Controlling reactivity of nanoporous catalyst materials by tuning reaction product-pore interior interactions: Statistical mechanical modeling

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Keywords
catalytic conversion, enhanced transports, irreversible reactions, nano-porous catalysts, reaction diffusion equations, linear equations, mathematical models, porous materials

Disciplines
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Comments

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Controlling reactivity of nanoporous catalyst materials by tuning reaction product-pore interior interactions: Statistical mechanical modeling

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I. INTRODUCTION

Advances in synthesis of nanomaterials have led to broad capabilities for multifunctionalization of mesoporous or nanoporous catalysts. Such capabilities allow for not only effective functionalization with catalytic groups but also the possibility to tune the interaction between reaction products and the interior pore environment.1–3 This can in turn significantly impact and potentially enhance catalytic reactivity. For example, creation of an unfavorable environment for product species within pores can lead to enhanced product ejection or inhibited product reentry. This feature would shift the equilibrium of reversible reactions towards completion. Other possible scenarios are discussed below.

One class of examples of the above type is provided by dehydration reactions such as esterification (acid + alcohol ↔ ester + water) in mesoporous silica nanoparticles (MSN). Multifunctionalization of MSN to include hydrophobic groups, as well as catalytic groups, has been observed to significantly enhance reactivity in several such systems.4–6 This effect has been explained as a result of functionalization converting an intrinsically hydrophilic interior pore surface of MSN into a hydrophobic environment thereby “expelling” the product water and shifting the equilibrium of the reversible esterification reaction. The greatest enhancement to date has been achieved through solvent-mediated control of the configuration of hydrophobic 3-(pentafluorophenyl) propyl groups which are induced to lie prone on silica surface thereby minimizing the interaction of the product water with the hydrophilic MSN surface groups.6, 7

In fact, there are several possible scenarios wherein functionalization to tune product-pore interactions can influence both the thermodynamics and the kinetics of transport and reaction, and thereby impact reactivity in meso- or nanoporous reaction systems. First, we discuss thermodynamic factors. Accounting for detailed balance requirements, it follows that creating an unfavorable environment for a reaction product within the pore increases the ratio of the rate of product desorption from the pore opening to that for product (re)adsorption. One should note that product readsorption can become significant for substantial conversion of reactant to product in the surrounding fluid. However, even constraining rates to satisfy detailed balance, there are still many distinct possibilities for rate behavior: (i) the product desorption rate could be tied to the rate of diffusion within the pore, and thus the rate of readsorption would be inhibited for stronger interior pore-product repulsion; (ii) the product readsorption rate could be tied to the rate of external diffusion, and thus the rate of desorption would be enhanced for stronger interior pore-product repulsion; (iii) more general cases where both rates change. Any of these cases will result in a shift of equilibrium for reversible reactions.

Second, we discuss other kinetic factors that can impact reactivity, but which are unrelated to shift of equilibrium for reversible reactions. Although not dictated by thermodynamic considerations, diffusive transport within the pore can also be modified by multifunctionalization. An unfavorable environment could enhance diffusion removing localized regions of strong binding and thereby “smoothing” interaction with the pore walls. Another possible scenario is that modifying the interior pore environment can change loading of product in the pore even for irreversible reactions. The loading can have a...
dramatic effect on effective transport for narrow pores, especially in the single-file diffusion (SFD) regime where species cannot pass each other in the pore, and this in turn greatly impacts reactivity. To test this latter effect, we will naturally consider the special case of irreversible reactions.

Our focus in this contribution is on exploring the effects of multifunctionalization for simple first-order catalytic conversion reactions (A to B) in mesoporous or nanoporous materials such as MSN consisting of parallel arrays of effectively identical linear nanopores. A key factor impacting reactivity is the extent to which reactants and products A and B can pass each other. Previous analyses for SFD or restricted passing\(^8\)\(^–\)\(^{15}\) reveal that reaction is strongly localized near the pore openings.\(^9\) While simple mean-field (MF) type reaction-diffusion equations\(^8\)\(^,\)\(^\text{11–13}\) are not adequate, recent studies have shown that behavior in this regime is captured by a “generalized hydrodynamic” (GH) formulation which accounts for both the effect of restricted passing on chemical diffusion as well as fluctuation effects in adsorption-desorption at pore openings.\(^14\) Here, we adopt the latter rather than computationally more expensive kinetic Monte Carlo (KMC) simulation which could also provide a precise characterization of model behavior.

In Sec. II, we describe our model for conversion reaction in linear nanopores, the associated exact master equations, and associated generalized hydrodynamic reaction-diffusion equations (RDE). In Sec. III, we present results for both irreversible and reversible conversion reactions focusing on reactivity (i.e., turn-over frequency) per pore as a function of the fraction of reactant converted to product, and contrasting behavior for pores where product entry in enhanced versus inhibited. Our conclusions are presented in Sec. IV.

II. SPATIALLY DISCRETE MODEL FOR CATALYTIC CONVERSION INSIDE LINEAR NANOPORES

A. Spatially discrete stochastic reaction-diffusion model prescription

Our model for catalytic conversion describes nanoporous materials which consist of a parallel array of linear pores by partitioning the continuous-space pores into adjacent cells labeled \(n = 1\) to \(L\).\(^8\)\(^–\)\(^{14}\) The cell width “\(a\)” is selected to be comparable to the species size \(\sim 1\) nm. Species within pores are regarded as localized to specific cells, and diffusive transport is treated as hopping or exchange between adjacent cells. To describe the surrounding fluid, we extend the 1D lattice of cells inside the pores to a 3D lattice outside. See Fig. 1.

We specify “external” reactant and product concentrations in the surrounding fluid at each stage of the reaction as \((A_{\text{out}})\) and \((B_{\text{out}})\), for a fixed total concentration \((X_{\text{out}}) = (A_{\text{out}}) + (B_{\text{out}})\). These correspond to the probabilities that sites or cells on the 3D lattice are occupied by various species, where fluid cell occupation is assumed random due to efficient stirring. Then, \((A_{\text{out}})\) will decrease from an initial value of \((X_{\text{out}})\), and \((B_{\text{out}})\) will increase from zero with increasing fraction, \(F = (B_{\text{out}})/(X_{\text{out}}) = 1 - (A_{\text{out}})/(X_{\text{out}})\), of the initial reactant converted to product.\(^14\)\(^,\)\(^{15}\)

Following most previous stochastic modeling of reaction-diffusion processes in linear nanopores,\(^8\)\(^–\)\(^{15}\) the simplest prescription for diffusion dynamics within the pores is that A and B hop to adjacent empty (E) sites at rate \(h\), corresponding to a diffusion rate of \(D_0 = a^2h\) for isolated particles. This simple prescription would correspond to single-file diffusion with a strict no-passing constraint. For a more general treatment of diffusional dynamics, we also allow positional exchange of adjacent A and B at rate \(P_{\text{ex}}\), thereby relaxing the strict single-file constraint. (Note that exchange of adjacent particles of the same type has no effect.) The passing propensity, \(P_{\text{ex}}\), will increase with the effective pore diameter, \(d\), from \(P_{\text{ex}} = 0\) for \(d\) below a threshold for SFD, to \(P_{\text{ex}} = 1\) for large \(d\) and unhindered passing.

In addition to hopping or exchange within the pore, the other mechanistic steps in the model (see Fig. 1) are as follows: (i) Adsorption of external reactant A (product B) to terminal pore sites \(n = 1\) and \(n = L\) at rate \(h\) (\(\alpha h\)), provided that these end sites are unoccupied or empty (E). We emphasize that the factor \(\alpha\) will account for the effects of multifunctionalization modifying the interior pore-reaction product interaction. (ii) Desorption of both the reactant, A, and product, B, from terminal sites of the pore at rate \(h\) provided that the fluid site just outside the pore is unoccupied (\(E_{\text{out}}\)). The probability for this fluid site to be unoccupied is given by \((E_{\text{out}}) = 1 - (X_{\text{out}})\). (iii) Conversion \(A \rightarrow B\) at catalytic (c) sites within the pore at rate \(k\), as well as the reverse reaction \(B \rightarrow A\) at rate \(k'\). Our model can treat general distributions of catalytic sites, but here we shall assume that all sites are catalytic. (iv) One could also consider exchange in and out of the pore.

FIG. 1. Schematic of the A to B conversion reaction model illustrating processes within pores (shaded light blue), as well as coupling to the surrounding fluid. In-out exchange processes are not shown (but are active in our modeling). “c” denotes catalytic sites.
One choice is to ignore such processes. Another plausibly more realistic choice is to specify that A (B) just outside exchanges with B (A) inside at $n = 1$ or L at rate $P_{ex}$ h ($\alpha P_{ex}$ h). Both choices (and others) are consistent with detailed balance. We expect that the choice will not greatly effect of reactivity (except in the special regime of both high $P_{ex}$ and high loading).

It should be emphasized that there is a natural “separation of time scales” for “local” relaxation (in time) of concentration profiles within the pore, and for “global” equilibration of the entire system including the fluid. Relaxation of concentration profiles to a local steady state form determined by the current values of $\langle A_{out} \rangle$ and $\langle B_{out} \rangle$ should be effectively instantaneous on the time scale of global equilibration of the entire system (which in experiments is on the order of hours). Thus, the main challenge is to solve the non-trivial statistical mechanical local steady state problem to determine reactant and product concentration profiles, and thus the reactivity, as a function of the fractional conversion, $F = \langle B_{out} \rangle / \langle B_{out} \rangle$, of reactant to product. It should also be noted that the global equilibrium values of $\langle A_{out} \rangle$ and $\langle B_{out} \rangle$, and thus of $F = \langle B \rangle_{eq}$, are determined not just by the equilibrium constant $K_c$ for the conversion reaction within the pores, but also by the parameter $\alpha$. This issue is addressed immediately below.

For the above model, it is clear that the “color-blind” dynamics for particles X = A + B (i.e., A or B) is described by a non-reactive diffusion process where particles hop within the pore and desorb at rate h. At a specified fractional conversion, $F$, particles adsorb at an effective rate $h_{ads} = h_{ads}(F)$ with $e_{ads} = e_{ads}(F) = (1 - F) + \alpha F$, where the first (second) term is the weighted contribution from A (B) adsorption. In the local steady state for fixed $F$, all sites within the pore are randomly occupied by particles, X, with equal probability $\langle X_{in} \rangle = \langle X_{in}(F) \rangle$, say. Then, balancing the adsorption flux, $J_{ads}$, and desorption flux, $J_{des}$, for particles X where

$$J_{ads} = h_{ads}(F)\langle X_{out}(1 - \langle X_{in} \rangle) \rangle \quad \text{and} \quad J_{des} = h(1 - \langle X_{out} \rangle)\langle X_{in}(1 - \langle X_{in} \rangle) \rangle \quad (1)$$

$$\langle X_{in} \rangle = e_{ads}(\langle X_{out} \rangle)/(1 + e_{ads} - 1)\langle X_{out} \rangle \rangle = [1 + (\alpha - 1)F]\langle X_{out} \rangle/(1 + (\alpha - 1)F)\langle X_{out} \rangle \}. \quad (2)$$

We recall that $\langle X_{out} \rangle$ remains constant at its initial value. As expected, (2) demonstrates that $\langle X_{in} \rangle$ exceeds $\langle X_{out} \rangle$ for $\alpha > 1$ (enhanced product reentry), and that $\langle X_{out} \rangle$ exceeds $\langle X_{in} \rangle$ for $\alpha < 1$ (inhibited reentry).

A simple analysis of individual species concentrations in the local steady state is not possible since these concentrations exhibit non-trivial spatial profiles within the pore. However, in the final global equilibrium state, concentrations of both species within the pore, $\langle A_{in} \rangle_{eq}$ and $\langle B_{in} \rangle_{eq}$, are spatially uniform, and satisfy $\langle B_{in} \rangle_{eq}/\langle A_{in} \rangle_{eq} = K_c$. Then, separately balancing the adsorption and desorption fluxes for species A and for species B yields

$$\langle A_{out} \rangle_{eq}(1 - \langle X_{in} \rangle_{eq}) = \langle A_{in} \rangle_{eq}(1 - \langle X_{out} \rangle) \quad \text{and} \quad \alpha\langle B_{out} \rangle_{eq}(1 - \langle X_{in} \rangle_{eq}) = \langle A_{in} \rangle_{eq}(1 - \langle X_{out} \rangle) \quad (3)$$

so that

$$\langle B_{out} \rangle_{eq}/\langle A_{out} \rangle_{eq} = \alpha^{-1}(\langle B_{in} \rangle_{eq}/\langle A_{in} \rangle_{eq}) = K_c/\alpha \quad \text{and} \quad F_{eq} = K_c/(K_c + \alpha). \quad (4)$$

The latter result characterizes the shift in equilibrium for our model associated with tuning of the reaction product-pore interior interaction via multifunctionalization. We thus find that $\langle X_{in} \rangle$ changes from its initial value of $\langle X_{out} \rangle$ at the onset of the reaction ($F = 0$) to

$$\langle X_{in} \rangle_{eq} = \alpha(1 + K_c)\langle X_{out} \rangle/(\alpha(1 + K_c)\langle X_{out} \rangle + K_c(1 - \langle X_{out} \rangle)), \quad (5)$$

when $F = F_{eq}$, at completion of the reaction. This result (5) recovers the requirement that $\langle X_{in} \rangle_{eq} = 0$ for blocked product reentry $\alpha = 0$. It also shows that for enhanced reentry with, e.g., $\alpha = 5$ and $\langle X_{out} \rangle = 0.8$ (the case considered below), one has $\langle X_{in} \rangle_{eq}/\langle X_{out} \rangle = (1 + K_c)/(1 + 0.84K_c) > 1$.

### B. Exact master equations and discrete reaction-diffusion equations

An exact description of our discrete reaction-diffusion model is provided by the master equations for the evolution of probabilities of various configurations within the pore. Often these are written in hierarchical form.\(^8,11-15\) Here, we use ($C_{eq}$) to denote the probability or ensemble averaged concentration for species C = A or B at site n (or for this site to be empty when C = E), ($C_{eq}E_{n+1}$) for the probability that C is at site n and for site n + 1 to be empty (E), etc. Then, the lowest-order equations in the hierarchy describe the evolution of single-site occupancies.

For A to B conversion in the case where all sites are catalytic, one has that

$$d/dt(A_n) = -k(A_n) + k'(B_n) - \nabla J_{A^{n-n+1}} \quad (6a)$$

and

$$d/dt(B_n) = +k(A_n) - k'(B_n) - \nabla J_{B^{n-n+1}} \quad \text{for } 1 < n < L, \quad (6b)$$

where we have defined the discrete derivative, $\nabla G_n = G_n - G_{n-1}$. The net diffusion flux, $J_{A^{n-n+1}}$, of A from site n to n + 1 due to both hopping and exchange is given by

$$J_{A^{n-n+1}} = h[(A_{E_{n+1}}) - (E_{A_{n+1}})] + P_{ex}h[(A_{B_{n+1}}) - (B_{A_{n+1}})]. \quad (7)$$

The expression for the net flux, $J_{B^{n-n+1}}$, of B is analogous. Separate equations for terminal sites reflect adsorption-desorption boundary conditions (BCs). In the presence of in-out exchange with rates as specified in Sec. II A, one has that

$$d/dt(A_1) = h(A_{out})/(E_1) - h(E_{out})(A_1) + P_{ex}h(A_{out})(B_1) - P_{ex}h(B_{out})(A_1) - k(A_1) + k'(B_1) - J_{A^{1-2}} \quad \text{and} \quad (8a)$$
and

\[
\frac{d}{dt}(B_1) = \alpha h(B_{\text{out}})(x) - h(E_{\text{out}})(x) + P_{\text{ex}} \alpha h(B_{\text{out}})(A_1) - P_{\text{ex}} h(A_{\text{out}})(B_1) + k(A_1) - k'(B_1) - J_B^{1.12},
\]

\[\text{(8b)}\]

with analogous equations for concentrations at site \( n = L \). If some sites are not catalytic, then the reaction terms are absent for such sites. Defining \( \Delta A_n = \langle A_n \rangle - K^{-1}_c(B_n) \) as the “excess” reactant concentration, the net overall rate of production of \( B \) per pore is given by

\[
R_{\text{ex}}^B = \sum_{n=c} (k(A_n) - k'(B_n)) = k \sum_{n=c} \langle \Delta A_n \rangle
\]

\[\text{(9)}\]

summing over all catalytic sites, \( c \).

Equations (6a) and (6b) couple to various pair probabilities in (7). Pair probability evolution is coupled to triples, etc., producing a hierarchy. Pair and multisite probabilities are not simply related to single-site probabilities due to spatial correlations. A simple MF factorization approximation, \( C_n E_{n+1} \approx C_n (E_{n+1}) \), etc., produces a closed set of discrete RDEs for single-site concentrations. However, this approximation, and even higher-order pair, triplet, etc., approximations, fundamentally fail to capture model behavior, at least for low reactivity \( k/h \ll 1 \) when \( P_{\text{ex}} \ll 1 \). Thus, below we discuss an alternative “generalized hydrodynamic” approach which does reliably describe model behavior. As an aside, in the special case \( P_{\text{ex}} = 1 \) (unhindered passing of \( A \) and \( B \)), (7) reduces exactly to \( J_A^{n \rightarrow n+1} = h[C_n] - \langle A_{n+1} \rangle = -h \nabla \langle A_n \rangle \), and similarly for \( J_B^{n \rightarrow n+1} \). This yields an exact set of discrete RDE matching the MF approximation.

C. Generalized hydrodynamic reaction-diffusion equations

For smoothly varying concentrations within the pore, it is natural to consider a coarse-grained description of the spatially discrete reaction-diffusion model which regards the species concentrations per unit length, \( C(x = na) \approx a^{-1}(C_n) \), as functions of a continuous spatial variable \( x \) (leaving the \( t \)-dependence implicit), and denote the total concentration by \( X(x) = A(x) + B(x) \). The continuum RDE for our \( A \) to \( B \) conversion reaction model with all sites catalytic then have the form

\[
\frac{\partial}{\partial t} A(x) = -k A(x) + k' B(x) - \partial / \partial x J_A \quad \text{and}
\]

\[
\frac{\partial}{\partial t} B(x) = +k A(x) - k' B(x) - \partial / \partial x J_B.
\]

\[\text{(10)}\]

If only portions of the pore are catalytic, then reaction terms appear just for those locations. BCs for (10) at the pore ends reflect the adsorption-desorption dynamics, i.e., one balances the diffusion fluxes at the end of the pore with the net adsorption-desorption rate for each species. Description of the diffusion fluxes, \( J_A \) and \( J_B \), is non-trivial.

Analysis from the theory of interacting particle systems\cite{17,18} for the hydrodynamic regime of slowly varying concentrations suggests the general form\cite{13,14,17,18}

\[
J_A = -D_0[1 - X^{-1}(1 - F_{\text{tr}})B] \partial A / \partial x
\]

\[\quad - D_0 X^{-1}(1 - F_{\text{tr}})A \partial B / \partial x.
\]

\[\text{(11)}\]

In this expression, one has \( D_0 = a^2 h \) and \( F_{\text{tr}} \) is related to a tracer diffusion coefficient for particles within the pore by \( D_0 = D_{\text{p}} F_{\text{tr}} \). In applying the form (11), we utilize the feature that the diffusive dynamics for both \( A \) and \( B \) within the pore is identical. An analogous expression applies for \( J_B \). Here, it suffices to consider the local steady state regime with uniform total concentration, \( X = \langle X_n \rangle = \langle X_n(k) \rangle \), corresponding to a counter-diffusion mode\cite{19} where \( \partial A / \partial x = -\partial B / \partial x \). Then, (11) and the analogous expression for \( J_B \) simply reduce to\cite{13,19}

\[
J_A = -D_0 \partial A / \partial x \quad \text{and} \quad J_B = -D_0 \partial B / \partial x.
\]

\[\text{(12)}\]

In the MF treatment, \( X^{-1}(1 - F_{\text{tr}}) \) in (11) is replaced by \( 1 - P_{\text{ex}} \) which corresponds to the assignment \( F_{\text{tr}} = F_{\text{tr}}(\text{MF}) = 1 - (1 - P_{\text{ex}}) X \). However, this MF choice overestimates diffusion fluxes within the pore, and thus overestimates overall reactivity, especially for the quasi-SFD regime, \( P_{\text{ex}} \ll 1 \) and \( F_{\text{tr}}(\text{MF}) \approx 1 - X \).\cite{12,13} A contrasting deterministic hydrodynamic (DH) formulation of \( F_{\text{tr}} \), applicable for large systems (very long pores) with slowly varying concentrations and negligible fluctuation effects, follows from a precise analysis of tracer diffusion for effectively infinite systems. One finds that the corresponding \( F_{\text{tr}} = F_{\text{tr}}(\text{DH}) = F_{\text{tr}}(X, P_{\text{ex}}) \) has the form shown in Fig. 2. Simple limiting behavior includes

\[
F_{\text{tr}}(\text{DH}) \rightarrow 1, \quad \text{as} \quad F_{\text{ex}} \rightarrow 1 \quad \text{and} \quad F_{\text{tr}}(\text{DH}) \rightarrow 0, \quad \text{as} \quad X \rightarrow 1; \quad \text{and}
\]

\[
F_{\text{tr}}(\text{DH}) \rightarrow 0, \quad \text{as} \quad P_{\text{ex}} \rightarrow 0 \quad \text{(for} \quad X > 0). \quad \text{(13)}
\]

The latter behavior for \( P_{\text{ex}} = 0 \) is in marked contrast to the MF form, and reflects the anomalous nature of SFD wherein the mean-square displacement of a tagged particle increases sublinearly.\cite{20} To account for the finite length of pores, we have considered a refinement of the DH choice where \( F_{\text{tr}} \sim 1/L \) for SFD when \( P_{\text{ex}} = 0.21 \) This modified choice was motivated by analyses of transport through channels across membranes of finite width.\cite{22} However, choosing either \( F_{\text{tr}} = 0 \) or \( F_{\text{tr}} \sim 1/L \) for SFD understimates diffusion fluxes at least

![FIG. 2. Behavior of the conventional (DH) tracer diffusion coefficient, \( F_{\text{tr}}(\text{DH}) \), for infinite systems as a function of pore loading \( X_m \) for various passing probabilities, \( P_{\text{ex}} \) (shown).](image-url)
near pore openings, and thus underestimates the overall reactivity.21

To address the shortcomings of the MF and DH approaches described above, we will utilize a GH treatment23 which incorporates a position-dependent $F_{tr}(x = na) = F_{tr}(GH)$. This $F_{tr}(x = na)$ is enhanced near pore openings above the deterministic hydrodynamic value of $F_{tr}(DH)$.14

This enhancement of $F_{tr}(GH)$ reflects the influence of stochastic adsorption-desorption processes which facilitate transport in and out of the pore near these pore openings.14 Results are shown in Fig. 3 where $F_{tr}(x)$ approaches $F_{tr}(DH)$ for $x$ or $n$ corresponding to the central region of the pore. The algorithm which we use to determine this location-dependent $F_{tr}(GH)$ is described in Ref. 14 and also in the Appendix. Roughly speaking, we set $F_{tr}(x = na) = t_x(x = na)/\langle x(x = na) \rangle$ where $t_x$ is time for a tagged particle starting at a specific location, $x = na$, in a pore with concentration $X$ of other particles to reach the closest pore opening. This choice is based on the classic result that diffusivity scales like the mean-square displacement divided by time. See Ref. 19 for an alternative formulation. Thus, it is immediately clear that $F_{tr}(x) \rightarrow 1$, as $X \rightarrow 0$ (as required). Introducing these variable $F_{tr}(x = na) = F_{tr}(n)$ into a discrete form of (10) and (11)24 recovers almost exactly the results of precise KMC simulations of model behavior, but much more efficiently.14 This formalism will be used to generate results in Secs. III A and III B.

III. CATALYTIC REACTION KINETICS: REACTIVITY VERSUS CONVERSION

In this section, we present simulation results for the reactivity (i.e., the turn-over frequency) per pore as a function of fractional conversion of reactant to product. We also provide more detailed information on concentration profiles within the pores. In all cases below, we consider a pore of length $L = 100 \text{ a}$ in which all cells are catalytic. The hop rate is set to unity $h = 1$, which determines the time scale. The rate of the forward reaction $A \rightarrow B$ chosen as $k = 0.001$. The initial reactant concentration, and thus the total concentration in the exterior fluid, is set to $\langle X_{out} \rangle = 0.8$. This high $\langle X_{out} \rangle$ results in a high loading inside the pore, and thus strong SFD effects in the absence of exchange diffusion when $P_{ex} = 0$. We will consider and compare behavior for three cases: (i) significantly enhanced product reentry with $\alpha = 5$ (mimicking hydrophilic pores for dehydration reactions); (ii) neutral product reentry with $\alpha = 1$; (iii) blocked product reentry with $\alpha = 0$ (mimicking strongly hydrophobic pores for dehydration reactions).

A. Irreversible reaction

For irreversible reaction, $A \rightarrow B$, where $k' = 0$, Fig. 4(a) shows the local steady state concentration profiles for $\langle A_{in} \rangle$ and $\langle B_{ex} \rangle$ versus $n$ at the onset of the reaction ($F = 0$) for various passing probabilities ranging from SFD ($P_{ex} = 0$) to completely unhindered passing ($P_{ex} = 1$). Behavior for $F = 0$ is independent of $\alpha$ due to the lack of product in the exterior fluid. Note the strongly enhanced penetration of reactant into the pore with increasing passing propensity, $P_{ex}$. This results in a strong increase in reactivity, $R_{\alpha}^{Brxn}$, as discussed further.

FIG. 3. Variation of the generalized hydrodynamic tracer diffusion coefficient, $F_{tr}(n) = D_{tr}(n)/D_0$, with distance $x = na$ into the left end of the pore for a pore on length $L = 100 \text{ a}$. The plateau value near the pore center corresponds to $F_{tr}(DH)$. Results are shown for fixed $\langle X_{out} \rangle = 0.8$ and varying $\langle X_{in} \rangle$ for: (a) single-file diffusion, $P_{ex} = 0$; and (b) exchange with $P_{ex} = 0.25$.

FIG. 4. Local steady state concentration profiles for irreversible reaction $A \rightarrow B$ with $L = 100 \text{ a}$, $k = 0.001$, $h = 1$, and $\langle X_{out} \rangle = 0.8$. A (B) is blue, solid (red, dashed). Behavior for: the onset of the reaction $F = 0$ (a) for all $\alpha$; and for $F = 0.625$ with (b) $\alpha = 5$; (c) $\alpha = 1$; (d) $\alpha = 0$. 

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below. Figures 4(b)–4(d) show the concentration profiles for \( A \rightarrow B \) when \( F = 0.625 \) for \( \alpha = 5, 1, \) and 0, respectively. Here, the \( \alpha \)-dependence on behavior is seen clearly not just in the increased values of \( \langle X_{\text{in}} \rangle \) for larger \( \alpha \), but also in the increased dominance of product over reactant within the pore.

Our main focus here is on a comprehensive characterization of the variation of reactivity during the “extended reaction.” Of particular significance is our demonstration of a dramatic difference between behavior for enhanced versus blocked product reentry to the pore. In Fig. 5, we show the reactivity, \( R_{\text{Brxn}}(F) \) as a function of the fraction, \( F \), of reactant outside the pore converted to product for the irreversible reaction \( A \rightarrow B \). The key observation is the contrasting strong decrease of \( R_{\text{Brxn}} \) with increasing \( F \) for enhanced product reentry (\( \alpha = 5 \)) versus the slow decrease of \( R_{\text{Brxn}} \) (or even an initial slight increase with \( P_{\text{ex}} = 0 \)) for blocked product reentry (\( \alpha = 0 \)). Thus, blocking reentry greatly enhances the effective reactivity of the system. The neutral case where reentry is neither enhanced or inhibited (\( \alpha = 1 \)) exhibits intermediate behavior with a linear decrease of \( R_{\text{Brxn}}(F) = (1 - F) \) versus \( F \), as explained below.

The enhanced reactivity upon converting from enhanced reentry (\( \alpha > 1 \)) to blocked reentry (\( \alpha = 0 \)) reflects the reduction in pore loading \( \langle X_{\text{in}} \rangle \). For example, when \( \langle X_{\text{in}} \rangle = 0.8 \) and \( F = 1/2 \), one has \( \langle X_{\text{in}} \rangle = 0.92 \) for \( \alpha = 0 \) versus \( \langle X_{\text{in}} \rangle = 0.67 \) for \( \alpha = 5 \). Lower \( \langle X_{\text{in}} \rangle \) (or higher \( \langle E_{\text{in}} \rangle \)) impacts the rate of adsorption of reactant \( A \) via hopping into the pores,

\[
R_{A_{\text{ads}}(\text{hop})} = h(A_{\text{out}})\langle E_{\text{in}} \rangle = h(X_{\text{in}})\langle E_{\text{out}} \rangle(1 - F)/(1 + (\alpha - 1)F(X_{\text{in}})].
\]

Thus, \( R_{A_{\text{ads}}(\text{hop})} \) increases with decreasing \( \alpha \) for \( F > 0 \), which naturally boosts reactivity. Note, however, that the rate of exchange adsorption of reactant for \( P_{\text{ex}} \) may decrease for lower \( \langle X_{\text{in}} \rangle \). More significantly, lower \( \langle X_{\text{in}} \rangle \) greatly increases the tracer diffusion coefficient \( F_{\text{t}}(\text{GH}) \) which strongly increases penetration and reaction into the pore, and thus also boosts reactivity. This strong increase in reactivity in changing from enhanced to blocked product readsoption is purely kinetic in origin rather than thermodynamic (noting that the reaction is irreversible).

Finally, we provide some further comments on reaction kinetics. First, for the neutral case \( \alpha = 1 \), we describe the origin of the linear decrease of \( R_{\text{Brxn}}(F) \alpha (1 - F) \) with \( F \). This behavior is a consequence of two features. One is the homogeneous \( F \)-independent linear form of the steady state master equations, \( 0 = -k(A_{\text{in}}) - V A_{\text{in}}^{n+1} \), noting that \( F_{\text{t}}(\text{GH}) = F_{\text{t}}(n) \) is independent of \( F \) when \( \alpha = 1 \). The other relates to the feature that the BC terms for \( A_{\text{in}} \) when \( n = 1 \) or \( n = L \) adopt an inhomogeneous linear form with driving term proportional to \( 1 - F \). This implies that all \( \alpha \geq 1 \) and thus one has \( R_{\text{Brxn}}(F) \alpha (1 - F) R_{\text{Brxn}}(0) \). A detailed derivation of the analogous result for the more general reversible case is provided in Sec. III B.

Second, we note that if \( \alpha \neq 1 \), \( R_{A_{\text{ads}}(\text{hop})} \) in (14) exhibits a nonlinear decrease with \( F \), and also the position-dependent tracer diffusion coefficient adopts a non-trivial nonlinear dependence of \( R_{\text{Brxn}}(F) \) on \( F \). As a result, it is not possible to provide a simple analytic expression for the nonlinear dependence of \( R_{\text{Brxn}}(F) \) on \( F \). For \( \alpha \neq 1 \).

Third, we emphasize that our results for the \( F \)-dependence of \( R_{\text{Brxn}}(F) \) encode complete information about the reaction kinetics through the equation

\[
d/\text{d}t(\langle A_{\text{out}} \rangle) = \epsilon R_{\text{Brxn}}(F), \quad \text{where} \quad F = 1 - \langle A_{\text{out}} \rangle/\langle X_{\text{out}} \rangle.
\]

Here, the constant \( \epsilon \) equals the number of pores in the system divided by the total number of 3D lattice sites associated with the fluid. Thus, for no product reentry \( \alpha = 0 \) where \( R_{\text{Brxn}}(F) \approx R_{\text{Brxn}}(0) \) is roughly independent of \( F \) (up to \( F \approx \frac{1}{2} \)), one has a sustained fast linear decrease in time of \( \langle A_{\text{out}} \rangle \approx \langle X_{\text{out}} \rangle/[1 - \epsilon R_{\text{Brxn}}(0)\langle X_{\text{out}} \rangle^{-1} \text{t}] \). For \( \alpha = 1 \) where \( R_{\text{Brxn}}(F) \alpha (1 - F) \), one has exponential decay \( \langle A_{\text{out}} \rangle \approx \langle X_{\text{out}} \rangle \exp[-\epsilon R_{\text{Brxn}}(0)\langle X_{\text{out}} \rangle^{-1} \text{t}] \). For \( \alpha > 1 \), one has slower decay. All cases exhibit the same \( \alpha \)-independent initial decay rate.

B. Reversible reaction

Next, consider the reversible reaction, \( A \leftrightarrow B \), with \( k = 0.001 \) as above, but now \( k' = 0.0005 \) is non-zero corresponding to a finite equilibrium constant \( K_e = 2 \). Figure 6(a) shows the local steady state concentration profiles for \( \langle A_{\text{in}} \rangle \) and \( (B_{\text{in}}) \) versus \( n \) at the onset of the reaction \( F = 0 \) for various passing probabilities \( P_{\text{ex}} \). Behavior for \( F = 0 \) is independent of \( \alpha \) as for irreversible reaction, and penetration of “excess” reactant, \( \langle A_{\text{in}} \rangle = \langle A_{\text{in}} \rangle - K_e^{-1}(B_{\text{in}}) \), into the pore is strongly enhanced with increasing passing propensity, \( P_{\text{ex}} \).
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Fig. 6. Local steady state concentration profiles for reversible reaction A ↔ B with L = 100 a, k = 0.001, K = 0.0005, h = 1, and (Xout) = 0.8. A (B) is blue, solid (red, dashed). Behavior for: the onset of the reaction (α = 1), to blocked reentry (α > 1) to blocked reentry (where 1 + Kc−1 = 1) to reversible reaction (where 1 + Kc−1 > 1). Equation (17) indicates that one should have quite similar values of (ΔAout) since k ≪ h (with (ΔA1) marginally lower in the reversible case), and (16) indicates that (ΔAout) should decay somewhat faster into the pore for the reversible case. Mainly the latter effect produces a slightly lower initial reactivity for the reversible case. In Fig. 8, we compare (ΔAout) profiles for irreversible and reversible cases to confirm this picture.

Third, nonlinear variation of RBrxn(F) on F when α ≠ 1 has similar origins to those for the irreversible case. Fourth, our results for the F-dependence of RBrxn(F) encode complete information about the reaction kinetics as discussed for the irreversible case.

Thus, the BC adopts an inhomogeneous linear form with driving term proportional to 1 − F/Feq. This implies that all (ΔAout) ∝ (1 − F/Feq), and thus one has RBrxn(F) = (1 − F/Feq) RBrxn(0).

Second, the above analysis is useful for understanding the change in initial reactivity (for F = 0 where behavior is independent of a) going from irreversible reaction (where 1 + Kc−1 = 1) to reversible reaction (where 1 + Kc−1 > 1).
IV. CONCLUSIONS

The catalytic activity of nanoporous materials containing multifunctionalized linear nanopores is shown to be strongly dependent on the tunable interaction between reaction products and the interior pore environment. Making the pore interior unfavorable to products not only modifies the reaction equilibrium towards completion but also reduces pore loading which can significantly enhance diffusivity and thus reactivity especially in the SFD regime. As noted in previous studies, catalytic activity is also strongly dependent on the propensity for passing of reactants and products within the pores.9, 14, 15, 21 Our generalized hydrodynamic formulation of reaction-diffusion phenomena provides an efficient tool to explore behavior over a broad phase-space of model parameters. This approach can reliably capture the complex interplay between reaction and restricted transport which results in subtle spatial correlations and fluctuations of reactants and products within the pore. These effects are not described by traditional mean-field approaches.

There are numerous possible modifications and extensions of our modeling which could be performed either utilizing refined generalized hydrodynamic RDE or with KMC simulation.

In this contribution, we have considered the benchmark case of equal mobility of reactants and products within the pore, following previous studies of conversion reactions in nanoporous systems.8-14 However, the basic features of the reaction-diffusion process and the variation for enhanced versus blocked product reentry to the pore will be preserved for unequal mobilities. Some comments pertaining to the required refinement of the GH formulation are found in Ref. 14. Another natural extension of our modeling is to consider different reaction mechanisms, e.g., A + B ↔ C + D better matching esterification reactions, and to consider the scenario where pore reentry of just one of the two products is enhanced versus blocked. The approximate MF and precise GH formalism described above are readily extended to treat this more complex situation, and preliminary studies reveal analogous behavior to that discussed above for the simpler A ↔ B conversion reaction mechanism.

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APPENDIX: RANDOM WALK ANALYSIS OF GH TRACER DIFFUSIVITY F_tr(n)

The position-dependent tracer diffusion coefficient, \( F_{\text{tr}}(x = na) = F_{\text{tr}}(n) \), for a tagged particle starting at cell \( n \) in a pore with a concentration \( X \) of other particles is central to our generalized hydrodynamic formulation. This quantity is determined by simulations involving a finite concentration of a single type of particle in the pore with dynamics of all particles identical to the tagged particle. This dynamics is naturally selected to match the (equivalent) dynamics A or B particles within the pore: hopping to neighboring empty sites at rate \( h \); exchange with adjacent particles within the pore at rate \( P_{\text{exh}} \); desorption from end sites \( n = 1 \) and \( n = L \) by hopping to empty sites just outside the pore. If the reaction model excludes (includes) exchange in and out of the pore, then this process is excluded (included) in the simulations to determine \( F_{\text{tr}} \). If included with rates described in Sec. II A, then the corresponding single-particle dynamics includes exchange in and out of the pore at rate \( e_{\text{exh}} P_{\text{exh}} \). This choice recovers the appropriate values for \( \alpha = 1 \) (where \( e_{\text{exh}} = 1 \) ) and for \( F = 1 \) with only B in the fluid (where \( e_{\text{exh}} = \alpha \).

Our explicit algorithm to determine \( F_{\text{tr}}(n) \) is based on a suitably defined “exit time” \( t_x(x = na) \) for the tagged particle to exit the pore (where exiting the pore corresponds to reaching a site just outside the pore opening). Given anomalous features of random walks in one dimension, such as long times in return-time distributions,20 a judicious choice of definition for \( t_x \) is appropriate. Rather than simply average exit times over many simulation trials, we define \( t_x(x = na) \) as the time when the root-mean-square displacement of the tagged particle reaches the distance to the closest pore opening (i.e.,...
a distance \( n \) for \( n < L/2 \). Then, we assign \( F_n(t) = t_0(n)/t_X(n) \), motivated by the classic result that diffusivity scales like the mean-square displacement divided by time. Here, \( t_0(n) \) corresponds to the exit time for an isolated particle in the pore, which can be determined analytically. Thus, one has that \( t_X(n) \sim t_0(n) \) and \( F_n(t) \to 1 \) for all \( n \), as \( X \to 0 \).

For a semi-infinite pore \( L \to \infty \), it is clear that \( F_n(t) \to F_c(t) = F_c(X, P_{ex}) \), as \( n \to \infty \), recalling that \( F_c(t) \) is the standard tracer diffusion coefficient for an infinite system. Thus, one has that \( t_X(n) \sim t_0(n) \sim 1/n^2 \) for classic diffusion. Together, these imply that \( F_n(t) \to 1/n^2 \), as \( n \to \infty \), for SFD. Numerical studies show that behavior is typical for \( L < \infty \), usually \( F_n(t) \to F_c(t) \) quickly upon entering the pore interior if \( P_{ex} > 0 \). See Fig. 3(b). For SFD \( P_{ex} = 0 \), numerical studies reveal that \( F_n(t) \) usually \( \sim 1/n^2 \) at the pore center.

To generate optimal numerical data for \( F_n(t) \), we sometimes smooth simulation results using a fit \( \delta F_n(t) = F_n(t) - F_c(t) \propto 1/(n^2 + an + c) \) over a broad range of \( n \). For finite pores \( L < \infty \), usually \( F_n(t) \to F_c(t) \) quickly upon entering the pore interior if \( P_{ex} > 0 \). See Fig. 3(b). For SFD \( P_{ex} = 0 \), numerical studies reveal that \( F_n(t) \) typically used to generate \( F_n(t) \) data for a selected set of values of \( X = \langle X_{in} \rangle \). Data for other intermediate \( X \)-values can be readily and reliably obtained by interpolation.

23 For irreversible reaction with \( \alpha = 1 \), one can show that net rate of reactant adsorption via hopping at \( n = 1 \) satisfies \( R_A^{\text{ads-hop}} = \frac{\langle 1 \rangle}{(n^2 + an + c)\langle \langle X_{out} \rangle \rangle} + R_A^{\text{des-hop}} = \frac{\langle 1 \rangle}{(n^2 + an + c)\langle \langle X_{out} \rangle \rangle} \).