Modeling reaction-diffusion processes within catalyst washcoats:

I. Microscale processes based on three-dimensional reconstructions

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Abstract

This paper develops a detailed analysis of reaction-diffusion processes within a porous rhodium-alumina catalyst washcoat. Focused-ion-beam-scanning-electron-microscope (FIB-SEM) techniques are developed and applied to reconstruct the actual catalyst-support microstructure. Three-dimensional transport processes within washcoat micro-pore structures are modeled using a dimensionless representation of reaction and diffusion rates based on the Damköhler number. Three-dimensional computational solutions for particular porous microstructures are modeled and interpreted. In a companion paper, these microstructural results are used to assist development of larger-scale models that can be incorporated into reactor-scale simulations.

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1. Introduction

The objective of this paper is to develop new qualitative and quantitative understanding of reaction-diffusion processes within catalytically active porous washcoats. At the microscale, catalyst washcoats are geometrically complex. Although notional models such as packed spheres can be qualitatively useful, they certainly do not represent the actual catalyst microstructure. At the reactor scale, models invariably represent the effective catalyst area as a multiplicative function of the geometrical surface area of the channel walls [1–3]. In other words, because the washcoat is porous, the effective catalyst area can be significantly larger than the channel wall area. Following the nomenclature of Deutschmann, et al. [2], the multiplicative factor may be called $F_{\text{cat,geo}}$. Albeit with knowledge of measured properties such as porosity, BET surface area, and chemisorption characteristics, the effective catalyst area is usually adjusted empirically. Moreover, $F_{\text{cat,geo}}$ is often taken to be a constant, independent of changes in reactor operating conditions. The results in this paper show that characteristics such as effective area and pore effectiveness are strong functions of the reaction chemistry and the pore microstructure.

This paper is composed of two primary elements. First, a focused-ion-beam–scanning-electron-microscope (FIB-SEM) method is developed and applied to reconstruct the washcoat microstructure from a commercial Rh- $\gamma\text{Al}_2\text{O}_3$ partial-oxidation catalyst monolith. The present study is based upon the catalyst shown in Fig. 1. Reconstruction results reveal microstructures,

24 with complex crack- and crevice-like features. Second, using the FIB-SEM re-
25 constructions, three-dimensional computational models are developed to sim-
26 ulate reaction-diffusion processes within the microstructural features. Seek-
27 ing some generality, the models are implemented in dimensionless form using
28 a characteristic Damköhler number.

29 A companion paper [4] is devoted to using the microstructural results
30 from the present study to inform large-scale models that can be practically
31 incorporated into full reactor-scale models. The macro-scale models are based
32 on more traditional concepts such as effectiveness factors and Thiele moduli.

33 [Figure 1 about here.]

34 Porous washcoats enable the dispersion of active metal (e.g., Pt, Pd,
35 Rh, Ni) with high surface-area-to-volume ratios. However, in designing and
36 synthesizing the porous microstructure, a compromise must often be made
37 between high surface area and internal diffusion limitations within the wash-
38 coat. Small pores within the catalyst (on micro and nano scale) present high
39 diffusive resistance from the high frequency collisions between the reactants
40 and the pore wall. At this scale, the diffusive resistance within a pore is
41 mainly Knudsen diffusion [5]. An optimum washcoat design compromises
42 between the gaseous diffusion rates and the accessible catalytic surface area.

43 1.1. *Prior research*

44 Detailed modeling of catalytic surfaces has been pursued in previous stud-
45 ies that incorporate three-dimensional representations of the physical cata-
46 lyst structures. Local variations are determined by simulating the three-
47 dimensional pore volumes, which may be either computer generated or re-

constructed from the actual catalyst. The computer-generated models synthesize three-dimensional random networks of catalyst support structures [6–9]. The pore-size distributions are obtained experimentally using a nitrogen absorption measurements or mercury porosimetry, while SEM and TEM images are used to determine the particle and pore sizes [6, 9]. Reconstructed models use recent advances in microscopy, enabling three-dimensional imaging of the porous catalytic materials at high resolution [10–14]. Methods for high-resolution microscopy include X-ray tomography [15–20] or FIB-SEM techniques [21–26] to reconstruct the microporous structure of the catalysts. The images are also used to explore the influence of the reaction rates and effective diffusions within the porous media, improve the accuracy of the chemical-kinetic models, and optimize the design of the washcoat structure [27]. Detailed simulations resolve the local variations in temperature and species concentrations, which can lead to understanding complex catalyst behavior such as deactivation and hot-spot formation [8].

Although FIB-SEM techniques have been used to characterize a variety of samples [13, 14, 28–36], the application of this technique on highly porous media is relatively new and challenging. Prill et al. [37, 38] used a FIB-SEM technique for 3D reconstruction of a highly porous media and reported that, unlike the batteries and dense surfaces with less porosity, the interpretation of the FIB-SEM data are quite difficult due to the “shine-through” artifacts. They developed an algorithm for post-processing of the images where these shine-through artifacts were corrected after imaging. Salzer et al. [31] presented a similar approach on a highly porous monolithic foam-like silica material. Because the threshold between the fill material and solid was not

73 clear in the FIB-SEM image, a postprocessing algorithm was developed to
74 sharpen phase contrast by adaptive local thresholding.

75 **2. Three-dimensional imaging**

76 *2.1. Sample preparation*

77 The selected porous sample for this study is a commercial catalyst, which
78 was designed for fuel reforming technologies at the industrial level. Fig-
79 ure 1 illustrates the Rh- γ Al₂O₃ catalyst washcoated onto a 900 cpsi (cells
80 per square inch) monolith made of cordierite (supplied by Umicore AG). The
81 monolith structure has square flow channels that are approximately 0.77 mm
82 on each side [39]. The washcoat varies between 5-10 μ m on the 60 μ m thick
83 cordierite monolith walls.

84 A sample pretreatment method was developed to create high-quality
85 FIB-SEM images with good contrast between the epoxy and the washcoat.
86 A mixture of 98 wt% low viscosity epoxy (Buhler) and 2 wt% conduc-
87 tive polymer (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) from
88 Sigma Aldrich) was prepared. The viscosity was further decreased by adding
89 3-5 mL acetone to the 25 mL mixture. At such low viscosity, the epoxy can
90 sufficiently impregnate even the smallest pores.

91 The sample was embedded in the conductive epoxy mixture under vacuum
92 conditions to avoid bubbling. A custom vacuum apparatus was designed for
93 this purpose. The sample was placed in a small volume (100 ml) erlenmeyer
94 flask and evacuated until the pressure was below 5 mbar. Once the volume
95 was fully evacuated the conductive epoxy mixture was introduced through a
96 capillary tube. The sample was dried at 35 °C for 12 h.

[Figure 2 about here.]

The final sample formed a thick epoxy layer (≤ 1 mm). The excess epoxy layer first was removed mechanically using a sand paper until the epoxy layer on the top of the surface was approximately $100\text{ }\mu\text{m}$. The surface cleaning was completed by using a cross-section polisher (JEOL IB-09010CP). The cross-section polisher uses an argon beam to controllably mill the specimen surface. The accelerating voltage was 6 kV and the milling rate was $10\text{ }\mu\text{m}$ per hour. After these preparations, the specimen was ready for the three-dimensional FIB-SEM imaging.

2.2. FIB-SEM instrument

Three-dimensional imaging was accomplished using an FEI Helios 600i DualBeam instrument using FEI's Slice and View software. A 30 kV Ga-ion beam operating at 65 nA was used to remove 300 slices of 100 nm each, covering a total thickness of $30\text{ }\mu\text{m}$. Between each slice, a SEM image was captured by the thru-lens detector using a 5kV accelerating voltage and 1.4 nA beam current. The detector and image settings were adjusted to optimize the contrast between the catalyst and epoxy phases. Images were collected at a 52° angle relative to the milling direction with tilt correction employed to adjust the aspect ratio to that for a 90° incidence. The horizontal field of view was $46.5\text{ }\mu\text{m}$ with each pixel being approximately 23 nm per side.

The FIB-SEM experiments produce approximately three hundred two-dimensional slices that account for $26.7\text{ }\mu\text{m} \times 13.8\text{ }\mu\text{m} \times 37.4\text{ }\mu\text{m}$ of catalyst volume. The original FIB-SEM images are rendered on a gray-scale and are systematically notch-filtered and exposure-corrected to easily identify

121 the difference between epoxy and catalytic material. An adaptive threshold-
122 ing technique is used to discriminate between phases. The black-and-white,
123 filtered, FIB-SEM images indicate the location of alumina in white and in-
124 filtrating epoxy in black. Figure 2 illustrates a typical FIB-SEM slice before
125 and after filtering.

126 The quality of the FIB-SEM data is greatly enhanced by filling the micro-
127 pore structures with an appropriate material to create good contrast between
128 the pore and the catalyst material. Filling the pores also assists in decreasing
129 the amount of curtaining in the images from the FIB milling. The fill ma-
130 terial should have a different density than the catalytic material to obtain a
131 good contrast and it should be conductive so that the quality of the electron
132 beam images is not compromised.

133 **3. Reconstruction**

134 The FIB-SEM images are reconstructed into a complete three-dimensional
135 object using the MIMICS software.¹ Due to the nature of the machining pro-
136 cess, filtering, and the three-dimensional generation, some sequential images
137 are not perfectly aligned and some of the gray-scale is not easily identifi-
138 able as epoxy or catalytic material. With these minor adjustments in mind,
139 it is reasonable to assume some smoothing should be applied to the recon-
140 structed three-dimensional object. Wiedemann et al. [40] performed similar
141 procedures to three-dimensionally reconstruct cathode microstructures for
142 lithium-ion batteries.

¹Materialize, NV; Leuven, Belgium; <http://www.materialise.com>.

143

[Figure 3 about here.]

144

Figure 3 illustrates the smoothed, reconstructed, three-dimensional catalyst with various undulations, pores, and crevices on the surface. The reconstructed catalytic sample is so complex that rendering the full volume mesh and performing simulations is computationally very expensive. To reduce the size of the mesh, and thus the computational time, several representative surface pores were selected from the microstructure and modeled separately for in-depth study. Each of the pores are unique in structure, depth, and surface area. The pore's three-dimensional surface meshes are exported from MIMICS in STereoLithography (STL) format, which interfaces well with finite-volume meshing software.

154

[Figure 4 about here.]

155

Figure 4 illustrates the pore volumes for five pores that are extracted from the reconstructed catalyst sample. The figure also illustrates the surface area for each of the pores with respect to depth. As illustrated in Fig. 4, Pore Volume 1 is a structure with high surface area near the pore entrance that decreases deeper into the pore. The surface area of Pore Volume 2 is more uniformly distributed along its depth and resembles a crevice-like structure. Pore 2 does have a large section near the bottom that is significantly restricted from the rest of the pore volume. Pore Volume 3 presents a similar crevice-like feature with large surface area concentrated at the bottom of the pore. Pore Volume 4 has long spindly structures connecting the top of the pore to the majority of the active catalytic area near the bottom of the pore. Pore Volume 5 is the shortest pore with the least surface area of the five

167 pores considered in this study. The surface-area versus depth graphs (Fig. 4)
168 further illustrate the uniqueness of the selected pores and give an idea of
169 where possible pinch points may exist. However, the graphs alone do not
170 express the tortuosity that is evident in the three-dimensional renderings.

171 To study pore effectiveness alone, without including the catalytic activity
172 occurring on the washcoat’s external surfaces, each reconstructed pore is
173 isolated from the top-surface structure and the pore opening is cut as a
174 planar surface. Additionally, any small fragments of pore volume captured
175 in the reconstruction that are not connected to the external surface do not
176 participate in the reaction and are therefore removed from the computational
177 domain during the meshing process.

178 Although only five pore volumes are selected for detailed study, these
179 pores represent qualitatively the range of behaviors that can be observed
180 throughout the washcoat. In principle, many more pores could be recon-
181 structed for the purpose of identifying statistical characteristics across a
182 wide variety of the random pores. However, the time and cost to do so
183 is prohibitively high.

184 **4. Microstructural modeling**

185 Although the microstructural geometry is highly complex (cf., Fig. 4),
186 the reaction-diffusion model is greatly simplified. The simplicity is beneficial
187 in two ways. First, the results can be generalized in terms of dimension-
188 less groups such as the Damköhler number. Second, the computation time is
189 greatly reduced compared to a model that considers detailed multi-step reac-
190 tion kinetics and high-fidelity molecular transport. However, as discussed in

191 Section 4.3, the modeling approach can be extended to more complex global
 192 reactions.

193 The model assumes only two generic gas-phase species, A and B. The
 194 catalytic chemistry is represented simply as a first-order irreversible reaction
 195 $A \rightarrow B$, with a rate constant of k . Any possible gas-phase reaction is ne-
 196 glected. Within the pore volume, steady-state gas-phase diffusion of A is
 197 represented as

$$\nabla \cdot (D_{\text{pore}} \nabla C_A) = 0, \quad (1)$$

198 where C_A represents the concentration of A and D_{pore} is an pore diffusion
 199 coefficient. Because the length scale of the pore microstructure is so small,
 200 the pore diffusion, D_{pore} , may be a combination of Knudsen and bulk diffu-
 201 sion [41]. This formulation neglects any pressure variations and convective
 202 fluid flow within the microstructure, which is usually a good assumption in
 203 microscale pore-volume features. The active catalyst is assumed to be uni-
 204 formly distributed over the entire surface of the pore volume. Finally, the
 205 model assumes isothermal conditions.

206 Equation 1 is an elliptic partial differential equation whose solution re-
 207 quires boundary conditions. At the gas-surface interfaces within the pore-
 208 volumes the boundary condition is

$$\mathbf{n} \cdot D_{\text{pore}} \nabla C_A = k C_A, \quad (2)$$

209 where $\mathbf{n}$ is the outward-pointing normal unit vector at the catalyst surface.
 210 As may be inferred from Fig. 5, there may be on the order of 10,000 finite-
 211 volume surface elements where Eq. 2 applies. At the top of the pore volume
 212 (where the pore volume interfaces with the flow channel), the mole fraction

213 of A is assumed to be unity. In some circumstances, a particular pore-volume
 214 feature may intersect with the edge of the full three-dimensional volume (i.e.,
 215 Fig. 3). In this case, symmetry boundaries are enforced.

216 To assist generalizing performance metrics, the model can be put into
 217 dimensionless form using the characteristic scale factors. The length scale is
 218 defined as

$$L = \frac{V_p}{A_s}, \quad (3)$$

219 where V_p and A_s are the pore volume's volume and surface area, respectively.
 220 Although the geometry is complex, these values can be easily extracted from
 221 the three-dimensional reconstructions. The characteristic concentration is
 222 taken to be $C_{A,\text{top}}$, which is assumed to be pure species A at the top of the
 223 pore. Using these scale factors, the dimensionless variables are

$$\hat{C}_A = \frac{C_A}{C_{A,\text{top}}}, \quad \hat{x} = \frac{x}{L}, \quad \hat{y} = \frac{y}{L}, \quad \hat{z} = \frac{z}{L}. \quad (4)$$

224 Upon transformation with these scale factors, the dimensionless form of the
 225 conservation equation and boundary condition can be expressed as

$$\nabla^2 \hat{C}_A = 0, \quad (5)$$

226

$$\mathbf{n} \cdot \nabla \hat{C}_A = \text{Da} \hat{C}_A. \quad (6)$$

227 A single dimensionless parameter, the Damköhler number, appears in the
 228 boundary condition,

$$\text{Da} = \frac{kL}{D_{\text{pore}}}. \quad (7)$$

229 The Damköhler number Da is parameterized by the first-order kinetic rate
 230 constant k , the pore diffusion coefficient D_{pore} , and the length scale, L . High
 231 reaction rates, compared to diffusion rates, lead to high Damköhler numbers.

Equation 7 unambiguously defines the Damköhler number that is used in the present study. However, it may be noted that alternative definitions of the Damköhler number are used in the chemical engineering literature, with their precise definitions depending on the context. For example, it is common to define a Damköhler number that represents the competition between diffusive resistance associated with the monolith channel-flow mass-transfer boundary layer and net the reaction rate at the washcoat interface. Because the present study is concerned entirely with reaction-diffusion behavior within pores, and not concerned with the monolith channel flow, such a Damköhler number definition is not appropriate.

4.1. Computational solution

Although the pore volumes are geometrically complex, the governing conservation equation is linear. The equation is solved on a finite-volume mesh using the ANSYS FLUENT software.

A finite-volume mesh for each reconstructed pore volume is generated using the ANSYS TGRID software² with a cut-cell meshing scheme. Cut-cell meshing adapts to the surface of the pore volume and increases in mesh density near edge interfaces. Figure 5 illustrates the cut-cell meshing scheme for one of the pores. With geometries as complex as the pore volumes, highly skewed or otherwise poor mesh volumes can be problematic. By using TGRID’s internal re-meshing and node optimization algorithms, low-quality mesh volumes are significantly decreased or eliminated. A typical pore contains about 500,000 finite-volume cells, with some pores requiring around a

²ANSYS, Inc; Canonsburg, PA; <http://www.ansys.com>.

255 million cells.

256 [Figure 5 about here.]

257 Once a mesh is generated, the equations are solved using the ANSYS
258 FLUENT software. Boundary conditions (Eq. 6) must be assigned to all
259 gas-surface interfaces. The present study models each of the five selected
260 pore volumes with five different values of Damköhler number ($10^{-5} \leq Da \leq$
261 10^{-1}). The computation times depend on the Damköhler number, with lower
262 Damköhler numbers requiring more computation because more of the pore
263 geometry is catalytically available. Simulation times varied between thirty
264 minutes to forty hours on sixteen parallel processors.

265 The output metrics for each pore volume are evaluated from the ANSYS
266 FLUENT solution through a User-Defined-Function (UDF). The UDF is writ-
267 ten to compute the area-normalized flux of the product species out of the
268 pores at their uppermost faces. Additionally, the reaction rates and mesh
269 statistics are evaluated on all the reactive surfaces within the pore volume
270 to determine the depths of reaction.

271 As in most large-scale finite-volume computational simulations, it is im-
272 portant to demonstrate that the results are independent of the mesh resolu-
273 tion. This study measured mesh independence in terms of the net product
274 flux from a pore volume. Especially for the lowest Damköhler numbers, where
275 most of the pore surfaces are catalytically available, the solutions can depend
276 significantly on mesh resolution. When mesh resolution is inadequate, the
277 product fluxes tend to oscillate and not reach a steady asymptotic result.
278 The meshes used for the reported results are always refined to the point that
279 the product fluxes are steady and independent of the meshing.

280 4.2. Pore performance metrics

281 Once a solution is found for a particular pore volume, summary perfor-
 282 mance metrics can be evaluated. Consider first the product species flux (here,
 283 species B) emerging from the pore opening, where the pore meets the flow
 284 channel. The flux can be evaluated as

$$J_p = \frac{\int_{\text{top}} D_{\text{pore}} \nabla C_B \cdot \mathbf{n} \, dA}{A_p}, \quad (8)$$

285 where A is the surface defining the pore-volume opening to free-stream flow,
 286 and A_p is the total pore-volume opening area. The integral is needed because
 287 the solution is represented locally on the discrete mesh network.

288 It is useful to normalize pore flux by the flux that would be produced by
 289 a catalytic flat plate with the same surface area as the pore-opening area.
 290 Continuing to assume first-order kinetics and fixed composition of species A,
 291 the flat-plate flux can be written as

$$J_o = C_{A,\text{top}} k. \quad (9)$$

292 The normalized pore flux Γ_p follows as

$$\Gamma_p = \frac{J_p}{J_o} = \frac{\int_{\text{top}} D_{\text{pore}} \nabla C_B \cdot \mathbf{n} \, dA}{C_{A,\text{max}} k A_p}. \quad (10)$$

293 In dimensionless terms, which is the form delivered from the three-dimensional
 294 simulations, the normalized effective product flux can be written as

$$\Gamma_p = \frac{1}{\text{Da}} \frac{\int_{\text{top}} \nabla \hat{C}_B \cdot \mathbf{n} d\hat{A}}{\hat{A}_p}. \quad (11)$$

295 The normalized flux compares the catalytic performance of a pore to an
 296 equivalent-area flat washcoat. A value of unity for Γ_p indicates that a pore

297 is producing an equivalent product species flux as a flat catalytic surface of
 298 the same area as the pore opening.

299 Another measure of pore performance is the pore effectiveness η_p , which
 300 is evaluated as

$$\eta_p = \Gamma_p \frac{A_p}{A_s}. \quad (12)$$

301 The pore effectiveness measures the flux of product leaving the pore volume
 302 compared to the maximum possible flux if all catalytic surfaces were exposed
 303 to free stream conditions. The pore effectiveness is unity if there are no mass-
 304 transport limitations within the pore.

305 Yet another relevant measure of washcoat performance is the pore depth
 306 beyond which any additional catalyst is unused. If reaction rates are high
 307 (relative to diffusion), then most reaction occurs near the pore opening and
 308 relatively shallow pores are appropriate. The present study measures the
 309 pore depth $\hat{Z}_{95}$ by which 95% of the catalytic reaction has been completed.

310 4.3. Possible extensions

311 The present model is based upon a single, irreversible, first-order reaction
 312 ($A \rightarrow B$), which enables the generalization in terms of a Damköhler number
 313 as a single dimensionless parameter. However, if the chemistry and transport
 314 can be represented with single parameters, the approach can be extended to
 315 more complex chemistry. Consider, for example, steam reforming that might
 316 be expressed globally as

317

318 Assume further that the process is rate-limited by the methane activation,
 319 with the water-gas-shift reaction remain in equilibrium. In this case, the
 320 single reaction-rate parameter is the forward rate constant for Eq. 13. Other
 321 parameters include the equilibrium constants, which depend on known gas-
 322 phase thermodynamics. Empirical representations of a steam-reforming rate
 323 expression are available (e.g., [42–44]). Additionally, modeling the microstruc-
 324 tural transport problem also requires at least pore diffusion coefficients for
 325 the four gas-phase species. A characteristic Damköhler number can be de-
 326 fined as a function of the ratio of the pre-exponential factor for forward rate
 327 constant associated with reaction 13 and the pore diffusion coefficient. The
 328 model must solve for four species gas-phase species, not two as in the present
 329 model. The local catalytic species production rates depend on the reaction
 330 orders in the empirical rate expression and the local species composition
 331 through the pore volume.

332 In principle, the model can also accommodate large elementary-step reac-
 333 tion mechanisms (e.g., [45–47]) and the software is in place to do so. However,
 334 the computational problem is very much larger. In addition to needing more
 335 gas-phase species, the reaction mechanisms also involve surface adsorbates.
 336 Moreover, with detailed chemistry there is no possibility to generalize the
 337 results in terms of a single parameter.

338 5. Illustrative results

339 [Figure 6 about here.]

340 [Figure 7 about here.]

341 [Figure 8 about here.]

342 [Figure 9 about here.]

343 [Figure 10 about here.]

344 Figures 6 - 10 show the influence of the Damköhler number on pore per-
345 formance within different pore volumes. Despite the qualitative shape dif-
346 ferences within the pores, similar Damköhler numbers produce qualitatively
347 similar species profiles. For example, species-A penetration depth is rea-
348 sonably well characterized by the Damköhler number within all of the pore
349 volumes. This is a desirable result in the sense that the important aspects
350 of the pore-scale reaction-diffusion processes may be represented in a di-
351 mensionless setting that only weakly depends on the detailed pore-volume
352 microstructural geometry. At relatively high Damköhler numbers, the reac-
353 tion is mainly concentrated at the pore openings leaving most of the catalytic
354 area deeper in the pores underutilized. However, as the Damköhler number
355 decreases the reaction is able to penetrate further into the pores. In this
356 case, the net reaction can depend on local diffusion resistances, such as small
357 necking regions.

358 The pore-volume simulations illustrate the influences of local geometric
359 features within pores. Figure 6 shows that Pore 1 has a highly tortuous
360 structure. As the Damköhler number decreases, Pore 1 contains more of
361 reactant species A. The species profiles indicate that as the kinetic rate is
362 decreased relative to the effective diffusion rate (low Damköhler number) the
363 reactant is able to reach more of the available catalytic surface. However,

364 there are significant choke points in Pore 1 near the bottom of the pore,
365 which limit access to some catalyst area.

366 Figures 7 and 8 illustrate species concentration simulation results for
367 Pores 2 and 3 respectively. Both of these pores contain significant choke
368 points. The simulation results indicate that the apparent pore tortuosity
369 greatly influences pore performance. Pore 2 (Fig. 7) and Pore 4 (Fig. 9)
370 present two different species rates of progress as a function of Damköhler
371 number. Pore 2 is characterized by a relatively open crevice-like structure.
372 Thus, the diffusion resistance is relatively low, enabling the reactant to pen-
373 etrate deep into the pore even at relatively high Damköhler numbers. In
374 Pore 2 a small change in diffusion rate can significantly increase the effective
375 utilization of catalytic surface area. On the other hand, Pore 4 is charac-
376 terized by long thin features that connect the opening of the pore to the
377 deeper catalytic surface areas. These thin capillary-like features restrict the
378 reactant from penetrating into the pore and subsequently limit the effective
379 surface area. Thus, Pore 4 is less sensitive to diffusion rate as compared
380 to Pore 2. The Pore 5 (Fig. 10) diffusion resistances are similar to those
381 in Pore 2. These pores are generally more open, without significant inte-
382 rior choke points, where the reactant can penetrate deep into the volume at
383 higher Damköhler number. Because Pore 5 is quite shallow compared to the
384 other four pore volumes, accessing all the available catalytic surface area is
385 easier.

386 [Figure 11 about here.]

387 Figure 11 illustrates some quantitative performance measures for the five
388 pore-volume simulations. The three plots show the effective normalized pore

389 flux Γ_p (top), pore effectiveness η_p (middle), and reaction depth $\hat{Z}_{95}$ (bottom)
 390 as functions of Damköhler number. Some expected trends are apparent. For
 391 high Damköhler numbers (relatively fast reaction) all measures tend toward
 392 zero (or unity in the case of Γ_p). Conversely, as the Damköhler number
 393 decreases (relatively high diffusion), reaction depth approaches 100%, pore
 394 effectiveness tends toward unity, and the respective normalized fluxes diverge
 395 from one another. This suggests the morphological differences between pores
 396 are largely only relevant to flux performance at low Damköhler numbers. It
 397 appears that while all the pore volumes sampled in this study produce near-
 398 unity effectiveness and near-100% reaction depth at low Damköhler numbers,
 399 there are clear performance differences from one pore to another. Pore 1
 400 produces approximately 70 times the effective normalized product species
 401 flux of a flat plate, while Pore 5 delivers only a factor of approximately 18.
 402 Referencing the pore-volume reactive surface area measures in Table 1, it
 403 is clear this effect is not simply a function of available catalytic area but
 404 also of more complex morphological differences (e.g., pinch points, pore-like
 405 features, crevice-like structures).

406 [Table 1 about here.]

407 6. Summary and conclusions

408 The catalyst washcoats from a commercial Rh- γ Al₂O₃ partial-oxidation
 409 monolith are reconstructed using focused-ion-beam–scanning-electron-microscopy.
 410 The three-dimensional reconstructions reveal complex microscale surface and
 411 pore morphology. The micro-morphology is quite different from notional
 412 models based on isotropic porous media or arrays of cylindrical pores. The

413 structure of individual pores can vary significantly, ranging from crevice-like
414 features to tortuous capillary-like features.

415 New models are developed and applied to investigate reaction-diffusion
416 processes within reconstructed pore volumes. Assuming first-order kinetics
417 and constant diffusion coefficients, the problem can be cast in dimensionless
418 variables with a Damköhler number emerging as a characteristic dimension-
419 less group. The three-dimensional reaction-diffusion problem is solved within
420 the geometrically complex pore structures. In addition to predicting local
421 concentration fields and reaction rates within the pore volumes, the model
422 also predicts summary information such as net product flux from the pore,
423 pore effectiveness, and reaction penetration depth. These results depend
424 greatly on the Damköhler number.

425 The paper contributes new quantitative insight about the performance of
426 actual catalyst washcoats. A companion paper [4] uses predicted results from
427 the microscale reconstructed pore volumes to develop macroscale models that
428 can be applied at larger length scales.

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Table 1: Reconstructed sample pore area statics

Parameter	Value
Pore 1 catalytic surface area, $A_{s,1}$,	190.5 μm^2
Pore 2 catalytic surface area, $A_{s,2}$	233.7 μm^2
Pore 3 catalytic surface area, $A_{s,3}$	203.9 μm^2
Pore 4 catalytic surface area, $A_{s,4}$	288.9 μm^2
Pore 5 catalytic surface area, $A_{s,5}$	54.9 μm^2