Diffusion limitations in stagnant photocatalytic reactors

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HIGHLIGHTS

- Analyzes of uneven absorption of light in photoreactors vs. counteracting diffusion.
- Describes the extremes of optically thick reactors and optically thin reactors.
- Provides a criterion for maximum allowable reaction rate for kinetic experiments.

ARTICLE INFO

ABSTRACT

This paper provides a simple criterion to determine when the performance of an unmixed photocatalytic slurry reactor becomes limited by diffusion. We use a 1D description of the reactor and the two-flux intensity model to describe the concentration profile in unmixed photoreactors. We show that the effect of diffusion limitation in optically thick photoreactors is negligible when the Dahmköhler number based on reactor length is smaller than 0.1 $\tau\gamma$, where τ is the optical thickness and γ is the exponent that describes how the reaction rate varies with light intensity. For optically thin reactors, in contrast, we find that the maximum Dahmköhler number scales with the inverse of $\tau\gamma$.

1. Introduction

This paper explores the effect of mass-transport limitations on photocatalytic reactors. Invariably, when mass transport is not fast enough to keep up with catalysis, the overall reaction rates changes. Classical examples include the effect of mass transport outside a catalytic particle [1], mass transport inside a catalyst particle [2] and axial dispersion in nearly-plug-flow reactors [3]. For all of these examples, the most useful analysis has been to define a criterion that teaches when change of the rate due to limitations exceeds a given threshold, typically 5%. Such an analysis captures the result of approximate or exact solutions of the governing component balances in a single criterion that can be used by experimentalists.

For photocatalytic reactors, such criteria are largely absent. The situation in photocatalysis is more complex: in addition to a non-uniform concentration field c, the optical field variable of relevance, i.e. the rate of photon absorption e_a by the particles, is also not constant throughout the reactor. This local volumetric rate of photon absorption e_a appears in the kinetic expression $r = f(c, e_a)$. Gradients in e_a lead to gradients in r, which in turn lead to concentration gradients, even if the catalyst is homogeneously dispersed and particle-level gradients can be ignored. Of course, vigorous stirring can eliminate such concentration gradients, but we find many examples [e.g. 4,5] of unstirred catalytic performance tests that lack forced convection (e.g., stirring) or reported natural convection (e.g., due to heating by incoming light or electron/hole recombination).

Herein, we analyze the simplest case of mass transport limitations in such stagnant photoreactors. To keep the problem tractable, we consider a reactor volume between parallel transparent plates, with light of intensity I_0 entering perpendicularly onto one side, and we use a two-flux model for the radiation transfer, as discussed below. This renders the problem one-dimensional. After a brief formulation of the problem, we define our five-percent criterion for the onset of mass transport limitations. We then explore limiting cases of optically very thin and optically very thick reactors. This gives analytical expressions for the asymptotes of the criterion, which have the most relevance in catalyst performance tests, and we use numerical calculations for the intermediate regime that is more important in design of efficient photoreactors. We mention here that there are other aspects of

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unmixed catalyst testing, such as aggregation and sedimentation of catalyst particles, concurrent possible diffusion limitation of oxygen from the air, and the likely natural convection from heating on the illuminated side, that are beyond the scope of this paper.

2. Problem formulation

2.1. Local rate of photon absorption

We first describe the local rate of photon absorption inside the slurry. The simplest analysis just uses the Lambert–Beer equation that ignores all scattering, resulting in an exponential decay of the light intensity I inside the reactor, $I(x) = I_0 \exp(-\beta x)$. The local rate of photon absorption is then given by

$$e_a = -dI/dx = \beta I_0 \exp(-\beta x). \tag{1}$$

where β is the extinction coefficient and x is the spatial coordinate that varies from $x = 0$ where the light enters to $x = L$ on the other end. A useful parameter is the optical thickness $\tau = \beta L$. A reactor is *thick* (opaque) if $\tau \gg 1$, indicating that very little light penetrates through the reactor. Conversely, a reactor is optically *thin* if $\tau \ll 1$.

Photocatalytic particles not only absorb light but also scatter it. Scattering occurs in all directions, and the full calculation of the radiation transfer equation is difficult. The two-flux model [6] simplifies the complex analysis of radiation transfer by assuming that light only travels in one direction. Light can be absorbed in a differential slice of thickness dx, or it can be scattered back, or it can pass through without changing path. The last option occurs because of a forward-scattering event or because the photon simply does not interact with any particle. Of course, backscattered light can be scattered again. For unidirectional light that enters the slurry at $x = 0$, this results in

$$e_a = \beta I_0 a_1 \left(a_2 e^{\beta x} + a_3 e^{-\beta x} \right) \tag{2}$$

where and a_1, a_2, a_3 are dimensionless coefficients. The term $a_2 \exp(\beta x)$ in Eq. (2) complicates the analysis, but it turns out that for thick reactors, a_2 is vanishingly small, such that we can write a pseudo-Lambert–Beer expression that consists only of an exponential decay term. Motegh et al. [7] showed that for optically thick photoreactors,

$$e_a = \beta I_0 [1 - q(\omega)] e^{-\beta x} \tag{3}$$

where $q(\omega) = \omega [1 + (1 - \omega^2)^{1/2}]^{-1}$ is the fraction of lost photons via backscattering out of the reactor. It depends on the scattering albedo $\omega = \sigma/\beta$, where σ is a scattering coefficient. Limiting values of ω are $\omega = 0$ when particles do not scatter but only absorb and $\omega = 1$ when particles only scatter but do not absorb light.

2.2. Kinetics

To use the local rate of photon absorption in a reactor model, we need a kinetic expression that relates the absorption of photons by particles to chemical conversion at the particle surface. Many such expressions have been proposed. Based on microkinetics, one can derive expressions for the reaction rate per unit slurry volume r of the form $r = k_1 f(c)[-1 + (1 + k_2 e_a)^{1/2}]$, where k_1 and k_2 are kinetic constants and $f(c) \in [0, 1]$ describes the surface saturation as a function of concentration c [8]. Most relevant photocatalytic processes are pollutant removals at low concentrations, for which surface saturation does not occur, such that the reaction is observed to be first order. At higher concentration, the observed reaction order can be smaller. The term in the square root describes the effect of electron–hole recombination. When e_a is small, electron–hole pairs migrate faster to the surface than they are generated, such that recombination is minimal and $r \propto e_a$. Conversely,

$r \propto \sqrt{e_a}$ when electron–hole pairs are generated much faster than they can migrate to the surface. Here, we shall use a power-law expression $r = k c^\alpha e_a^\gamma$, where the kinetic constant k can be any value and the kinetic constants $0 < \alpha \leqslant 1$ and $0.5 < \gamma < 1$, typically.

2.3. Governing component balance

Without convection, the transient component balance for concentration $c(x, t)$ only has a diffusion term and a reaction term:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - k e_a^\gamma c^\alpha, \tag{4}$$

with initial condition $c(x, 0) = c_0$ and no-flux boundary conditions $\partial c/\partial x(0, t) = \partial c/\partial x(L, t) = 0$. Note that r and e_a are defined per unit volume of the slurry mixture, such that the catalyst concentration is "hidden" in k. We are interested in the concentration profile in the entire reactor, so we scale length as $X = x/L$. The concentration falls from the initial value c_0 to zero, so we have for dimensionless concentration $C = c/c_0$. The characteristic time is either the diffusion time L^2/D or the reaction time $\left[k c_0^{\alpha-1} (\beta I_0)^\gamma \right]^{-1}$. The ratio of these characteristic times is the Dahmköhler number

$$Da = \frac{k c_0^{\alpha-1} (\beta I_0)^\gamma L^2}{D}. \tag{5}$$

The significance of Da is shown in Fig. 1: small values, in Fig. 1(a) and (b), indicate that gradients are small, whereas for $Da \gg 1$ in Fig. 1(c) and (d), gradients in concentration are significant. We scale time with the diffusion time, i.e. $T = (L^2/D)^{-1} t$, and obtain

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial X^2} - Da E_a^\gamma C^\alpha. \tag{6}$$

where $E_a = e_a/\beta I_0$ is the dimensionless rate of photon absorption. The scaled initial condition and boundary conditions are $C(X, 0) = 1, \partial C/\partial X(0, T) = \partial C/\partial X(1, T) = 0$.

3. Criterion for mass transfer limitations

A good instantaneous measure for diffusion limitations is the difference in concentration between the illuminated end and the dark end of the reactor. We define a time-averaged version over the entire conversion as

$$\epsilon = \frac{\int_0^\infty [C(1, T) - C(0, T)] dT}{\int_0^\infty C(1, T) dT} \tag{7}$$

and define as a criterion for the absence of mass transport limitations $\epsilon < 0.05$. As discussed above, we limit ourselves to $0 < \alpha \leqslant 1$. As is generally the case, for first-order reactions the concentration asymptotically approaches zero, whereas for fractional-order reactions ($0 < \alpha < 1$) the concentration becomes zero in finite time. From numerical solutions of Eq. (6) where non-negativity of concentration was ensured, we found for first-order reactions that we could truncate the integration at $T \sim 10$, with negligible change in ϵ upon continued integration. For fractional-order reactions, ϵ reaches a finite value when the concentration becomes zero everywhere, which happens in finite time. In other words, ϵ never diverges to infinitely for the range of α that we are interested in and gives a good time-averaged measure for the extent of diffusion limitations.

The criterion $\epsilon = 0.05$ will depend on the Dahmköhler number Da, the optical thickness τ, the scattering albedo ω and the reaction orders α and γ. The problem is well tractable for the first-order reactions without scattering, i.e. the case $\alpha = 1, \omega = 0$, which we will describe in detail. This will reveal the important features of the boundary, which we write as $\epsilon(Da, \tau\gamma) = 0.05$, because it will turn out $\tau\gamma$ always appear together as a group. Subsequently, we