p	48.0 μm^2
Total Catalytic Area, A_c	4270.4 μm^2
External surface area, A_o	1273.3 μm^2
Geometric surface, A_{geo}	668.4 μm^2
Effective pore-volume aspect ratio based on η_p	
Parameter	Value
Pore 1 average aspect ratio, $\alpha_{1,\text{eff}}$	43.06
Pore 2 average aspect ratio, $\alpha_{2,\text{eff}}$	23.59
Pore 3 average aspect ratio, $\alpha_{3,\text{eff}}$	28.89
Pore 4 average aspect ratio, $\alpha_{4,\text{eff}}$	33.02
Pore 5 average aspect ratio, $\alpha_{5,\text{eff}}$	13.33