Chemical Engineering Science 71 (2012) 367–374

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Headspace diffusion limitations on heterogeneous catalysis in unstirred batch reactors

Baron Peters [a,b,*]

[a] Chemical Engineering, University of California, Santa Barbara, CA 93106, USA
[b] Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA

ARTICLE INFO

Article history:
Received 19 September 2011
Received in revised form
23 November 2011
Accepted 10 December 2011
Available online 20 December 2011

Keywords:
Diffusion limitations
Heterogeneous catalysis
Batch reactor
Catalyst screening
Reaction engineering
Reactor modeling

ABSTRACT

Headspace gas diffusion can affect measurements of catalytic rate constants in unstirred batch reactors when the reaction occurs in a small pile of catalyst within the reactor. To quantify these effects, the governing equations for catalysis in a round-bottom flask were solved numerically in a toroidal coordinate system. We also introduce a simpler model reactor geometry that preserves the essential characteristics of a typical bench-scale flask-reactor. The preserved characteristics include the reactor volume, an averaged diffusion length scale, and the area of the catalyst pile. An eigenfunction expansion solution for the model reactor closely parallels the full numerical solutions in the round-bottom flask reactor, thus confirming the validity of the simplified model reactor. Solutions for the model reactor show that concentrations measured above the catalyst pile decay exponentially to equilibrium even when transport limitations are important. Therefore, exponential decay rates in these reactors should not be equated to first order (or pseudo-first order) reaction rate constants without first checking carefully for diffusion limitations. Two dimensionless parameters govern the reactor performance. Effectiveness factors are computed for unstirred catalytic batch reactors over a wide range of the two dimensionless parameters. Our findings show quantitatively when headspace stirring is and is not necessary. When stirring is inconvenient or impossible, the tabulated effectiveness factors can be used to design reactors that are small enough, with kinetics that are slow enough, and with the catalyst dispersed over a large enough area to avoid headspace diffusion limitations.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Mass transfer effects in heterogeneous catalysis are typically a concern for industrial reactor design (Aris, 1957; Carberry, 2001; Fogler, 1992; Froment and Bischoff, 1990; Luss and Amundson, 1967; Thiele, 1939; Vannice, 2010). However, this paper shows that diffusion limitations can also affect catalyst screening in bench-scale chemistry experiments. Much of the literature on transport limitations in catalysis concerns diffusion (and also conduction) through porous catalyst pellets and through films at the surface of catalysts in flow reactors (Aris, 1957; Carberry and Kulkarni, 1973; Hutchings and Carberry, 1966; Luss and Amundson, 1967; Schilson and Amundson, 1961; Smith et al., 1975; Thiele, 1939). Concentration gradients over scales much larger than the catalyst particles have also been studied, for example, in packed bed membrane reactors (Hara et al., 1999; van Sint Annaland et al., 2007).

This paper discusses very small reactors where mass transfer effects might seem to be negligible. Catalysis experiments for screening catalysts are often performed in bench-scale batch reactors with a large gas-phase headspace and a small amount of solid catalyst in the reactor. These experiments often use a stir bar to mix the reactants and products. However, with some *in situ* measurements or with easily poisoned catalysts it may be easier not to include a stir bar. One must then worry about possible diffusion limitations in the stagnant headspace. There is, to our knowledge, no prior literature to help decide which catalytic rates and reactor characteristics require a stirred headspace and which do not.

This paper analyzes the performance of an unstirred batch reactor with a small pile of solid catalyst at the bottom. The coupled diffusion and reaction processes can be modeled numerically (and effectively exactly) in a toroidal coordinate system. Via an approximate geometric transformation, we obtain a simple model for which the coupled reaction-diffusion problem can be solved quickly and analytically. The simplified model closely parallels the full solutions. Importantly, the simplified model reveals two dimensionless parameters that govern the overall rates of conversion in the reactor. The two dimensionless parameters include the expected properties and parameters: diffusivity in the reactor headspace, length scale of the

---

* Corresponding address: Chemical Engineering, University of California, Santa Barbara, CA 93106, USA.
E-mail address: baronp@engineering.ucsb.edu

0009-2509/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2011.12.013

headspace, length scale of the catalyst pile, and the intrinsic catalytic rate parameters. We derive and compute effectiveness factors for a wide range of the dimensionless parameters. The tabulated effectiveness factors provide a simple resource to design batch reactors that avoid headspace diffusion limitations in catalysis experiments.

2. Well-stirred reactor model

The reaction which motivated this study (olefin metathesis) converts propylene to butenes and ethylene (Vicente et al., 2011). The actual chemistry is complicated by secondary reactions between the products and reactants, but a simplified first-order model of the kinetics has been given and successfully fit to the rate data. For the remainder of this paper, we let A=propylene, and B=unspecified products. Note that we will not separately consider the ethylene and butene products. Representing the active site by *, the simplified mechanism is

$$\mathrm{A}+*\leftrightarrow *+\mathrm{B} \tag{1}$$

We consider batch catalysis experiments performed in round-bottom flasks with a diameter of $L=6$ cm. During the experiments, composition is monitored by withdrawing small aliquots of gas through a septum port near the top of the flask. In each experiment a small amount (tens of milligrams) of solid catalyst powder is placed at the bottom of the reactor. The small pile of catalyst is spread over an area of approximate diameter $\ell=2$ cm. The flask is shown in Fig. 1. Temperature is maintained at 298 K throughout the experiments. The thin layer of catalyst is in direct contact with the controlled temperature of the glass walls, so we do not consider thermal gradients in this analysis.

If the reactor was well-stirred, the composition as a function of time would follow the equation

$$V\frac{dA}{dt}=-k_1WA+k_{-1}W(A_0-A), \tag{2}$$

here $V=\pi L^3/6$, W is the mass of catalyst used, and A is the concentration of species A. The initial condition is $A(0)=A_0$. The rate constant would therefore have units $[=]$ mol g^{-1} M^{-1} s^{-1}. The steady state solution is $A_{eq}=A_0k_{-1}/(k_1+k_{-1})$. We can change Eq. (1) to an equation for the deviation from steady state by introducing $\Delta=A-A_{eq}$.

$$\frac{d\Delta}{dt}=-\frac{(k_1+k_{-1})W}{V}\Delta \tag{3}$$

Thus the well-stirred model predicts an exponential decay to equilibrium. As seen in the work by Vicente et al. (2011)) the kinetics resemble an exponential decay to equilibrium. Eq. (3) describes the rate of a first order reaction in a well-stirred batch reactor. However, as ℓ becomes small and L becomes large in an unstirred reactor, diffusion limitations will begin to affect the conversion rate.

3. Averaged reactor length scale

Typically one develops a model and then non-dimensionalizes all variables in the model by some characteristic length scale in the problem. One could use either length scale, L or ℓ, in Fig. 1 to model the diffusion and reaction processes in the reactor. The physical results typically would not depend on the choice of length scale, as long as all subsequent analyses are performed correctly. However to compare results for two different reactor geometries later in the paper, we first determine a special averaged length scale $\mathscr{L}$ for diffusion from the catalyst to points across the reactor. To obtain $\mathscr{L}$ we compute a root mean square distance, averaged on a per unit area basis as seen from the bottom of the sphere. Fig. 2 defines the quantities used for this calculation. Note that we do not consider any effects from the neck of the flask in this work.

$$\mathscr{L}=\left[\frac{\int_0^{2\pi}\xi(\Omega)^4\sqrt{1+\xi'(\Omega)^2}d\Omega}{\int_0^{2\pi}\xi(\Omega)^2\sqrt{1+\xi'(\Omega)^2}d\Omega}\right]^{1/2}=\sqrt{\frac{3}{5}}L \tag{4}$$

We note that corresponding length scales have been derived by different approaches elsewhere. The most similar analysis to average a length-scale for diffusion was by Beekman and Froment (Beekman and Froment, 1982) for defining tortuosity inside porous catalyst particles. Also in the context of intrapellet mass transfer, Aris suggested defining the length scale for irregular particles by matching the volume-to-surface area ratio between the irregular catalyst pellet and a sphere (Aris, 1957; Froment and Bischoff, 1990). Aris' prescription is not valid for our application.

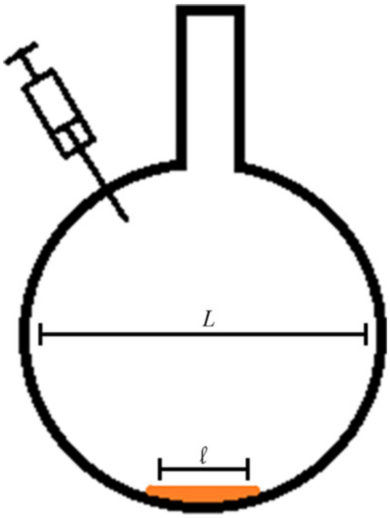

Fig. 1. Schematic of an unstirred batch reactor with catalyst at the bottom and septum port at the top for sampling composition. The analysis here is for a round bottom flask geometry.

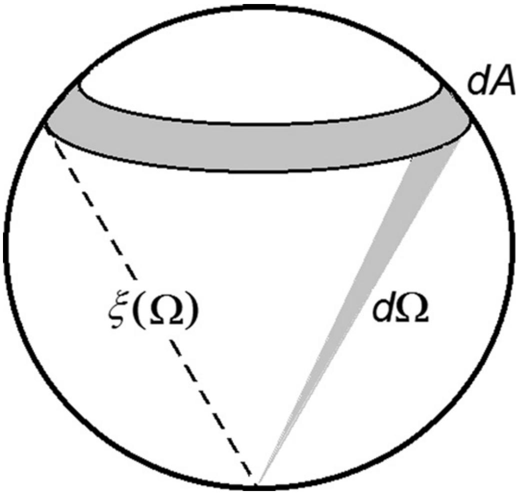

Fig. 2. Solid angle dependent length $\xi(\Omega)$, differential solid angle $d\Omega$, and corresponding differential area $dA=\xi^2(\Omega)(1+\xi'(\Omega)^2)^{1/2}d\Omega$ used to average the transport length scale. Note that $\xi(\Omega)=L\cos[2\ \mathrm{arcs\ in}\sqrt{}(\Omega/4\pi)]$ a result from the geometry of solid angle sectors.

Download English Version:

https://daneshyari.com/en/article/155766

Download Persian Version:

https://daneshyari.com/article/155766

Daneshyari.com