Multiphase flow regimes for hydrogenation in a catalyst-trap microreactor

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Abstract

Multiphase reactions, namely gas–liquid reactions involving solid catalyst, play a critical role in many industries. In particular, hydrogenation reactions are carried out on a large scale in the pharmaceutical industry. Nearly 20% all reaction steps in a typical fine chemical synthesis are catalytic hydrogenation. The use of microreactor geometry would greatly benefit chemical process miniaturization in the pharmaceutical and other industries.

A silicon microreactor has been developed to investigate multiphase mass transfer in the context of gas–liquid–solid catalytic reactions. The reactor employs a three-channel "catalyst-trap" design, whereby solid catalyst is suspended in the liquid channel by an arrangement of posts. Such a device has advantages in that commercial catalysts are supported, and that pressure drop across the bed can be reduced by engineering the packing density. In this paper, a model incorporating the transport and kinetic effects is developed to design this kind of reactor. We have chosen the liquid-phase hydrogenation of *o*-nitroanisole to *o*-anisidine to serve as a prototype reaction. The reaction is carried out across a range of gas and liquid flow rates that encompass three distinct flow regimes, termed gas-dominated, liquid-dominated, and transitional.

Variations of the reactor design are used to study the flow regimes in detail. A two-phase "flow map" is generated for each reactor type. Kinetic experiments seek to assign a reaction conversion to each point in this two-phase "flow map," in order to subsequently reconcile differences in performance with the characteristics of the respective flow regime. We observe the highest reaction conversion in the transitional flow regime, where competition between the two phases results in the generation of a large amount of gas–liquid interfacial area. The experimental conversion is greater than that predicted by the initial plug-flow model, an effect attributable to the mass transfer enhancement induced by transitional flow. Flow maps for each reactor variation show that liquid channel dimensions and trap density can be manipulated to maximize the region of transitional flow. In addition, we explore operation at elevated pressures to enhance hydrogen solubility. This reactor architecture may be useful for catalyst evaluation through rapid screening, or in large numbers as an alternative to macroscale production reactors.
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1. Introduction

Miniaturization of chemical processes is motivated by the quest for clean and efficient on-site, on-demand, and on-time distributed production of chemicals. To this end, the term "microreactor" is broadly used to describe devices with critical geometry ranging from tens of microns to approximately 1 mm in size. Microreactor technology possesses significant advantages over conventional macroscale reactors. Because of their small size, microreactors have inherently large surface-to-volume ratios, allowing for superior mass and heat transport. Surface-to-volume ratios of $20,000 \, m^2/m^3$ or more are not uncommon, compared to $1000 \, m^2/m^3$ for a conventional reac-

tor. Laminar flow is typically impressed by microgeometry, but because the overall heat transfer coefficient is inversely proportional to channel diameter, values for liquids are on the order of $10,000 \, W/(m^2 \, K)$, roughly one order of magnitude higher than in conventional heat exchangers [1–8].

In the case of catalytic reactions, where competition exists between the rate of diffusion to the catalyst sites and the rate of reaction, microreactors are able to virtually eliminate mass transport resistance, making them an extremely useful tool for isolating reaction kinetics. Excellent heat transfer properties ensure a uniform temperature throughout the reactor and prevent the formation of hotspots in the case of an exothermic reaction. In a stirred-tank reactor, for example, hotspots can lead to undesired changes in local concentration or pH. Low residence time and ease of heat removal also make microreactors more suitable for flammable service, where the potential for explosion or fire from runaway reactions is greatly reduced [9,10].

Nomenclature

a_h	gas–liquid interfacial area
c_i	liquid-phase concentration of species
H_i	Henry's law constant for species i
k	reaction rate constant
k_L	liquid-phase mass transfer coefficient
K_i	absorption constant for species i
P_i	partial pressure of species i
t	time
u_L	liquid superficial velocity
w_c	weight of catalyst per unit volume of reactor bed
z	length coordinate
ε	reactor void fraction

Fig. 1. Illustration of gas/liquid flow regimes.

In this paper, we consider the use of a microreactor for gas–liquid–solid catalytic reactions, where the rate of diffusion of gas into the liquid phase can also limit the observed reaction rate. Thus, we would like to be able to address both intra- and inter-particle diffusion. The former can be accomplished with reasonable certainty simply by using small-sized catalyst particles. In general, catalyst particles with a diameter smaller than $100\,\mu m$ (1×10^{-4} m) exhibit sufficiently low transport resistance to enable their use with most reactions [11]. The latter is a function of gas–liquid interfacial area and driving force for transport, both of which depend on the gas–liquid flow regime. Similar to the development of macroscale packed or trickle bed reactors, mass transfer in two-phase flow has been studied extensively in microchannel or capillary geometry, and here we wish to extend these principles to reactive systems.

For our purposes, three traditional flow regimes are adequate to describe the two-phase behavior, although other papers present more precise delineations [12–17]. Bubble flow is characterized by liquid as the continuous phase, with bubbles of gas dispersed into a fully wetted channel. As the ratio of gas-to-liquid velocity increases, the Taylor (slug) flow regime emerges, in which alternating segments of gas and liquid occupy the channel. The relative lengths of each segment are constant for a given set of inlet conditions. As gas-to-liquid velocity further increases, annular (for a capillary) or trickle (for a wide reaction channel) flow occurs. In annular or trickle flows, gas is the continuous phase, and the liquid flows as a thin film along the channel walls [12–17]. Analogs of these distinct flow regimes develop within both macro- and microscale devices over varying gas and liquid ratios. Fig. 1 illustrates the three flow regimes, where u_G and u_L are the gas and liquid superficial velocities, respectively.

In the context of a gas–liquid–solid catalytic reaction with reaction occurring in the liquid phase, two characteristics are critical in evaluating the advantages and disadvantages of a particular flow regime. First, we desire good mass transport between gas and liquid, which depends on the driving force for mass transport and the gas–liquid interfacial area created. Second, we desire a high liquid–solid interfacial area to effectively utilize the catalyst for rate of production. The highest liquid–solid interfacial area will be achieved when liquid is the continuous phase.
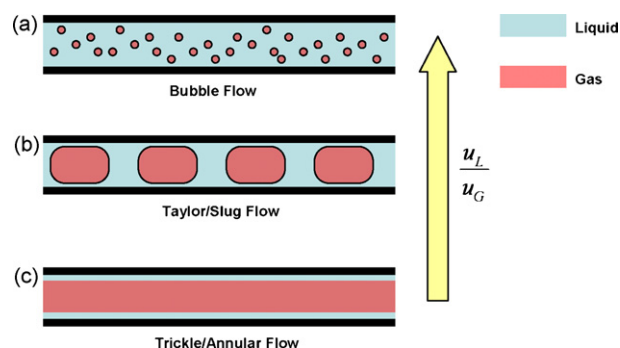
Taking the example of a capillary, the slug flow regime is typically associated with the best gas–liquid mass transport because of the high shear rates that have been observed to develop between liquid slugs and their intervening fluid [12–17]. The high velocity gradient within the liquid slug provides a chaotic mixing effect, so a constant refreshing of the gas–liquid interface occurs. This provides a high driving force for diffusion of gas across the interface. Despite good mass transport properties, slug flow does not maximize the liquid–solid interfacial area because gas still occupies a significant portion of the channel. Bubble flow, in contrast, exhibits both a high liquid–solid and gas–liquid interfacial area. Because liquid is the continuous phase with only a relatively small fraction of gas present, essentially all of the catalyst is in contact with liquid [18]. Thus, we can generalize that slug flow will possess the best gas–liquid mass transport, owing to both interfacial area and driving force, and that bubble flow, although less turbulent, will have the highest liquid–solid interfacial area. On the basis of these mass transfer arguments, we speculate that the best reactor performance will fall in either the bubble or slug flow regimes. Likewise, we suppose that trickle flow, with the lowest liquid–solid and gas–liquid interfacial areas, will be the least effective for these types of reactions. We proceed to design the device and subsequent experiments with this hypothesis in mind.

2. Reactor modeling, design, and fabrication

The reactor is designed for operation across the spectrum of flow regimes, while making use of the advantages of microchemical systems to relieve various transport resistances. The design is pictured in Fig. 2.

The reactor is used for the liquid-phase hydrogenation of o-nitroanisole to o-anisidine, with methanol as an inert solvent. The catalyst is 5% Pd by weight on carbon. Hydrogen gas enters along the two outside channels, and is allowed to diffuse into the liquid channel through a slotted wall, shown at the top inset. The reaction occurs in the liquid channel, where an arrangement of posts, or catalyst traps, holds the catalyst particles in place (Fig. 2b, lower inset). Each trap is a trapezoidal arrangement of four posts spanning the depth of the channel. The posts are spaced to "catch" catalyst particles during the catalyst loading process and hold them in place during the reaction processing, so one can imagine the liquid sees the particles stacked single-file