Selectivity for Patch-Distributed Reactive Spherical Surfaces

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The selectivity of reactions on active patches over those on a partially active carrier surface is investigated for patch-covered spheres. The effects of relevant parameters including patch and carrier reactivities, patch coverage, patch size, and patch separation state are studied. The selectivity is found to increase with increasing relative dominance of the patch reactivity over the carrier reactivity and patch coverage, as expected. Interestingly, it also increases with decreasing patch size and increasing patch separations. Decrease in patch size creates more patch–carrier interfaces and thus enhances the competition effectiveness of the patches against the carrier surface. With respect to the patch separation state, more complete utilization of the patches is achieved for well-separated patches and thus enhances the selectivity toward the patches. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 475–478, 2007

Introduction

Diffuse-and-incorporate processes are commonly encountered in nature and industrial processes, such as heterogeneous catalysis, ligand-receptor binding, crystal growth, and capture of aerosol pollutants, to cite just a few.[1–3] These processes involve diffusion of small entities onto much larger and relatively immobile inclusions and subsequent incorporation of these small entities into the inclusions. Although the majority of the past work in this field has assumed fully active spheres for the inclusions, there are still a number of works devoted to the partially active inclusion problem,[4–11] which in fact is a more realistic representation of the inclusions. A good example involves the binding between freely moving biological ligands and their affinity receptors distributed over the cell surfaces.[12] Researchers further observed that receptors partially covering the cell surfaces could change their distribution states in response to external disturbances or microenvironmental changes.[13–15] The relevant thermodynamic implications for the phenomenon of receptor redistribution were discussed in our previous study.[16]

One interesting but previously untreated problem relevant to the partially active inclusion system is the selectivity problem. As shown in Figure 1, the covering patches on the inclusion (the carrier) are assumed reactive, whereas the rest of the inclusion surface also possesses a certain degree of reactivity. As a result, competitions arise between the patch and carrier surfaces for incoming reactant species, and the results of such competitions may be characterized as selectivity. Good examples regarding this sort of problem can be found in the field of immunology: study of two competitive receptors on T cells[17] and catalysis for promoter patches on metal carrier surfaces.[18] Selectivity thus serves as a good measure of intermolecular competition or the effectiveness of the reactive patches in achieving their intended task and is an important parameter for the diffuse-and-incorporate processes.

Evidently, one would expect selectivity to depend on the reactivities of the patch and carrier surfaces and the patch coverage fraction. Furthermore, patch size[9] and patch separation state[16] have also been shown to play important roles in determining the overall rate constants of the system and thus

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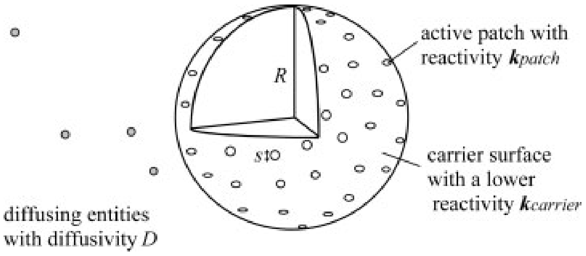

Figure 1. Schematic of the system.

Small entities diffuse toward a suspending sphere of radius of R to react on the surfaces of the patch covered sphere. Active patches of radius of s are distributed over the sphere surface. The patches possess a reactivity of k_{patch}, higher than that of the carrier surface, k_{carrier}.

are expected to affect selectivity. In this regard, this article extends our previous study on partially active inclusion problems to discuss the selectivity issue arising from competitions between active patches and noninert carrier surfaces. The key parameter—*selectivity*—is defined and investigated with respect to variations in key factors including relative reactivity, patch coverage, patch size, and patch separation state.

Simulation of Incorporation Selectivity

The diffuse-and-incorporate system for this study includes small mobile reactant species and a much larger static and suspending sphere whose surface the species steadily diffuse onto and become incorporated with. The sphere surface is covered with active circular patches of a coverage fraction of f_{cover} and the carrier is assumed a nonzero reactivity. The intrinsic rate constants at the patch and carrier surfaces are denoted as k_{patch} and k_{carrier}, respectively. The active patches are assumed uniform in size with a radius of s, and distributed, subject to the nonoverlapping constraint, on the surface of the carrier sphere of radius R. The relative dominance of surface reaction over diffusive mass transfer can be characterized by dimensionless parameters P_{patch} ($=D/k_{\text{patch}}R$) and P_{carrier} ($=D/k_{\text{carrier}}R$) for the two different surfaces, where D is the diffusivity of the reactant species. The process is surface-reaction limited if P tends to infinity and is diffusive-mass-transfer limited if P is zero. The distribution of the patches is characterized with a geometric mean pair distance defined in our previous study[16] as

$$d = \left(\prod_{i=1}^{N_p} \prod_{\substack{j=1 \\ j \neq i}}^{N_p} \left| \mathbf{x}_i - \mathbf{x}_j \right| \right)^{\frac{1}{N_p(N_p-1)}} \tag{1}$$

where $\mathbf{x}_i$ is the position vector of the center of the ith patch, $|\mathbf{x}_i - \mathbf{x}_j|$ is the curved distance between the centers of the ith and jth patches along the sphere surface, and N_p is the number of patches. A separation index, I_s, for quantification of the separation state of the patch distribution, is further defined by normalizing d with respect to the maximum and minimum d values of the well-separated and most compact distributions of the patches, respectively as follows:

$$I_s = \frac{d - d_{\min}}{d_{\max} - d_{\min}} \tag{2}$$

With the above normalization, the values of I_s range from 0 to 1, corresponding to the most compact and well-separated distribution states of the patches. The patches are positioned onto the carrier surface sequentially in a random and nonoverlapping procedure. They are then moved around in a biased way to achieve the desired separation index I_s. A movement of the patch is forbidden and retried if the movement results in a greater deviation from the target I_s. Note that a specific I_s can be realized with different patch distributions.

In this study, the accelerated Brownian dynamic scheme, developed by Lu[9] and colleagues[19,20] by incorporating the first-passage technique, with the Brownian dynamics algorithm proposed by Zhou et al.,[21] is adopted to evaluate the selectivity of reactions occurring on the two distinct surfaces: the patches and the carrier. The details of the accelerated Brownian dynamic scheme can be found in Lu,[9] Lu et al.,[20] and Zhou et al.[21] The basic idea to accelerate the Brownian dynamic simulation is to replace a large number of random-walk steps with a big jump to the surface of a virtual homogeneous sphere, spending some statistically average time, so that the simulation time can be dramatically reduced.[22]

The suspension is assumed dilute. More specifically, the interactions between partially active spheres in the suspension can be neglected and the suspension can be modeled as a single sphere suspended in an infinitely large domain. In the simulation, a sufficient number of test reactant species are released, one at a time, from a fixed outer spherical surface to move to an inner suspending sphere. The trajectories are traced until the species either are reacted on the sphere surface or escape to infinity. Here, the judgment as to whether the species would escape to infinity is made based on a statistical argument as detailed in Lu et al.[20] By collecting the number of reactions occurring on both patch (NR_{patch}) and carrier (NR_{carrier}) surfaces, the selectivity of the patch over carrier surfaces, S, can be defined as

$$S = \frac{NR_{\text{patch}}}{NR_{\text{patch}} + NR_{\text{carrier}}} \tag{3}$$

Two different patch sizes, s/R values of 0.314 and 0.063, are considered in this study with patch numbers of 2 to 16 and 10 to 405, respectively, to demonstrate the size effect on the selectivity under the same patch coverage fraction. For the present work, results for selectivity are averages of 100 patch configurations, each probed with 10^6 test reactant species released one at a time.

Results and Discussion

Figure 2 shows selectivity as a function of P_{patch} with P_{carrier} as a varying parameter. The patch coverage fraction is fixed at 0.3 and the patch size at $0.0628R$. First, a validity check was conducted by examining the special case of $P_{\text{patch}} = P_{\text{carrier}}$, at which the reactivities of the patch and carrier surfaces are the same and the selectivity should simply be equal to the patch coverage fraction. In Figure 2, we mark two points with a cross sign. These two points were obtained at the condition of $P_{\text{patch}} = P_{\text{carrier}}$ and the corresponding selectivities were exactly equal to the patch coverage fraction, 0.3 here, as expected.

For a given P_{carrier}, one expects the selectivity to increase with decreasing P_{patch}. Recall that a smaller P_{patch} corresponds to a higher patch reactivity and thus more dominance

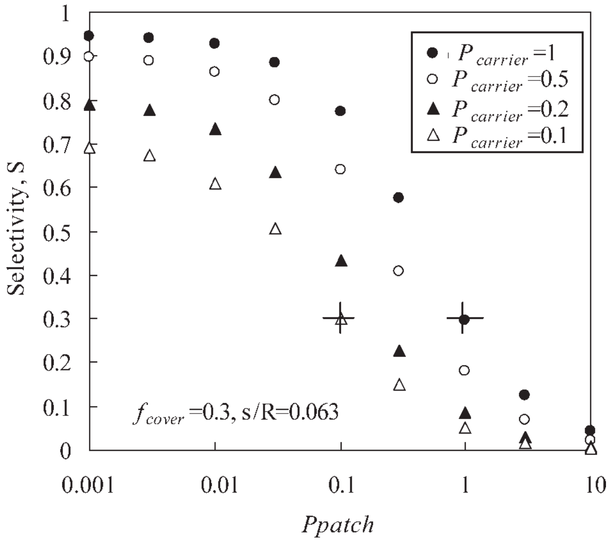

Figure 2. Selectivity vs. P_{patch} with varying parameter of $P_{carrier}$ of 1, 0.5, 0.2, and 0.1.

Patch size $s/R = 0.0628$, patch coverage fraction = 0.3, and separation index $I_s = 1$. The selectivity is equal to the coverage fraction, 0.3, at the two points marked with crosses corresponding to cases of equal P_{patch} and $P_{carrier}$ of 0.1 or 1.

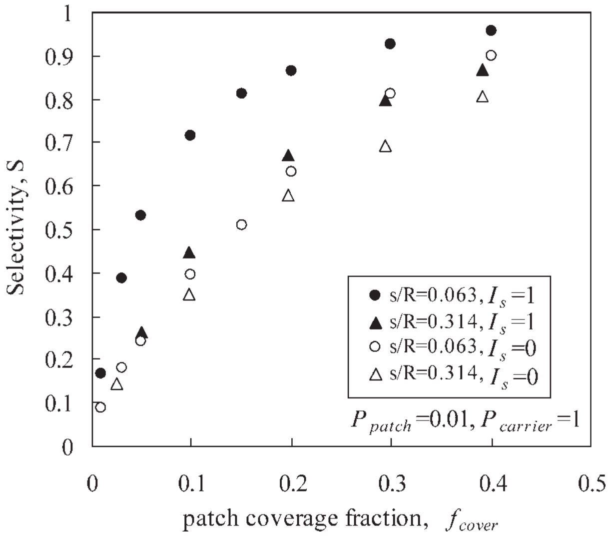

Figure 3. Selectivity vs. patch coverage fraction for patch sizes, *s/R*, of 0.0628 and 0.314 distributed in two extreme patch-separation states.

$P_{patch} = 0.01$ and $P_{carrier} = 1$.

of the patch over the carrier for consuming the incoming reactant species, leading to higher selectivities. On the other hand, the carrier surface becomes dominant when P_{patch} increases to large values, causing the selectivity to approach zero. These trends are clearly observed in Figure 2. In fact, a typical curve of Figure 2 shows the sigmoidal shape, with the two ends leveling off to constant values. Toward the two ends of the curve, the disparity between P_{patch} and $P_{carrier}$ grows, making one of the two surfaces dominant and thus diminishing variations in selectivity.

Lu[9] investigated the patch size effect on overall rate constants and concluded that decreasing patch size leads to higher overall rate constants. Wu and Lu[16] further showed that separation state of the patches on the inclusion surface also significantly affects the overall rate constant. Well-separated patches are more fully utilized and thus give higher overall rate constants than the compact ones, as observed by Northrup.[6] The competitions between neighboring patches for incoming reactant species lower the concentration gradients necessary to drive the diffusional flux toward patches.[23] Consequently, for the present study, both patch size and separation state are expected to play important roles in selectivity. Figure 3 shows the effects of both patch size and separation state on selectivity. The selectivities of two different size patches distributed in two extreme separation states—the well-separated and most compact—are examined in Figure 3, under the condition of P_{patch} of 0.01 and $P_{carrier}$ of 1.

If examined closely, three points can be made from Figure 3.

(1) At the same f_{cover} and patch size, the well-separated patches give higher selectivities than those of the closely packed ones. As discussed in Lu,[9] well-separated patches can be more fully utilized and thus enhance the competitiveness of the patches. Higher selectivities are thus acquired.

(2) The effect of patch separation state is most pronounced at intermediate f_{cover}, but diminishes at low and high f_{cover} values. This phenomenon can be understood as follows. At dilute patch concentrations, patches are far away from one another and their mode of distribution does not cause much difference in the utilization of the patches. At a high f_{cover}, the patches are crowded together, and thus insufficient space is left for the patches to move around to experience significant variations of separation state. Consequently, the effect of separation state diminishes.

(3) At the same f_{cover} and I_s, the selectivity for smaller size patches is higher than that for the larger size patches. As shown in Lu,[9] smaller size patches give higher overall rate constants, translating to higher selectivities in this work. In fact, the competition for incoming reactant species is most

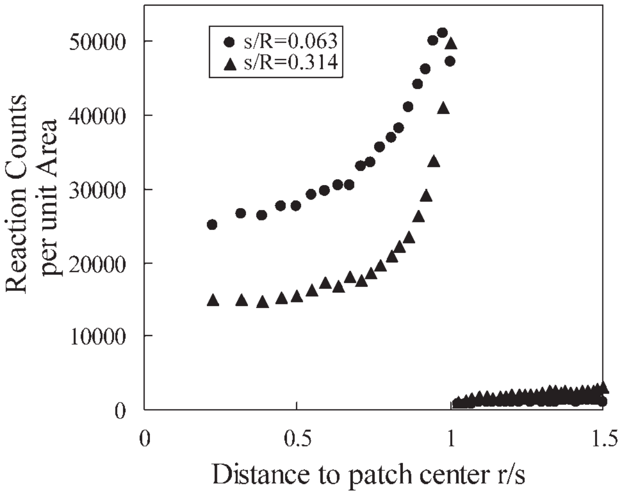

Figure 4. Distribution of reaction count per unit area along the radial direction of the patch.

Here, $s/R = 0.0628$ or 0.314, $f_{cover} = 0.1$, $I_s = 1$, $P_{patch} = 0.01$, $P_{carrier} = 1$, and $I_s = 1$. Reaction counts beyond $r/s = 1.5$ are not shown in the figure.

intense at the patch–carrier boundaries. In Figure 4, we show the distributions of reaction counts per unit area along the radial direction of the patch for two patch sizes. The curve peaks at the patch–carrier interface, with the largest reaction counts per unit area appearing at the patch side of the interface and a sharp drop across the interface. This signifies that the deciding competition between the patch and carrier for incoming reactants, which determines the selectivity, occurs around the patch–carrier interface. With this, one can expect the selectivity to increase with decreasing patch size at fixed patch coverage because smaller patch size gives rise to more patch–carrier interfaces and thus more competition battlegrounds that favor the patch. As shown in Figure 4, the curve for the case of smaller patch size does increase above that of the case of larger patch size in the patch domain, whereas the trend is reversed in the carrier domain, leading to higher selectivity for the smaller patch size system.

Conclusion

The selectivity of reactions on active patches over the noninert carrier surface for a patch-covered sphere is studied with the accelerated Brownian dynamic simulations. The selectivity is found to increase with increasing patch reactivity, patch coverage, and patch separation, but decreasing patch size. The patch size and patch separation state do play important roles in determining selectivity. These factors should be taken into account in the design of relevant processes such as heterogeneous catalysis and biosensing devices to achieve the highest patch efficiency with least usage of expensive functional materials.

Notation

D = diffusivity of the reactant
d = geometric mean pair distance of distributed patches
$d_{\max}$ = geometric mean pair distance of well-distributed patches
$d_{\min}$ = geometric mean pair distance of the most compacted distributed patches
f_{cover} = patch coverage fraction
I_s = dimensionless separation index, $(d - d_{\min})/(d_{\max} - d_{\min})$
$I_{s,rand}$ = average separation index of the random distribution
$k_{carrier}$ = intrinsic rate constants at the carrier surface
k_{patch} = intrinsic rate constants at the patch surface
N_p = total number of patches
$NR_{carrier}$ = reaction count occurring on the carrier surface
NR_{patch} = reaction count occurring on the patch surface
$P_{carrier} = D/k_{carrier}R$
$P_{patch} = D/k_{patch}R$
p = appearing probability of a patch distribution
R = radius of the carrier sphere
S = reaction selectivity, $NR_{patch}/(NR_{patch}+NR_{carrier})$
s = radius of patch
$\mathbf{x_i}$ = position vector of the center of the ith patch

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