Overall mass transfer coefficients and controlling regimes in catalytic monoliths

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ABSTRACT

It is well known that the performance of a catalytic monolith is bounded by two limits: the kinetic regime at low temperatures (or before ignition for the case of exothermic reactions) and the external mass transfer controlled regime at sufficiently high temperatures (or after ignition). The washcoat diffusional resistance can also be significant over an intermediate range of temperatures. The transition temperatures at which the controlling regime changes from kinetic to washcoat diffusion to external mass transfer depend on the various geometric properties of the monolith, flow properties, the catalyst loading and washcoat properties. We present analytical criteria for determining these transition temperatures. These are derived using the recently developed low-dimensional model and the concepts of internal and external mass transfer coefficients. The criteria are more general than those in the literature and are useful in analyzing the experimental data. Further, we present an explicit expression for the experimentally measurable dimensionless apparent mass transfer coefficient (Sh_{app}) in terms of individual transfer coefficients in each phase. It is shown that Sh_{app} can be lowered by orders of magnitude compared to the theoretical upper bound obtained in the limit of external mass transfer control. Low values of Sh_{app} are obtained due to a small value of effective diffusivity in the washcoat, low catalyst loading or a reaction with low activation energy. The analytical criteria may be used for the design of monolith properties and experimental conditions so that the performance of the monolith approaches the upper limit defined by the external mass transfer controlled limit.

1. Introduction

The catalytic monolith reactor has been widely used as a pollution abatement device because of its structural integrity and unique advantages such as high heat and mass transfer rates per unit of pressure drop, high specific interfacial area, and ease of scale-up compared to packed-bed or ceramic foam reactors. It consists of a matrix of a large number of parallel channels of about 1 mm hydraulic diameter. The catalyst is deposited in the form of a washcoat (of typical average thickness of $10-50\,\mu m$) on the inner walls of the channel. As the reacting fluid flows along the channel, the reactants diffuse transverse to the flow direction from the bulk gas phase into the washcoat where they diffuse and react on the active catalyst sites.

For the case of a single exothermic reaction carried out in a monolith operated at low temperatures, the reaction rate is typically much lower than the external mass transport rate. This results in a nearly uniform concentration and temperature profiles in the

transverse direction in the channel. In the literature, this operating regime is usually referred to as the *kinetic regime*, wherein the external and internal mass transfer resistances are negligible and the observed rate is limited by the kinetics. As the operating temperature increases, the reaction rate increases rapidly, and in most applications, this increase is exponential with temperature (Arrhenius dependence). However, since the diffusivities of the reacting species in the gas phase and washcoat are weak functions of temperature, the external and internal mass transfer rates increase only slightly with temperature. Thus, at high operating temperatures, the resistance due to reaction becomes negligible and the main resistance is due to external and internal mass transfer (washcoat diffusion). We refer to this transition regime as the *combined (pore diffusion and external) mass transfer controlled regime*. As we show in this work, the range of temperatures over which this regime exists depends strongly on the washcoat and monolith channel properties as well as reaction kinetics (and in some cases this regime may not even exist and we move to the third regime discussed below).

Finally, at sufficiently high temperatures, the reaction is confined to a very thin boundary layer near the fluid–washcoat interface and the resistance due to pore diffusion as well as chemical reaction becomes negligible. In the literature, this regime is referred to as the *external mass transfer controlled regime*. For the case of irreversible (or

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far from equilibrium) reactions, this regime defines the highest conversion that can be obtained for a given set of geometric and flow properties (and the conversion is nearly independent of temperature or catalyst loading). Thus, for a given pressure drop, the external mass transfer limited regime defines the upper limit of performance of a monolith.

Typical operating variables (such as inlet temperature and reactant concentration, gas flow rate) and design parameters (such as channel dimensions, channel shape, catalyst loading and washcoat properties) encountered in laboratory and industrial scale monoliths can vary over a wide range. For example, the lab-scale monoliths are typically about 0.25–5 cm long while the industrial monoliths are about 10–100 cm long. In spite of the difference in the length, the space velocities for the lab-scale monoliths are matched to the values used in the industrial applications. Thus, for a typical gas phase Reynolds number (Re) of, say, 200 in a lab-scale monolith, the flow development length is about 10 channel diameters. As a result, the flow may not be fully developed along most (or all) of the channel length in the lab-scale monolith. The flow conditions before the entrance to the monolith channels may be quite different in the lab-scale and industrial applications. In most lab-scale experiments, the flow is laminar before entrance to the channels but in applications it can be turbulent. Moreover, in the lab-scale monolith, the use of same space velocities with different lengths can lead to higher dispersion effects and larger width for various fronts (such as adsorption and temperature) that propagate through the monolith due to time varying inlet conditions. For these reasons, it is convenient to have some simple quantitative criteria that can be used to determine the various regimes of operation of the monolith, to study the impact of scale-up on these regimes, to interpret lab-scale experiments and estimate the kinetic or mass transfer parameters and so forth. The main goal of this work is to provide such criteria. Specifically, we study the effect of flow rate, temperature, channel dimensions, catalyst (precious metal) loading and washcoat properties on regime transition.

This paper is organized as follows. In the next section, we present a literature review on experimental and theoretical studies on the mass transfer coefficients in catalytic monoliths. Then, we review briefly the recently developed low-dimensional model to analyze catalytic reactions in washcoated monoliths. Using this model, we derive the criteria for characterizing various regimes in catalytic monolith. Then, we analyze the effect of various operating and design parameters on the regime transition. We also illustrate the usefulness of these criteria with examples and compare the findings with previous results from the literature.

2. Literature review

In the literature, the process of overall mass transfer in a monolithic channel is simplified by dividing the process into two parts: external (or inter-phase) mass transfer from bulk fluid phase to washcoat and internal (or intra-phase) mass transfer with chemical reaction in the washcoat. The external mass transfer is approximated by using the concept of mass transfer coefficient (or in dimensionless form as the external Sherwood number, Sh_e) and inter-phase concentration gradient, while the process of internal diffusion and reaction is simplified by effectiveness factor concept (η). Extensive literature in the form of experimental and theoretical studies is available on Sh_e. A large number of studies have been presented on effectiveness factor calculations (Aris, 1975; Froment and Bischoff, 1990).

External (or inter-phase) mass transfer coefficient: A large number of experimental and theoretical correlations for the dimensionless external mass transfer coefficient (Sh_e) have been

presented in the literature. First we discuss the theoretical studies. Ramanathan et al. (2003) presented correlations for the external mass transfer coefficient (Sh_e) for various cases of developing boundary layers. For the case of fully developed laminar flow but a developing concentration boundary layer, the following expression describes the local mass transfer coefficient:

$$Sh_e(z) = \frac{k_{me}(z)4R_{\Omega_1}}{D_f} = \begin{cases} 3.28\left(\frac{R_{\Omega_1}^2\langle u\rangle}{zD_f}\right)^{1/3}, & 0 < z < \frac{R_{\Omega_1}^2\langle u\rangle}{D_f}\left(\frac{3.28}{Sh_{H_1,\infty}}\right)^3, \\ Sh_{H_1,\infty}, & z \geq \frac{R_{\Omega_1}^2\langle u\rangle}{D_f}\left(\frac{3.28}{Sh_{H_1,\infty}}\right)^3. \end{cases}$$

(1)

When the velocity field is also developing along with the concentration profile, the following expression gives the local mass transfer coefficient:

$$Sh_e(z) = \frac{k_{me}(z)4R_{\Omega_1}}{D_f} = \begin{cases} \frac{1.4}{Sc^{1/6}}\left(\frac{R_{\Omega_1}^2\langle u\rangle}{zD_f}\right)^{1/2}, & 0 < z < \frac{R_{\Omega_1}^2\langle u\rangle}{D_f}\frac{1}{Sc^{1/3}}\left(\frac{1.4}{Sh_{H_1,\infty}}\right)^2, \\ Sh_{H_1,\infty}, & z \geq \frac{R_{\Omega_1}^2\langle u\rangle}{D_f}\frac{1}{Sc^{1/3}}\left(\frac{1.4}{Sh_{H_1,\infty}}\right)^2. \end{cases}$$

(2)

Here, $Sc(=\nu/D_f)$ is the Schmidt number, and $Sh_{H_1,\infty}$ is the asymptotic Sherwood number for the channel with constant flux boundary condition. Gupta and Balakotaiah (2001) examined in some detail the dependence of $Sh_e(z)$ on the local Damkohler number, ϕ_s^2 (defined as the ratio of the transverse diffusion time to the reaction time). The general observation is that $Sh_e(z)$ decreases with increasing ϕ_s^2 and attains a lower bound in the limit of $\phi_s^2 \to \infty$ (infinitely fast wall reaction). This lower bound on $Sh_e(z)$ corresponds to the value attained in the case of constant wall concentration boundary condition, $Sh_T(z)$. This variation in $Sh_e(z)$ with ϕ_s^2 is typically of the order of 20% of the value and is often ignored in applications. For example, for the case of a circular channel, the asymptotic Sherwood number varies from $48/11 = 4.364$ (for $\phi_s^2 \to 0$) to 3.656 (for $\phi_s^2 \to \infty$).

Balakotaiah and West (2002) presented an analytical expression for Sh_e for a channel of arbitrary cross section for the case of fully developed laminar flow and in the limit of an infinitely fast wall reaction:

$$Sh_e(z) = 4\frac{\sum_{i=1}^{\infty}\alpha_i\mu_i\exp(-\mu_i/P)}{\sum_{i=1}^{\infty}\alpha_i\exp(-\mu_i/P)}, \quad P = \frac{R_{\Omega_1}^2\langle u\rangle}{zD_f}.$$

(3)

The eigenvalues μ_i and the Fourier coefficients α_i for various common geometries were presented by Balakotaiah and West (2002). In the same article, the authors presented a simple approximation that can be used for any arbitrary geometry:

$$Sh_e(z) = Sh_{e\infty} + \frac{1.4\sqrt{P}}{Sc^{1/6}}.$$

(4)

A correlation based on theoretical results has been presented by Tronconi and Forzatti (1992) which is of the form

$$Sh_e(z) = Sh_{e\infty} + \gamma_1 P^{\gamma_3}\exp\left(-\frac{\gamma_2}{P}\right),$$

(5)

where γ_i ($i = 1, 2, 3$) are numerical constants that depend on geometry and Schmidt number. This correlation takes into account the variation of the Sherwood number with both P and Sc but the constants γ_i have to be fitted for each geometry and Schmidt number. Bhattacharya et al. (2004) presented a theoretical analysis on the asymptotic Sherwood number ($Sh_{e\infty}$) and showed that in the kinetic regime, $Sh_{e\infty}$ approaches a new asymptote which depends on the flow as well as washcoat geometries.

Apart from these theoretical studies, many experimental correlations are available in the literature. Hawthorn (1974) proposed a correlation based on the analytical solutions presented by Kays and