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Chemical Engineering Journal 133 (2007) 105–111

Chemical Engineering Journal

www.elsevier.com/locate/cej

Fluid segment configuration for improving product yield and selectivity of catalytic surface reactions in microreactors

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Received 27 August 2006; received in revised form 8 February 2007; accepted 13 February 2007

Abstract

Ordered laminar flow and mixing driven mainly by molecular diffusion in microreactors enables operation using fluid segments. This paper discusses the effects of configuration of fluid segments including reactants at the reactor inlet for catalytic surface reactions in a microreactor. Irreversible and reversible parallel and series–parallel reaction systems were investigated. The rate-controlling step of these reaction systems is diffusion in the channel or diffusion in the catalyst layer. Under some diffusion-controlled conditions, appropriate fluid segment configuration gives higher selectivity of the desired product than reactors where the reactants are mixed at the reactor inlet. Configurations in which reactants with different reaction orders in parallel reactions or consumed only in the reaction producing the desired product are placed on the catalyst surface are suitable to improve the selectivity of the desired product. The configuration to maximize the yield of the desired product depends on the reaction system and rate-controlling step. To obtain a given selectivity of the desired product, the required fluid segment size depends on the configuration. The results reported here indicate an advantage of fluid segment, which is a typical fluid operation in microreactors, for enhancing the yield and selectivity of desired products.

Keywords: Catalytic surface reaction; Microreactor; Yield and selectivity; Fluid segment; Reaction order

1. Introduction

Microreactors are miniaturized reactors including microchannels with characteristic dimensions in the sub-millimeter range. Channel miniaturization provides a high surface-to-volume ratio and laminar flow [1,2]. High surface-to-volume ratios lead to enhanced heat and mass transfer, and thus lead to efficient catalytic surface reactions. Examples of catalytic surface reactions in microreactors are as follows: ammonia oxidation on a platinum catalyst [3], degradation of 4-chlorophenol on titanium dioxide as a photocatalyst [4], methanol steam reforming using a $CuO/ZnO/Al_2O_3$ catalyst [5], production of hydrogen from ammonia on alumina [6], reforming/oxidation of methanol on thin metallic wires containing Cu and Zn [7], and 1-pentene epoxidation on a TS-1 (titanium silicalite-1) catalyst [8]. Numerical investigations of catalytic surface reactions in microreactors have also been performed [9,10].

Laminar flow leads to mixing driven mainly by molecular diffusion. The mixing time by molecular diffusion scales with the square of diffusion length. Therefore, a short diffusion length is necessary for rapid mixing. Mixing operations by which reactant fluids are separated into many micro fluid segments are often used for this purpose. Examples of the micromixers using this mixing principle include the interdigital mixer [11], the static V-micro-jetmixer [12], the SuperFocus mixer [13], the K-M mixer (Kyoto University-MCPT; Research Association of Micro Chemical Process Technology) [14,15], and the dual pipe mixer [16]. To achieve efficient mixing realizing controlled reaction conditions, we have proposed guidelines to determine design factors of fluid segment, such as width, arrangement, and shape using dimensionless numbers representing the ratio of reaction rate to mixing rate and the ratio of the diffusion rates in the horizontal and vertical directions in the cross-section of a reactor [17,18].

We have also examined the effects of fluid segment configuration, *i.e.*, combinations of reactant concentrations, width, and arrangement of laminated fluid segments on product distribution of multiple reactions [19]. For the fixed mean fluid segment size, the selectivity of the desired product for series–parallel

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doi:10.1016/j.cej.2007.02.006

reactions depends on the configuration. Ordered laminar flow and mixing driven by molecular diffusion enables this operation.

In catalytic surface reactions, the reactions occur only in the catalyst layer. The concentration profile near the catalyst layer dominates the product distribution in a reactor. Configuration of reactants at the reactor inlet is expected to enable the concentration of reactants on the catalyst surface to be controlled and thus to be useful to improve yield and selectivity of the desired products in such reactions. To establish the effectiveness of fluid segment configuration in catalytic surface reactions, we investigated the effects of the arrangement of fluid segments including reactants at the reactor inlet for catalytic surface reactions in microchannels. We applied irreversible and reversible parallel and series–parallel reaction systems proceeding in the channel between two parallel plates into CFD (computational fluid dynamics) simulations. We also examined the effects of the following rate-controlling steps of the reaction systems: surface diffusion and diffusion in the catalyst layer. Moreover, we studied the effects of fluid segment size on the selectivity of the desired product and discuss channel size to achieve a certain yield of the desired product for each fluid segment configuration.

2. Simulation settings

First, the settings for all CFD simulations in this study are explained. We simulated mixing by molecular diffusion, reaction, and flow in reactors with a channel between two parallel plates of width W (two-dimensional simulations) and various configurations of fluid segments that will be described in the subsequent sections. A commercial CFD code, Fluent 6.2.16, was used for the CFD simulations. This code solves mass, momentum, and energy conservation equations by the control volume method [20]. The laminar flow and the finite-rate model were applied. The SIMPLE (semi-implicit method for pressure-linked equations) algorithm was used to solve the pressure–velocity coupling equation. The second-order upwind scheme was used to solve mass and momentum conservation equations. The discretization method of the simulation domain is mentioned in subsequent sections. We confirmed that the solutions of the CFD simulations are independent of the further increase in number of mesh elements.

The diffusion coefficient of every species D was assumed to be $10^{-9}\,\mathrm{m^2\,s^{-1}}$, which is the typical order of the diffusion coefficients for liquid phase reactions [21]. The physical properties of the two-reactant fluids are as follows: the density is $1000\,\mathrm{kg\,m^{-3}}$, and the viscosity is 0.001 Pa s. The inlet velocity of the reactant fluids u was fixed at $0.001\,\mathrm{m\,s^{-1}}$.

Using the settings described in the following sections, we performed CFD simulations to obtain concentration profiles of the species in the reactors and then calculated relations between the yield of the desired product C, Y_C, and conversion of the reactant B, x_B, in the reactors as a measure of reactor performance. These relations were obtained from the mass-weighted average concentration of each species on the plane perpendicular to the axial direction at each axial position.

2.1. Effects of fluid segment configurations for each multiple reaction system

Fig. 1 shows a schematic of the reactor channel and simulation settings applied in the CFD simulations with various reaction systems. Diffusion from the reactor channel to the catalyst surface was assumed to be the rate-controlling step. The catalyst is loaded on the bottom of the channel and this is where the reactions take place. Analogous catalyst loading is realized by placing a membrane catalyst on the bottom of the reactor channel [22]. The no-slip boundary condition was assumed on both channel walls. The reaction formulas and the rate equations of the multiple reactions proceeding in the reactors were as follows:

(1) Parallel reactions (irreversible),

$$\mathrm{A + B \rightarrow C}, \quad r_1 = k_1 C_A C_B,$$
$$\mathrm{A + B \rightarrow D}, \quad r_2 = k_2 C_A C_B^{0.5}, \tag{1}$$

where $k_1 = 1\,\mathrm{m^4\,kmol^{-1}\,s^{-1}}$ and $k_2 = 0.1\,\mathrm{m^{2.5}\,kmol^{-0.5}\,s^{-1}}$;

(2) Parallel reactions (reversible),

$$\mathrm{A + B \rightleftarrows C}, \quad r_1 = k_1 C_A C_B - k_{-1} C_C,$$
$$\mathrm{A + B \rightleftarrows D}, \quad r_2 = k_2 C_A C_B^{0.5} - k_{-2} C_D, \tag{2}$$

where $k_1 = 1\,\mathrm{m^4\,kmol^{-1}\,s^{-1}}$, $k_2 = 0.1\,\mathrm{m^{2.5}\,kmol^{-0.5}\,s^{-1}}$ and $k_{-1} = k_{-2} = 0.01\,\mathrm{m\,s^{-1}}$;

(3) Series–parallel reactions,

$$\mathrm{A + B \rightarrow C}, \quad r_1 = k_1 C_A C_B,$$
$$\mathrm{B + C \rightarrow D}, \quad r_2 = k_2 C_B C_C, \tag{3}$$

where $k_1 = 1\,\mathrm{m^4\,kmol^{-1}\,s^{-1}}$ and $k_2 = 0.1\,\mathrm{m^4\,kmol^{-1}\,s^{-1}}$.

In the reaction formulas, A and B are the reactants, C is the desired product, D is the by-product, r_i and k_i are the reaction rate ($\mathrm{kmol\,m^{-2}\,s^{-1}}$) and the rate constant of the ith reaction, respectively, and C_j is the molar concentration of the species j. The reactants were assumed to react isothermally, and the rate constants were fixed. The reaction order of B for the reaction producing C was higher than that for the reaction producing D. The channel width was 200 μm, which is of the typical order of microchannel size [23]. The channel width affects the rate-controlling step. The reactor length L was set to 0.1 m, *i.e.*, the mean residence time of the reactants in the reactors τ was

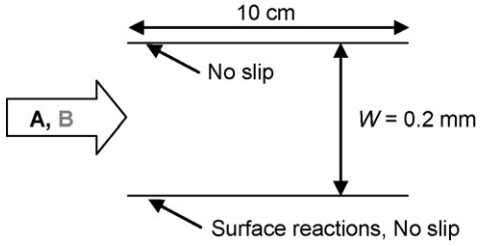

Fig. 1. Simulation settings of the reactor under channel diffusion-controlled conditions.