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On the use of internal mass transfer coefficients in modeling of diffusion and reaction in catalytic monoliths

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ABSTRACT

We utilize the recently developed concept of internal or intraphase mass transfer coefficient to simplify the problem of diffusion and reaction in more than one spatial dimension for a washcoated monolith of arbitrary shape. We determine the dependence of the dimensionless internal mass transfer coefficient (Sh_i) on washcoat and channel geometric shapes, reaction kinetics, catalyst loading and activity profile. It is also reasoned that the concept of intraphase transfer coefficient is more useful and fundamental than the classical effectiveness factor concept. The intraphase transfer coefficient can be combined with the traditional external mass transfer coefficient (Sh_e) to obtain an overall mass transfer coefficient (Sh_{app}) which is an experimentally measurable quantity depending on various geometric and transport properties as well as kinetics. We present examples demonstrating the use of Sh_{app} in obtaining accurate macro-scale low-dimensional models of catalytic reactors by solving the full 3-D convection–diffusion–reaction problem for a washcoated monolith and comparing the solution with that of the simplified model using the internal mass transfer coefficient concept.

1. Introduction

In the traditional reaction engineering literature, mathematical models of catalytic monolith reactors in more than one spatial dimension are often simplified by using the concept of external (heat and mass) transfer coefficients and (internal) effectiveness factors. The external transport problem of flow and diffusion in the fluid phase is decoupled from the internal problem of diffusion and reaction in the washcoat and approximated by using an external mass transfer coefficient between the bulk fluid phase and the fluid–solid (catalyst) interface. The concept of catalyst effectiveness factor is used to simplify the internal problem of diffusion and reaction in the washcoat. These simplifications reduce the local (transverse) degrees of freedom while retaining the qualitative features and quantitative accuracy that is sufficient for most applications. The resulting two-phase models of catalytic reactors have been used extensively in the literature.

Extensive literature is available on external mass transfer coefficients in monolithic catalytic reactors. Unlike the more complex case of packed beds and other irregular porous media, the external heat and mass transfer problem in monoliths can be treated theoretically, especially when the flow in the channels is laminar, which is the case in most applications. The theoretical relations for estimating heat and mass transfer coefficients in ducts of various shapes in which the flow is laminar have been presented and discussed in Shah and London (1978), Tronconi and Forzatti (1992), Groppi and Tronconi (1997), Gupta and Balakotaiah (2001), Ramanathan et al. (2003), Bhattacharya et al. (2004) and many other researchers. Experimental correlations for the same were presented and discussed by Votruba et al. (1975), Bennett et al. (1991), Ullah and Waldram (1992), Holmgren and Andersson (1998), West et al. (2003), and Santos and Costa (2008a, 2008b) among others.

Washcoat diffusional limitations can play an important role in determining the light-off behavior of monoliths (Ramanathan et al., 2003). Santos and Costa (2008b) reported that even at high temperatures, the purely external mass transfer controlled regime is hard to obtain under realistic operating conditions and most catalytic monolith reactors used in exhaust gas after-treatment operate in a mixed regime in which both the internal and external mass transfer resistances are significant. Inclusion of washcoat diffusional effects in the monolith models requires the solution of a 2-D diffusion–reaction problem in the washcoat at each axial position. Since this slows the computations considerably, several simplifications have been proposed in the literature for determining the effectiveness factor. Bhattacharya et al. (2004) presented explicit expressions to calculate effectiveness factor for washcoated monoliths for the case of first order kinetics. Hayes et al. (2005) proposed a method for the

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determination of effectiveness factors in a monolith channel in which the washcoat thickness varies in the circumferential direction. Papadias and Edsberg (2000) presented a simplified method to calculate the effectiveness factors in irregular geometries of washcoats.

It should be pointed out that the classical two-phase models of catalytic reactors that utilize the external mass transfer coefficient with the effectiveness factor have some limitations and conceptual difficulties. For example, the effectiveness factor concept does not reduce the local degrees of freedom and requires the solution of the full multi-component diffusion–reaction problem in the washcoat, which, as stated above, can be computationally demanding. Second, it is difficult to generalize for non-uniform or irregular washcoat and channel geometric shapes and multiple reactions with no clearly defined limiting reactant(s). Third and most importantly, for multi-component systems, it is difficult to combine the external transfer coefficient concept with the effectiveness factor concept to describe the overall mass transfer coefficient that can be measured experimentally. For example, the low values of the experimentally observed overall Sherwood number cannot be explained by any existing theoretical or empirical correlations on external mass transfer coefficient (Votruba et al., 1975; Bennett et al., 1991; Ullah and Waldram, 1992; Santos and Costa, 2008a).

In this work, we utilize the recently developed (Balakotaiah, 2008) concept of internal mass transfer coefficient (Sh_i, in dimensionless form) to simplify the problem of diffusion and reaction in the washcoat. We combine Sh_i with the traditional external mass transfer coefficient (Sh_e, in dimensionless form) to obtain an overall mass transfer coefficient (Sh_{app}), an experimentally measurable quantity that depends on catalyst activity profile, washcoat and channel geometries and species diffusivities in the gas phase and washcoat. The focus of this work will be on determining the dependence of Sh_i on various washcoat–channel geometric shapes, reaction kinetics, catalyst loading and activity profile. We also reason that the concept of intraphase transfer coefficient is more useful and fundamental than the classical effectiveness factor concept. We present examples demonstrating the use of the internal and external transfer coefficients in obtaining accurate macro-scale low-dimensional models of catalytic monolith reactors by solving the full 3-D convection–diffusion–reaction problem for a washcoated monolith and comparing the solution with that of the simplified models. The extension of this concept to more important and practical case of multi-component system will be considered in a subsequent publication.

In the next section, we review the concept of internal mass transfer coefficient and how it may be used to develop a simplified 1-D model for an isothermal catalytic monolith reactor. Then, we present some theory and calculations of internal mass transfer coefficients for various washcoat–channel geometries, reaction kinetics and activity profiles. We also present an analogy between internal and external transfer coefficients and a theoretical explanation for the lower values of experimentally observed overall mass transfer coefficients. Finally, we use the low-dimensional model along with the concept of overall mass transfer coefficient for reactor scale modeling and bifurcation analysis of a washcoated monolith and compare the predictions with the solution of the full model.

2. Low-dimensional model and overall mass transfer coefficient

In this section, we review briefly the recently developed simplified model for analyzing catalytic reactions in washcoated monoliths of arbitrary shape and the concepts and usefulness of individual and overall mass transfer coefficients. For details on the low-dimensional models, we refer the reader to the recent article by Joshi et al. (2009). Since the rigorous derivation of the model is documented in the cited

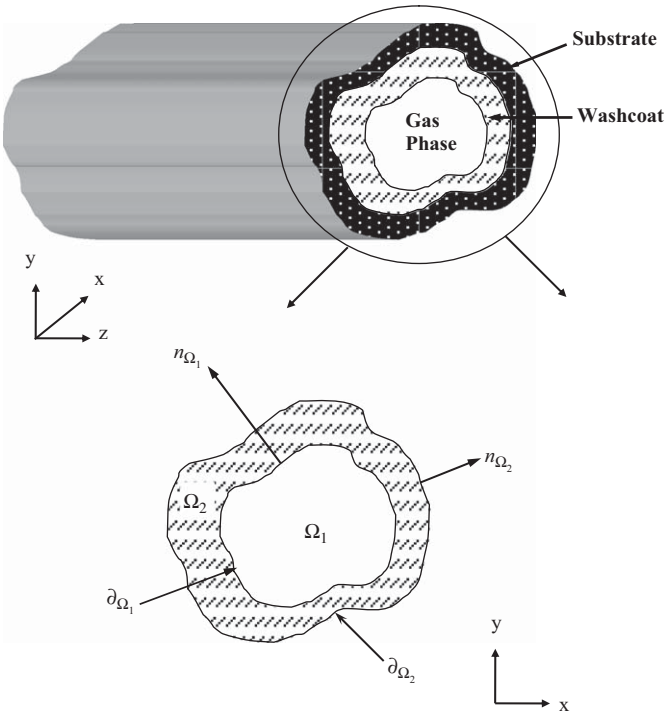

Fig. 1. Schematic diagram of a monolith channel and notations used for washcoat of arbitrary shape.

article, we show here a more physically revealing alternate derivation that applies the conservation laws at the intermediate scales. We consider a single straight channel of arbitrary shape as shown in Fig. 1 (Joshi et al., 2009). The catalyst is distributed uniformly within the porous washcoat deposited on the inner wall of the channel. It is assumed that the cross-section of the channel is invariant with the axial position, but the washcoat thickness may vary along the circumferential perimeter. We can write three balance equations: one for each phase and one at the interface using a control volume as shown in Fig. 2.

Gas phase species balance: As in the classical approach, we assume that the entire resistance for mass transfer in the gas phase resides in a stagnant film of a certain thickness in which the concentration drops from C_{fm} (in main stream) to $\overline{C_s}$ (at the fluid–washcoat interface). Fig. 2 shows the film resistances and gradient for mass transfer. Thus, we can write steady state species balance in the gas phase as

$$(A_{\Omega_1}\langle u\rangle C_{fm})|_z - (A_{\Omega_1}\langle u\rangle C_{fm})|_{z+\Delta z} - (P_\Omega \Delta z)k_{me}(C_{fm} - \overline{C_s}) = 0.$$

Dividing by $(A_{\Omega_1}\Delta z)$ and taking the limit as $\Delta z \to 0$, we get the steady-state gas-phase species balance equation as

$$\langle u\rangle \frac{dC_{fm}}{dz} = -\frac{1}{R_{\Omega_1}} k_{me}(C_{fm} - \overline{C_s}). \tag{1}$$

Washcoat species balance: Similar to the gas phase, we write a volume averaged balance equation in the washcoat assuming that the hypothetical film in the washcoat describes the intra-phase or internal mass transfer resistance in the washcoat. Assuming no diffusional limitations in the bulk washcoat, the concentration drops from $\overline{C_s}$ (at the fluid–washcoat interface) to a constant value of $\langle C_{wc}\rangle$ in the bulk washcoat as shown by the approximate concentration profile in Fig. 2. The reaction rate is evaluated at this volume averaged concentration ($\langle C_{wc}\rangle$):

$$(P_\Omega \Delta z)k_{mi}(\overline{C_s} - \langle C_{wc}\rangle) - (A_{\Omega_2}\Delta z)R(\langle C_{wc}\rangle) = 0.$$