Coarse-graining of diffusion–reaction models with catalyst archipelagos

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HIGHLIGHTS

- Reduced order model is developed for diffusion and reaction in supported catalysts.
- The mesoscale kinetic constants in a single-mode model are diffusion disguised.
- The two-mode model retains the true kinetics and up-scales the microscale effects.
- Mass-transfer coefficient in two-mode model depends on crystallite distribution.

GRAPHICAL ABSTRACT

Activity (crystallite) distribution (left) and the corresponding concentration at the wall in the axial and azimuthal directions (right) for diffusion and reaction in a cylindrical pore.
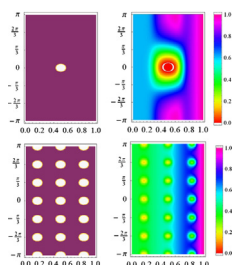
ABSTRACT

We consider the problem of diffusion and reaction in a supported catalyst in which the active sites are located on the crystallites that are distributed in the form of islands (archipelagos) on the pore walls. We determine the coarse-grained mesoscale kinetic constants in terms of the true crystallite scale constants, catalyst activity distribution, pore size and species molecular diffusivities. We analyze the effect of different catalyst archipelagos on the mesoscale rate constants. We also develop a two-mode coarse grained model to describe diffusion and reaction accurately in such systems and develop criteria under which the pore and crystallite scale gradients can be neglected. A significant result is that for moderately fast reactions, the kinetics is disguised in the coarse-grained model if a single pore space averaged concentration mode is used. However, the true kinetics may be represented accurately with the use of two concentration modes, the second mode being the activity weighted concentration.

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1. Introduction and literature review

A fundamental understanding of the coupling between diffusion and reaction in supported porous catalysts is essential for the design and scale-up of catalytic reactors. In the classical catalytic reaction engineering literature, this problem is analyzed at the macro- (or catalyst particle) scale by using a one-dimensional diffusion–reaction model with global reaction kinetics and effective diffusivities. For example, for the case of a catalyst that is in the form of a thin plate or a straight cylindrical pore with no

gradients in the radial (or azimuthal) direction, this classical one-dimensional diffusion–reaction problem in dimensionless form may be expressed as (Aris, 1975; Froment and Bischoff, 1990; Jackson, 1977)

$$\frac{d^2c}{dx^2} = \phi^2 R(c); \quad 0 < x < 1$$

$$c'(0) = 0; \quad c(1) = 1, \tag{1}$$

where c is the dimensionless concentration and ϕ^2 is the (square of the) Thiele modulus defined as the ratio of the characteristic diffusion time to the reaction time and $R(c)$ is the dimensionless reaction rate. The solution to the above one-dimensional model for

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the case of linear kinetics ($R(c) = c$) is given by

$$c(x) = \frac{\cosh(\phi x)}{\cosh(\phi)}; \quad \phi^2 = \frac{k_v L^2}{D_m}, \tag{2}$$

and leads to the well known expression for pore effectiveness factor η as

$$\eta = \frac{\tanh(\phi)}{\phi}, \tag{3}$$

which has the two asymptotes:

$$\eta = \begin{cases} 1, & \phi \ll 1 \\ \frac{1}{\phi}, & \phi \gg 1. \end{cases} \tag{4}$$

In other words, in the limit of slow reactions ($\phi \ll 1$), the observed (macroscopic) reaction rate constant k_{obs} is independent of molecular diffusivity. For the case of a cylindrical pore, we have

$$k_{obs} = k_v = a_v k_s; \quad a_v = \frac{2}{r_p} \tag{5}$$

where k_v is the reaction rate constant based on the pore volume; k_s is the rate constant based on the pore surface area, and a_v is the specific surface area of the pore (r_p = pore radius). If only a fraction of the pore surface is catalytically active and k_0 is the intrinsic rate constant based on the active surface area of the pore, we have

$$k_s = \frac{a_c}{a_v} k_0, \tag{6}$$

or

$$k_{obs} = a_c k_0 \tag{7}$$

where a_c is the exposed active catalytic area of the pore. Thus, in this kinetic limit, the observed rate constant depends only on the intrinsic kinetic parameters, namely the active surface area (a_c) and the microscale rate constant (k_0), or in this case, the product $a_c k_0$.

When the characteristic reaction time is much smaller than the species diffusion time based on the pore length, or for fast reactions ($\phi \gg 1$), the observed rate constant is given by

$$k_{obs} = \frac{1}{L}\sqrt{\frac{2k_s D_m}{r_p}} = \frac{1}{L}\sqrt{a_c k_0 D_m} \tag{8}$$

where D_m is the molecular diffusivity (assuming that diffusion in the pore is in the molecular regime). In this limit, the pore length as well as the species diffusivity enter the observed rate constant.

As pointed out by Bischoff (1966) and Aris (1975), the above one-dimensional treatment may not be valid for short pores or fast reactions where the gradients in the transverse direction of the pore may become important. More recently, Balakotaiah and Gupta (2000) analyzed the pore-diffusion problem in two dimensions and presented new forms of solution (for linear kinetics). They derived the exact expression of the effectiveness factor for classical Bischoff–Aris pore diffusion problem as follows:

$$\eta = \sum_{n=1}^{\infty} \frac{2\alpha I_1(\alpha v_n)}{v_n\left[\alpha v_n I_1(\alpha v_n) + \left(\frac{\phi^2 \alpha^2}{2}\right) I_0(\alpha v_n)\right]}, \tag{9}$$

where $\alpha^2 = r_p^2 / L^2$ is the ratio of axial to transverse diffusion time; L is the pore length; I_0 and I_1 are zeroth and first order modified Bessel functions of first kind, respectively; and $v_n = (n - \frac{1}{2})\pi$. Unlike the traditional effectiveness factor plot, a plot of Eq. (9) may show up to three asymptotes:

(I) $\quad \phi \ll 1$ & $\alpha\phi \ll 1$: $\eta = 1$; $\quad k_{obs} = k_v = \frac{2k_s}{r_p} = a_c k_0$, $\tag{10}$

(II) $\quad \phi \gg 1$ & $\alpha\phi \ll 1$: $\eta = \frac{1}{\phi}$; $\quad k_{obs} = \frac{1}{L}\sqrt{\frac{2k_s D_m}{r_p}} = \frac{1}{L}\sqrt{a_c k_0 D_m}$,

$$\tag{11}$$

(III) (a) $\quad \phi \gg 1$ & $\alpha\phi \gg 1$: $\eta = \frac{4}{\alpha\phi^2}\left[\frac{1}{\pi}\ln\left(\frac{2\alpha^2\phi^2}{3\pi}\right) + 0.251\right]$;

(b) $\quad k_{obs} = \frac{4D_m}{Lr_p}\left[\frac{1}{\pi}\ln\left(\frac{2a_c k_0 r_p^2}{3\pi D_m}\right) + 0.251\right]$. $\tag{12}$

The first two asymptotes are same as those predicted by the 1-D model. The third asymptote, in which the observed reaction rate constant is a logarithmic function of the true surface rate constant, is realized for fast reactions or short pores where strong concentration gradient exists in both the axial and radial directions. In this limit, the observed rate constant depends on the pore dimensions (r_p and L) as well as species molecular diffusivity and is a very weak function of the intrinsic constants (k_0 or a_c). Further, this limiting case is attained when the square of the Thiele modulus based on the pore radius, i.e.

$$\phi_s^2 = \alpha^2 \phi^2 = \frac{2k_s r_p}{D_m} = \frac{a_c k_0 r_p^2}{D_m} \tag{13}$$

exceeds unity. From a physical point of view, this limiting case is attained when the characteristic reaction time is smaller than the species diffusion time based on the pore radius so that transport in the entire pore (in the radial as well as axial directions) is diffusion limited.

The prior work reviewed above assumes that the reactant concentration gradients extend only to the pore dimensions and the activity on the pore wall does not vary along the axial or azimuthal directions. However, in practice, the active sites in supported catalysts are located on the crystallites which are distributed in the form of islands (archipelagos) on the pore walls and cover only a small fraction (typically 1–2%) of the pore surface area. For example, as shown in Fig. 1, the active sites (metal crystallites) form archipelagos on the pore wall of a porous catalyst in a typical monoliths used in a three-way catalytic converter. This non-uniform distribution in catalyst activity within a pore is not taken into account in most prior modeling of diffusion and reaction in supported porous catalysts. This is the main focus of the current work. Specifically, we consider the problem of three dimensional (3-D) diffusion and reaction in a cylindrical pore in which the reaction takes place only on the pore walls and the active sites form an archipelago. Based on the discussion above, it
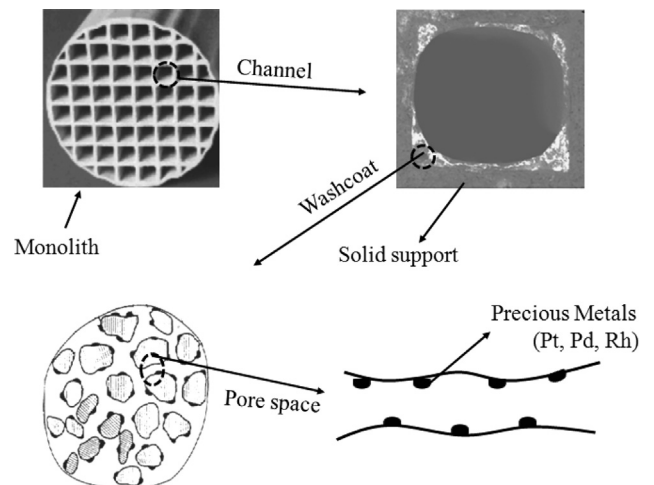

Fig. 1. Schematic diagram illustrating various length scales and crystallite distribution in the porous washcoat of a three-way catalytic converter.