

Ministructured Catalyst Bed for Gas-Liquid-Solid Multiphase Catalytic Reaction

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A ministructured reactor concept improves the performance of multiphase gas-liquid-solid reactions over conventional packed-bed and trickle-bed reactors. In the mini-structured reactor, the catalyst bed is structured at the particle level by dividing the bed into a number of identical, parallel flow channels with the channel walls being catalyzed. The hydraulic diameter of each channel opening is from 0.2 to 2 mm, comparable to the conventional particle size. The mini-structured reactor can be assembled using monolith catalyst modules that have been a proven material technology for gas-phase reactions. Two types of gas-liquid-solid reactions, olefin hydrogenation and toluene saturation, are used to test the fundamental feasibility of the mini-structured reactor under steady-state reaction conditions in a cocurrent down flow mode. The new reactor shows an order of magnitude increase in the activity compared to a trickle-bed operation for reaction conditions of practical interest. This degree of activity improvement is larger than estimates based on conventional analyses of catalyst geometric surface area and/or characteristic pore diffusion lengths. Individual catalyst particles are significantly underutilized in a trickle-bed reactor. More ideal contacting of gas, liquid and catalyst, as well as the enhancement of overall mass-transfer processes in the mini-structured reactor, makes it possible to dramatically improve the gas/liquid multiphase reaction performance over solid catalysts.

Introduction

It is known that the chemical process industry requires significant capital expenditure for reactor and process equipment. After feedstock costs, capital recovery is often the second largest fraction of the total product cost. For new plants, reduction of equipment size is an obvious pathway to reduce capital cost. In existing plants, however, gaining a significant increase in capacity or productivity by de-bottlenecking or retrofitting equipment on the ground is a very attractive way to realize substantial cost savings and recoup a high profit. Hydrogenation and hydrotreating processes represent one very important category of gas-liquid-solid catalytic reactions, used for the production of a variety of chemicals and refined products. Since high-pressure hydrogen is often used, enhancing reactor productivity for these processes is highly desirable from both capital and operation points of view. Trickle-bed and slurry reactors are commonly used by the industry (Al-Dahhan et al., 1997; Biardi and Baldi, 1999; Gianetto and Specchia, 1992). For example, trickle-bed reactors using packed beds of catalyst pellets of various forms have

been widely used to conduct hydrotreating reactions for fuel upgrade in the refining industry. In contrast to increasingly stringent requirements to the quality of these refined products, these conventional reactors are perceived as a mature process technology. Refinements to fixed-bed reactors include optimizing catalyst size, shape, and packing method, and tuning the operating regime. However, recent improvements are mostly incremental and have not resulted in a large increase in the performance of these processes.

Development of novel reactor technologies to enhance gas/liquid reaction efficiency has long been a chemical engineering research endeavor. Recently, the microreactor concept has been promoted as smaller and safer reactors in the future (Hendershot, 2000; Stankiewicz and Moulijn, 2000). However, there are several practical problems associated with its potential application in chemical plants, such as plugging and fouling of microchannels, cost and availability of microreactor modules for large-scale commercial reactions, catalyst preparation, and so.

A mini-structured reactor idea is proposed here as a realistic approach for the short term to achieve a fundamental improvement in conventional packed-bed and trickle-bed reactor performance. The mini-structured bed can be constructed by the use of monolith catalyst modules that are a proven material technology for gas-phase catalytic reactions. The term, "monolith reactor," has been loosely used in the literature without fundamental and experimental elaboration. The mini-structured reactor concept, instead of the monolith reactor, is emphasized in this article to highlight the importance for discovery of new reaction engineering sciences associated with this type of reactor structure. A fundamental analysis will be presented in this article as a foundation for future studies. Specific comparisons will be made between a mini-structured reactor and a trickle-bed operation for model compound hydrogenation reactions under multiphase conditions of practical interest.

Mini-structured Reactor and Monolith Catalyst

Figure 1 illustrates the concept of a gas/liquid catalytic reaction in a mini-structured catalyst bed. The catalyst comprises an array of reaction channels with each channel wall being catalyzed. The channels have uniform dimensions and are vertically oriented parallel to each other. Bulk gas and liquid feed streams are delivered co-currently into the channels of the mini-structured catalyst through a gas/liquid (G/L) distributor device, and the reaction occurs on the catalyzed wall as the two-phase flow passes through the channels. In contrast to the random flow patterns of gas and liquid in conventional packed beds, the flow paths in the mini-structured catalyst bed are highly ordered.

The mini-structured reactor is different from conventional structured beds in the reactor scale and microreactors having micron scale dimensions. The bed structure is characterized by reaction channels having hydraulic diameters on the order of 0.2 to 2 mm. These dimensions are generally larger than those envisioned for microstructured reactors, but smaller than the dimensions of conventional structured packings used in distillation towers or reactors structuring on a more macroscale, such as baffles. Channel openings in the mini-structured catalyst bed are comparable to the dimensions of the interparticle void formed by randomly packed catalyst pellets. Thus, channel plugging is not expected as a major problem for practical applications involving "dirty" feedstock, such as hydrotreating processes.

In theory, many different kinds of materials can be used to construct the mini-structured catalyst bed. Among all potential options, ceramic monolith catalysts appear to be the most presently feasible. Table 1 lists properties of some monolith substrate materials that have been reported in the literature (Williams, 2001). Monolith substrates can be made as blocks having various forms such as cylinders, ovals, or squares, and large-scale assemblies of blocks to fill large chemical reactors can be envisioned.

Monolith materials made of cordierite, $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, have been successfully used in automotive catalytic converters for nearly three decades, and the mechanical and chemical durability of this type of substrate has been well demonstrated. More recently, selective catalytic reduction (SCR) of nitrogen oxides over monolith catalysts made of transition metal oxides for flue-gas clean up has been commercialized (Nakjima and Hamada, 1996), demonstrating that large reactors having mini-structured catalyst beds are feasible and practical.

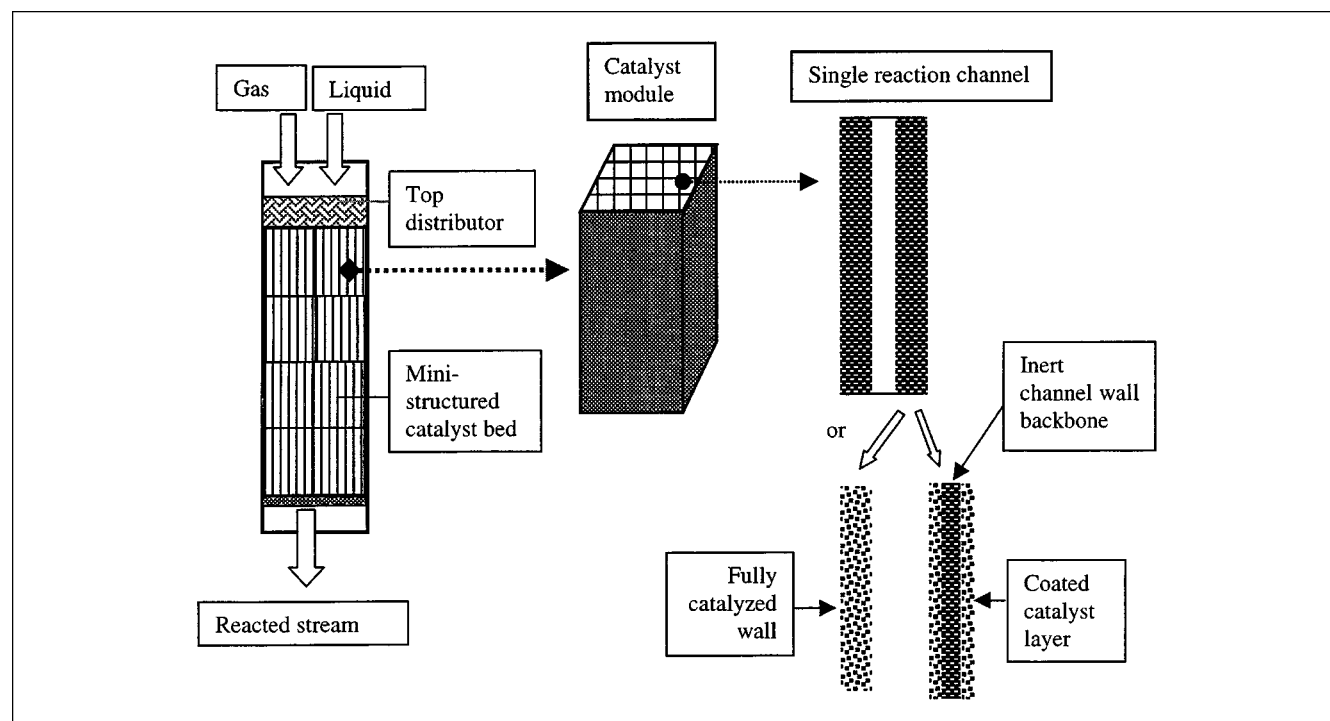


Figure 1. Technology components of mini-structured catalyst bed for gas/liquid catalytic reactions.

Table 1. Monolith Catalyst Substrate Materials*

Materials	Channel Density #/in ² (cpsi)	Channel Opening, mm	Surface Area, m ² /g
Cordierite	25 to 900	0.5 to 5	Determined by catalyst support materials to be coated. 30 wt. % alumina coating is typical.
Alumina	25 to 400	0.5 to 5.0	1-5 for α -Alumina 50 ~ 300 for γ -Alumina
Alumina-silica	25 to 400	0.5 to 5.0	200 ~ 600
ZSM-5, silicalite	25 to 600	0.5 to 5.0	200 ~ 2,000
Iron oxide	25 to 400	0.5 to 5.0	0.5 to 15
Carbon	25 to 1,200	0.5 to 5.0	50 to 1,200

*Made by Corning Inc.

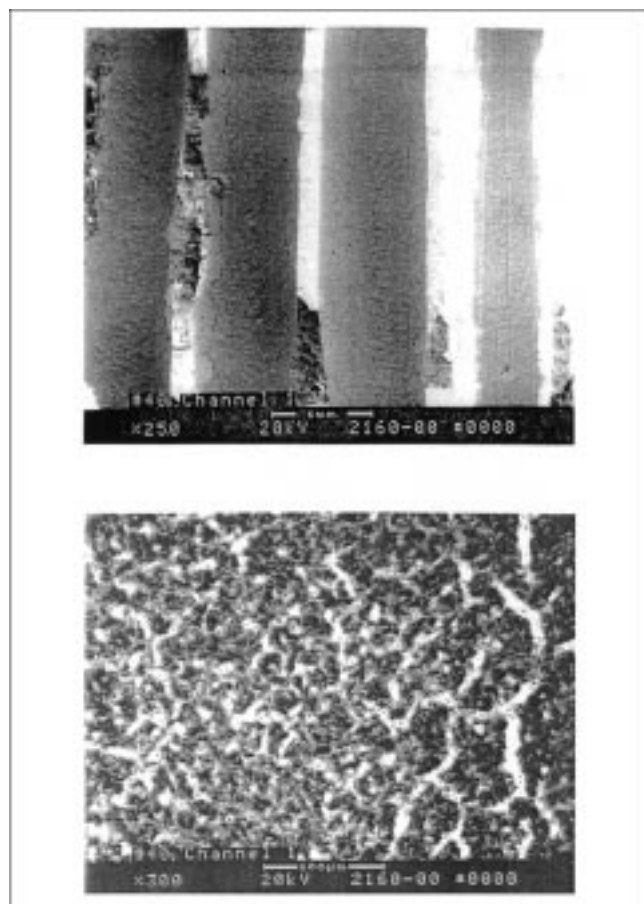


Figure 2. Texture of minireactor channel made of washcoating Ni/alumina catalyst on 400 cpsi cordierite monolith substrate.

Cell density of 400/in², nominal channel opening of 1.0 mm square, wall thickness of ~ 0.18 mm, catalyst layer thickness of 70 μ m; 4.0 wt. % NiO loading, BET surface area of 37 m²/g, average catalyst pore size of 9.5 nm.

The cordierite monolith has low surface areas and macroporous walls, and is generally not well suited as catalyst supports. Thus, additional catalyst support material is coated on the cordierite substrate. Washcoating the cordierite substrate with a layer of γ -alumina powder is an established commercial process. Since γ -alumina is a common catalyst support, many active metal catalysts can be applied onto the alumina

support by impregnation methods. Figure 2 shows the wall texture of minireactor channels made from a cordierite monolith substrate deposited with a layer of nickel oxide-impregnated γ -alumina washcoat support. With commercial washcoating techniques, the cordierite substrate can be fully covered with a dense layer of alumina having minimal cracks or macropores. The pore-size distribution of the washcoated alumina is similar to that of alumina catalyst beads used in commercial packed bed reactors. For the monolith catalyst tested in this work, the average pore size of the catalyst layer is about 9.5 nm.

Monolith parts can also be extruded directly from γ -alumina thereby avoiding the need for washcoating. This approach provides a higher alumina weight loading in the reactor bed compared to thin alumina layers on cordierite substrates. Figure 3 shows the texture of ministructured reactor channels made of an alumina extruded monolith support. In this example, the γ -alumina monolith is impregnated with about 9 wt. % NiO, and the nominal wall thickness and channel opening for this sample are about 0.18 and 1.0 mm, respectively. Even though there is some variation in wall thickness among different channels, the wall texture in a given channel is uniform and dense. The average pore size (7.5 nm), and BET surface area (200 m²/g), are comparable to conventional Ni/ γ -alumina catalyst pellets. The dense wall structure makes it possible to confine the gas and liquid inside each channel, and convective flow in the radial direction through channel walls is eliminated.

The low-pressure drop advantage of the structured system is well recognized, while its performance advantage for the multiphase reaction needs to be demonstrated and understood. A considerable amount of basic research has been conducted to understand the application of monolith catalysts to gas/liquid catalytic reactions, hydrogenation of nitrocompounds (Hatziantonlou et al., 1986), competitive hydrodesulfurization and hydrogenation (Irandoost and Gahney, 1990), glucose oxidation (Kawakami et al., 1989), oxidation of acetic acid (Klinghoffer et al., 1998), and olefin hydrogenation (Smits et al., 1996). However, most of the reaction conversion data reported in the literature for monoliths have been generated in differential reactors operating at low on-pass conversion levels and in a flow regime that is characterized by a high liquid linear velocity and a low G/L ratio, which is not typical to most commercial processes. Direct comparisons between the performance of monolith catalyst reactors and trickle beds for gas/liquid reactions have been difficult to make. In addition, the gas/liquid distribution in the previous studies has not been well characterized, so that

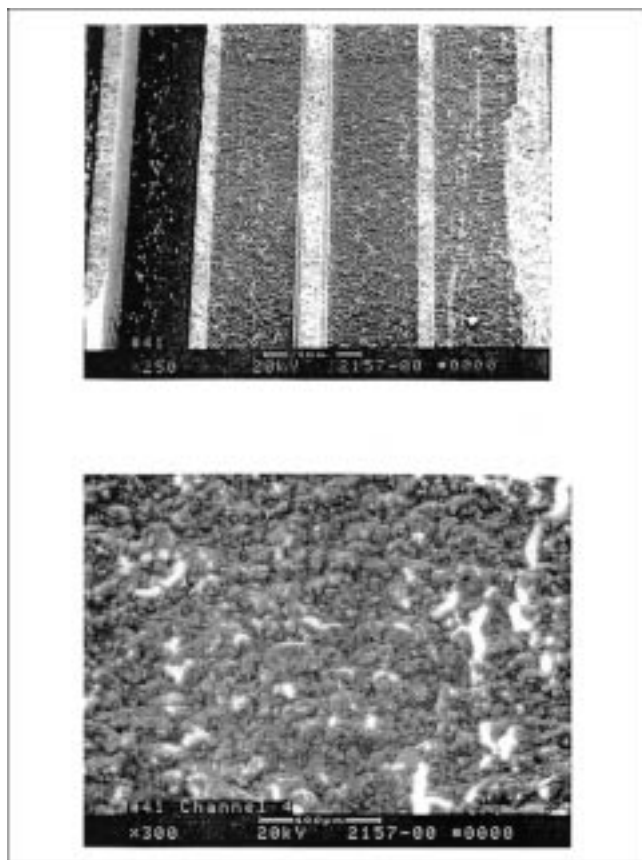


Figure 3. Texture of minireactor channel made of Ni-impregnated 400 cpsi γ -alumina monolith substrate.

Cell density of 400/in², nominal channel opening of 1.0 mm square, catalyst wall thickness of 0.18 mm, 9.0 wt. % NiO loading, BET surface area of 200 m²/g, average catalyst pore size of 7.5 nm.

the intrinsic performance is hard to know. This article is intended to clarify some fundamental and experimental issues, and pave the way for future studies.

Fundamental Analysis of Ministructured Catalyst Bed

An important goal of the present study is to develop ways of dramatically improving reactor efficiency. Based on conventional reaction engineering assumptions about multiphase reactors, however, it may be difficult to understand how mini-structured reactors can show performance benefits compared to the trickle beds containing catalyst pellets. A theoretical framework to describe processes occurring in the ministructured reactor is introduced here. This background will be needed later to understand significance of the experimental results, compare the performance of ministructured reactor beds against conventional trickle-bed reactors, and justify more systematic studies in the future.

The first issue is about catalyst loading density, that is, the amount of catalyst per unit of reactor volume. In general, for gas/liquid catalytic reactions in a given reactor vessel, the conversion increases with the amount of catalyst pellets that can be packed inside the reactor. It is a common practice to

improve the reactor conversion of kinetically slow reactions by maximizing the catalyst loading density and minimizing the void fraction. In this regard, a ministructured catalyst bed does not offer much advantage compared to conventional catalyst pellets even though both may be made out of the same material. This is due to the low packing density and high void fraction of the structured system. For monoliths, the void fraction is a function of cell density, commonly described by the number of cells per square in. (cpsi), and wall thickness. Void fractions for commonly used monolith substrates having square channel openings can be varied from 60–80%. This is typically much higher than random packed beds, such as 35–40%, where void fraction is primarily a function of particle size and shape and the reactor loading method. The void fraction of monolith catalysts can be decreased by increasing the wall thickness to a level comparable with the particle diameter of conventional packed-bed catalysts. However, increasing the wall thickness reduces the specific geometric surface area (m²/m³) and increases the mass-transfer resistance inside the catalyst wall. Thus, significant performance advantage of ministructured systems cannot be rationalized from the point of view of the catalyst loading density.

The second controversial issue is about geometric surface area. It is generally believed that the external mass-transfer rate is proportional to the catalyst external surface area per unit of reactor volume, that is, specific geometric surface area. For fast reactions that are constrained by mass-transfer inside the catalyst pore, a monolith catalyst is perceived to be advantageous because of its thin catalyst layer and higher catalyst effectiveness factor. Such an activity enhancement is ultimately a geometric surface area enhancement. Monolith catalysts can have higher specific geometric surface areas compared to packed beds, and do so at a significantly lower-pressure drop. However, the specific geometric surface area advantage is limited, depending on what monolith cell density can be practically manufactured and what catalyst pellet size is compared to.

Figure 4 compares the specific surface areas of monoliths used in ministructured reactors to randomly packed catalyst spheres used potentially in trickle-bed applications. For these calculations, the void fraction of the packed catalyst particle is assumed to be 0.35. It is known that the specific surface area of the packed catalyst particle rapidly increases with a decrease of the particle size. At the constant void fraction, the specific surface area of monolith catalysts increases with cell density. At the same cell density, the monolith catalyst surface area increases with an increase of the void fraction. When compared to a 3.2 mm catalyst bead, a typical 400 cpsi monolith catalyst has an advantage, but if the catalyst bead diameter is reduced to about 1.6 mm, such an edge no longer exists. The manufacturing difficulty and the cost of monoliths rapidly increases with the cell density. Cylindrical extruded 1.6 mm catalyst pellets are commonly used in industrial trickle bed reactors. As a result, significant performance benefits from ministructured reactors would not be expected based on the specific surface area compared to trickle beds.

It is proposed here that realization of a dramatic performance improvement with the ministructured bed lie in the bed structure itself that fundamentally changes the way how gas-liquid-catalyst contacts. Figure 5 illustrates conceptually

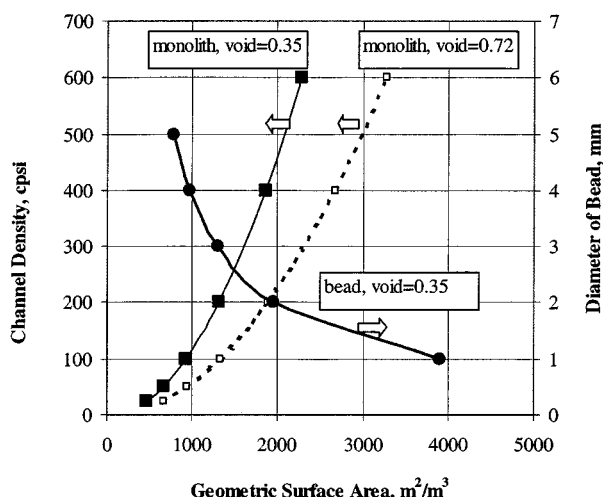


Figure 4. Comparison of geometric surface area of monolith to bead.

cpsi = number of channel/ in^2 .

possible differences in two-phase flow patterns for a random packed bed and a ministructured channel system. The flow is assumed to be gas continuous and liquid dispersed. Analysis of potential problems with the packed catalyst pellet bed is the starting point.

As the two-phase mixture flows co-currently through the packed catalyst pellets, the liquid contacts the pellet and wets the catalyst external surfaces. The spreading liquid tends to fill voids both inside the pellet and the larger spaces between adjacent catalyst pellets. Liquid in the interpellet space is preferentially trapped by capillary forces depending on the

characteristic dimension of the local void volume. Wherever this phenomenon occurs, the gas stream must find alternate passages through the bed that are not blocked by bound liquid until the pressure drop through the bed is balanced. The liquid holdup in the bed will have both static and dynamic contributions and in local areas the holdup may fluctuate. Thus, portions of the liquid feed that are trapped in the void spaces are relatively inaccessible to the reactant gas stream. This effectively reduces catalyst utilization, and at the same time increases the chance of secondary reactions such as coking that can occur in stagnant liquid zones due to the relative unavailability of gaseous co-reactant. Since the liquid holdup results from the way catalyst pellets are arranged in these reactors, such a fundamental disadvantage is inherent in the packed-bed reactors.

Fundamental problems with the trickle-bed reactor were pointed out by Ng and Chu (1987). The authors depicted various flow features, such as film, liquid pocket, rivulet, liquid filament, and so on, to illustrate the nonuniformity of the flow pattern within the trickle bed at the particle level. Thus, emphasis on physics at the particle level was proposed for future study of the trickle-bed reactor. Some of these flow features are experimentally confirmed by the recent study with magnetic resonance imaging technique (Sederman and Gladden, 2001). Research results of trickle-bed reactors under unsteady-state flow modulation provide some indication to the liquid pocket problem (Khadikar et al., 1999). However, critical problems, such as how the reactor conversion performance is affected by these flow features and what solution may be used to eliminate them, are not resolved yet for the trickle-bed reactor.

Thus, the following two key assumptions are formulated for research and development of the ministructured reactor to replace the conventional packed bed:

Assumption I. Catalyst in the conventional packed bed is significantly underutilized due to serious nonuniformity at the particle level. The catalyst utilization is improved in a ministructured reactor due to a better liquid/catalyst contacting and enhancement of overall gas/liquid/catalyst mass-transfer process.

Assumption II. Convective flow between adjacent channels in a ministructured reactor is negligible or secondary to the main channel flow so that each reaction channel works as if an independent reaction unit.

As illustrated in Figure 5, gas and liquid flows are confined inside individual channels in the ministructured catalyst bed so that liquid and gas flow could not segregate. Liquid contacting the channel walls tends to spread on channel surfaces similar to packed beds, but there are no horizontally oriented voids that can trap the liquid. Moreover, gas flowing through the open channel space is likely to minimize liquid holdup and promote good contact between gas, liquid, and the solid surface. Under Assumption I, a significant activity improvement is realized in a ministructured reactor by fully utilizing the catalyst external surface and through significant enhancement of the overall mass-transfer processes between gas, liquid, and solid. Under Assumption II, the ministructured catalyst bed can be analyzed by decoupling reactions occurring inside the channel from the influence of external gas and liquid distribution.

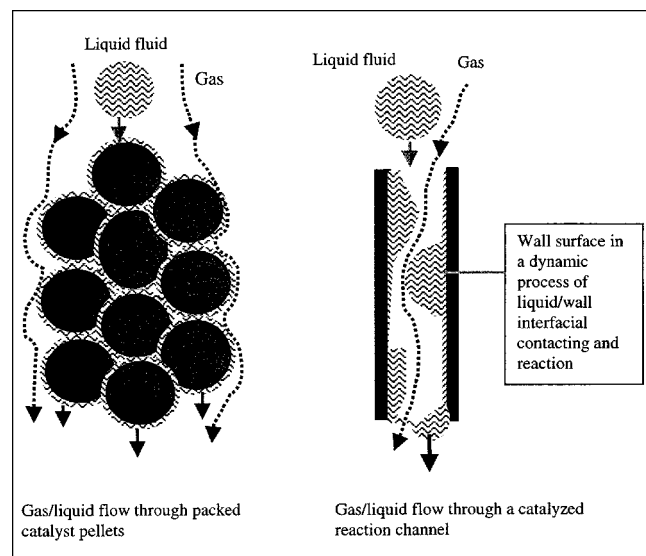
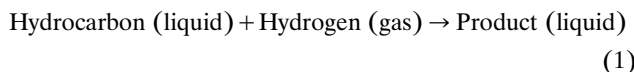


Figure 5. Characteristic of gas/liquid flow pattern through packed catalyst pellets vs. through minireactor channel.

Controlling Factors for Ministructured Reactor Performance

The ministructured catalyst bed as a new reactor system needs to be delineated and studied in a systematic manner. Its performance can be affected by various controlling factors in a way that is very different from the conventional packed-bed reactor. A conceptual analysis of the ministructured reactor is presented in this article for a reaction of unsaturated hydrocarbon molecules with hydrogen as an example



For a given catalytic reaction system, the conversion through a single channel is generally expressed as

$$\chi_C = \chi_C(X_{\text{Flow}}, X_{\text{Geometry}}, X_{\text{Reaction}}) \quad (2)$$

The above equation shows that the conversion through a reaction channel is determined by three groups of controlling factors. X_{Flow} is related to the flow condition inside the channel that can be characterized by superficial liquid and gas linear velocities $\{V_L, V_G\}$. X_{Geometry} is related to the channel geometry that can be defined by a group of parameters (channel opening, catalyst layer thickness, and channel shape). X_{Reaction} represents typical reaction conditions (reaction temperature, pressure, feed composition, and contact time).

It is noted that the above controlling factors are not an exhaustive list. Instead, they are basic variables/parameters to define a specific ministructured reaction system. The flow condition is proposed as basic controlling factors to highlight its importance, relative to the trickle-bed reactor. For co-current downflow operation of the ministructured reactor, it is expected based on the falling film theory that adequate liquid flux or velocity is needed to get the solid surface fully wetted. The channel geometry has a significant effect on the reaction performance and is the core of the structured bed. For example, the channel shape can be made into square, circular, or other forms. For a two-phase flow inside a square channel, the liquid tends to be preferentially trapped in the corner area (Heibel et al., 2001). Thus, both the flow pattern and catalyst effectiveness factor can be affected by the channel shape.

The overall conversion rate through an array of reaction channels (such as structured catalyst bed) is a sum of individual channels.

$$\chi_{\text{Bed}} = \frac{\sum_i \chi_{C,i}(V_{L,i}, V_{G,i}, X_{\text{Geometry},i}, X_{\text{Condition},i}) \cdot V_{L,i} \cdot A_i}{F_{\text{total}} \cdot A_{\text{Bed}}} \quad (3)$$

where $V_{L,i}$ and $V_{G,i}$ are liquid and gas superficial linear velocities in i th channel, respectively, $X_{\text{Geometry},i}$ is geometries of i th channel, $X_{\text{Condition},i}$ is the reaction conditions in i th channel, A_i is the cross-sectional area of i th channel, A_{bed} is

the overall bed cross-sectional area for the flow passage, and F_{total} is the volumetric liquid feed flow rate. For a ministructured reactor comprised of a number of identical reaction channels, the conversion equation is simplified as

$$\chi_{\text{Bed}} = \chi_C(V_{L,\text{avg}}, V_{G,\text{avg}}, X_{\text{Geometry}}, X_{\text{Condition,avg}}) \cdot \eta_{\text{Bed}} \quad (4)$$

$$\eta_{\text{Bed}} = \frac{\sum_i \chi_{C,i}(V_{L,i}, V_{G,i}, X_{\text{Geometry}}, X_{\text{Condition},i}) \cdot V_{L,i} \cdot A_i}{F_{\text{total}} \cdot A_{\text{Bed}} \cdot \chi(V_{L,\text{avg}}, V_{G,\text{avg}}, X_{\text{Geometry}}, X_{\text{Condition,avg}})} \quad (5)$$

where $V_{L,\text{avg}}$ and $V_{G,\text{avg}}$ are average liquid and gas superficial linear velocities, respectively, $X_{\text{Condition,avg}}$ is average reaction conditions inside the channel, and η_{bed} is considered as a G/L distribution factor.

The conversion Eq. 4 carries a strong physical meaning. Essentially, the reaction conversion in the ministructured catalyst bed is decoupled into a single-channel conversion and a gas/liquid distribution factor. The distribution factor is primarily determined by the details of gas and liquid distribution at the entrance to the channels. The initial G/L distribution is important to all the multiphase reactor operations. However, the situation is particularly critical to the ministructured bed performance. In conventional trickle-bed reactors, the randomly oriented void volume allows for radial flow paths and gives the possibility to correct some flow maldistribution along the bed depth. In contrast, once gas and liquid enter the channel of a structured bed, there are no viable flow paths that would alter the distribution along the reactor length. Thus, the ministructured reactor has a much more stringent requirement to the initial distribution of bulk gas and liquid feed flows. Both gas and liquid flow need to be delivered into individual channels. With uniform gas and liquid distribution among all channels, $\eta_{\text{Bed}} = 1.0$ for a catalyst bed under the same reaction condition and performance potential of the ministructured reactor is fully reached. For severe mal-distribution, such as segregated gas and liquid flows, the gas and liquid reactants do not meet inside the channel, $\eta_{\text{Bed}} \approx 0$. In this scenario, the ministructured reactor performance is very poor regardless of how good the structured catalyst really is.

Equation 4 tells for a given reaction system, it is impossible to understand the ministructured reactor performance without knowing the G/L distribution profile at the channel level. The single-channel reaction performance and G/L distribution comprised of two essential technology components for the ministructured catalyst bed. Fortunately, under Assumption II stated in the previous section, these two problems may be decoupled and addressed separately. Assumption II can be met with most of the practical monolith modules containing a dense layer of catalyst coating.

From the above analysis, we can see that understanding the single-channel reaction performance is a key to assessing the potential advantage of the ministructured reactor compared to conventional packed beds. Even for the single channel, the performance can be affected by many factors and each of these factors deserves a systematic study. A simple, liquid/solid (L/S) interfacial reaction model is proposed here to illustrate the relationship of the single-channel perfor-

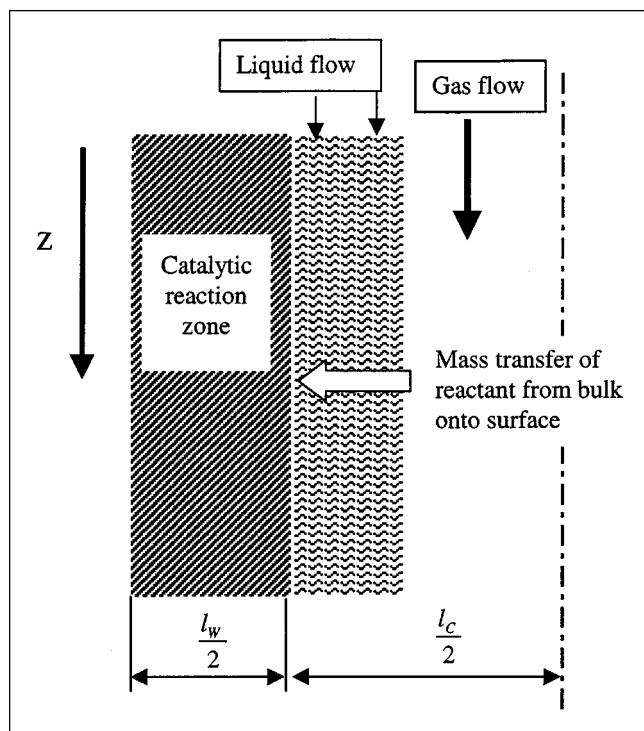


Figure 6. 1-D liquid/solid (L/S) interfacial reaction model.

mance with some of the controlling factors. The model would be helpful for understanding of the experimental results to be presented later.

Figure 6 shows a simplified, one-dimensional (1-D) reaction model with the following major assumptions:

(1) Mass transfer of liquid reactant from bulk onto the catalyst surface and diffusion into catalyst pores are rate-determining processes under all possible flow regimes inside the channel.

(2) Pseudo-first-order kinetics to the liquid reactant.

(3) Square channel wall is fully and uniformly catalyzed.

(4) Plug-flow reactor and isothermal catalyst bed.

A mass balance of the liquid reactant A gives

$$-F_{\text{feed}} \frac{dC_{A,B}}{dz} = \theta_{LS} \cdot 4l_c \cdot k_{LS} \cdot (C_{A,B} - C_{A,S}) \quad (6)$$

A fudge factor θ_{LS} is incorporated in the above rate equation. It represents the fraction of external catalyst surface that is actively involved in the reaction process

$$4l_c \cdot k_{LS} \cdot (C_{A,B} - C_{A,S}) = \left[(l_c + l_w)^2 - l_c^2 \right] \cdot k_V \cdot \eta_w \cdot C_{A,S} \quad (7)$$

$$-V_L \frac{dC_{A,B}}{dz} = \theta_{LS} \cdot \frac{4k_{LS}}{l_c} \cdot \frac{l_w(2l_c + l_w) \cdot k_V \cdot \eta_w}{4l_c k_{LS} + l_w(2l_c + l_w) \cdot k_V \cdot \eta_w} \cdot C_{A,B} \quad (8)$$

The apparent reaction rate constant on bed volume basis

(channel + wall)

$$k_{\text{app,bed}} = \theta_{LS} \cdot \frac{4k_{LS}}{l_c} \cdot \frac{l_w(2l_c + l_w) \cdot k_V \cdot \eta_w}{4l_c k_{LS} + l_w(2l_c + l_w) \cdot k_V \cdot \eta_w} \cdot \frac{l_c^2}{(l_c + l_w)^2} \quad (9)$$

$$\eta_w = \eta_w(\phi) \quad (10)$$

$$\phi = \frac{l_w}{2} \sqrt{\frac{k_V}{D_{\text{eff}}}} \quad (11)$$

$$k_V = k_S \cdot C_{B,W} \quad (12)$$

wherein $C_{A,S}$ is the concentration of reactant A at the catalyst outer surface, $C_{A,B}$ is the concentration of reactant A in the bulk flow, $C_{B,W}$ is the kinetically averaged concentration of reactant B inside the catalyst wall, D_{eff} is the effective diffusivity of reactant A inside the catalyst, k_{LS} is the liquid/solid mass-transfer constant, k_V is the mono-molecular rate constant based on catalyst volume, k_S is the bi-molecular rate constant based on catalyst volume, $k_{\text{app,bed}}$ is the observed rate constant based on bed volume, l_w is the catalyst wall thickness, l_c is the square channel opening, z is the reactor length, ϕ is Thiele modulus of the reaction inside the catalyst wall, and η_w is the effectiveness factor of the catalyst wall.

Equation 12 shows that the rate constant is directly proportional to the concentration of hydrogen inside the catalyst layer

$$\text{let } \delta_{MR} = \frac{4k_{LS}}{k_V \cdot \eta_w}$$

Equation 9 is rewritten as follows

$$\frac{k_{\text{app,bed}}}{\theta_{LS}(k_V \eta_w)} = \frac{\delta_{MR}}{l_c} \cdot \frac{l_w(2l_c + l_w)}{\delta_{MR} \cdot l_c + l_w(2l_c + l_w)} \cdot \frac{l_c^2}{(l_c + l_w)^2} \quad (13)$$

δ_{MR} is a parameter that takes into account the reaction rate constant and mass-transfer terms. Equation 13 is an explicit expression on the effect of channel geometry on the reaction rate. Figure 7 shows plots of the relative activity vs. channel opening at various values of parameter δ_{MR} for 0.1 mm channel wall thickness. The relative activity is a measure of how much catalytic activity can be realized in a ministructured reaction channel. For a given δ_{MR} number, the activity increases as the channel opening is decreased from 5 mm to about 0.1 mm. The range of the δ_{MR} parameter from 1 to 500 mm is likely to cover most of the operating conditions in practical operations. The simulation results suggest that within the range of channel openings suitable for ministructured reactors, small sizes are generally preferred.

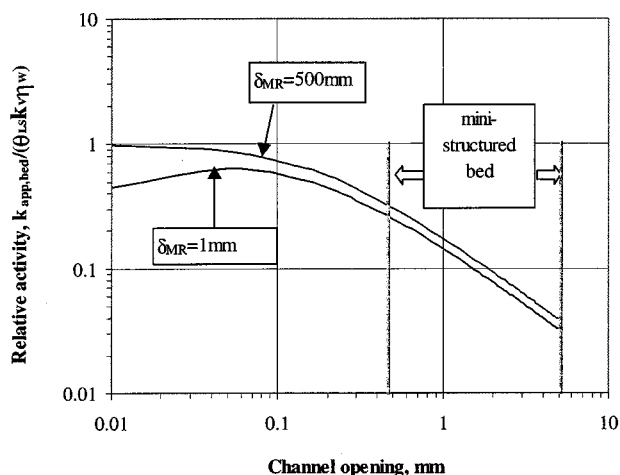


Figure 7. Model projection about effect of channel opening on bed volume-based activity.

Wall thickness, $l_w = 0.1$ mm.

Experimental Method

Catalyst performance tests of the ministructured reactor concept were conducted by directly injecting gas and liquid reactants into a single reaction channel. Direct injection of a two-phase mixture avoids any potential problems with maldistribution that could easily occur with multiple channel openings in a laboratory-scale reactor. Figure 8 shows the reactor containing a monolith catalyst module. The module consists of a ceramic monolith piece having multiple channels with catalyzed walls. A single, centrally located reaction channel is isolated from the others by plugging the top and bottom openings of all remaining channels with inorganic ce-

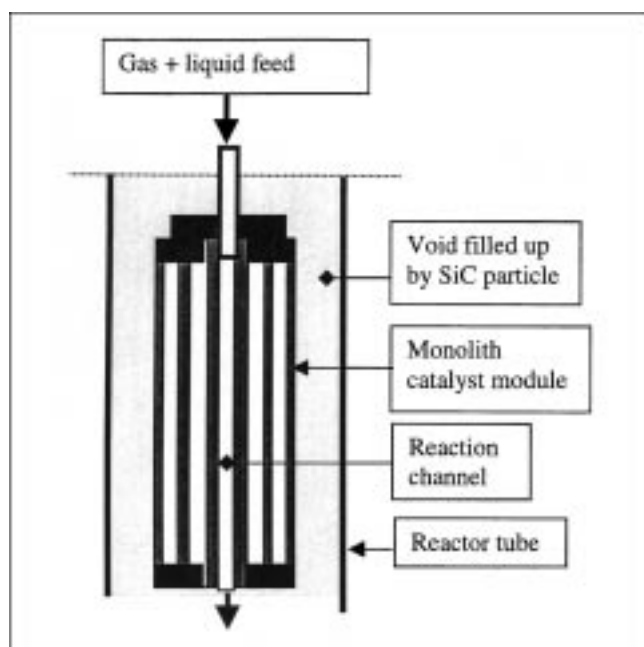


Figure 8. Reactor loading for single-channel reaction testing.

ment, as illustrated in Figure 9. A feed delivery tube is mounted onto the top of the open channel and sealed by cement. The gas and liquid feed mixture is introduced into the reaction channel via the delivery tube and flows through the channel in a co-current downflow mode. The entire catalyst module is housed inside a steel reactor tube to contain pressure. The void space in the annular region between the ceramic monolith and the tube is filled with fine SiC particles to minimize the impact of any potential leakage. Reaction products exit in the bed and are collected for analysis by gas chromatography.

As constructed, the central, open reaction channel represents the lowest pressure drop route for fluid flow. Cold flow testing confirmed that there is no appreciable leakage of liquid from the reaction channel into other adjacent channels. Furthermore, the porous catalyst wall is permeable to hydrogen gas so that the whole catalyst module, including the isolated, unused channels, is kept at the same static pressure. Consequently, there is little driving force for the liquid to flow through the catalyst wall into adjacent channels and all the liquid and gas flows straight through the central reaction channel. With washcoated and bulk alumina monolith catalysts, the catalyst channel wall has a dense texture, as shown in Figures 2 and 3, with a mostly mesoporous structure having an average pore from 6 to 10 nm.

Gas-liquid-solid catalytic reaction testing was performed under steady-state reaction conditions. Two reaction systems of different kinetics were studied to obtain a good assessment and fundamental understanding of the mini reactor. For clarity, certain process variables used in this article are defined below.

Three liquid hourly space velocities can be defined based on the channel configuration shown in Figure 9

$$LHSV_{\text{Cat}} = \frac{F_{\text{feed}}}{V_{\text{Cat}}} \quad (14)$$

$$LHSV_{\text{Channel}} = \frac{F_{\text{feed}}}{V_{\text{Channel}}} \quad (15)$$

$$LHSV_{\text{Bed}} = \frac{F_{\text{feed}}}{V_{\text{Bed}}} \quad (16)$$

where F_{feed} = volumetric flow rate of the liquid feed at feed conditions, V_{Cat} = volume of catalyst material that is exposed to the liquid reactant, V_{Channel} = volume of the reaction channel in which the reaction occurs, and V_{Bed} = total volume of the packed bed that is exposed to the liquid reactant, catalyst volume plus the void space. Thus, $LHSV_{\text{Cat}}$, $LHSV_{\text{Channel}}$, and $LHSV_{\text{Bed}}$ are the space velocity relative to the catalyst volume, channel volume, and catalyst bed volume, respectively.

Superficial liquid linear velocity is a measure of how fast the liquid flows through the open channel. In reality, the channel is not fully occupied by liquid alone in a two-phase flow

$$V_L = \frac{F_{\text{feed}}}{SA_{\text{Channel}}} \quad (17)$$

where SA_{Channel} = cross-sectional area of the channel.

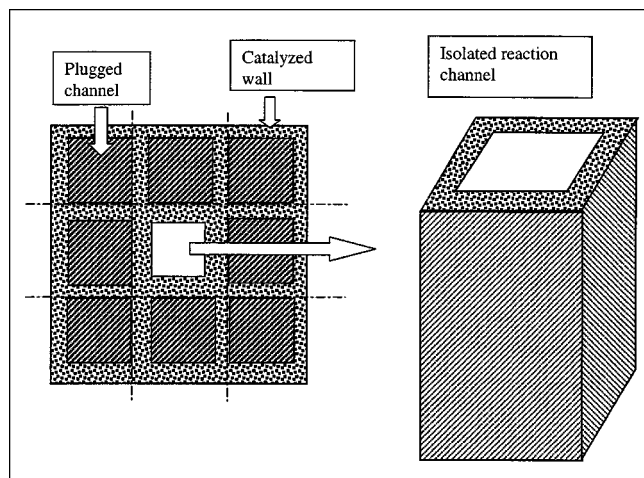
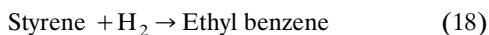


Figure 9. Single reaction channel isolated from a multi-channel catalyst module.

Experimental Result and Discussion of Olefin Hydrogenation

Hydrogenation of styrene to ethylbenzene and 1-octene to n-octane are used as model reactions for studying fast kinetics in a ministructured reactor. There are literature data available for this reaction system (Smits et al., 1996)



The feed is prepared by mixing styrene and 1-octene with toluene; 100% hydrogen is used as the co-reactant. Benchmark olefin hydrogenation in a trickle bed was conducted over Ni/alumina catalysts using catalyst particles of different sizes. This study is necessary to understand the performance of the same reaction within the ministructured reaction channel. Particles are prepared by crushing 3.2 mm Ni/alumina catalyst beads and sieving the crushed particles into two different sizes: 335 μm and 132 μm on average. Catalyst particles are blended with 60 mesh silicon carbide to improve particle wetting in the packed reactor and to reduce the tendency for fluid bypassing at the wall, and the blend is loaded into a laboratory-scale trickle-bed reactor having a 25 mm diameter. The catalyst is reduced *in-situ* prior to reaction by flowing hydrogen through the reactor at a pressure of 15 bar and a temperature of 673 K for about 10 h. Following the reduction, hydrogen and the olefin/toluene blend are fed to the reactor at the same pressure and temperatures between 303 and 373 K. At these conditions, flash calculations indicated that the reactor was operating in a gas/liquid two-phase flow mode.

Figure 10 shows variations of styrene and 1-octene conversion with LHSV_{Bed} at two different temperatures. Under reaction conditions used in this work, the conversion data are fitted by first-order kinetics. An apparent rate constant is derived to represent the hydrogenation activity

$$k_{\text{app}} = -\ln(1 - \chi) \cdot \text{LHSV}/3,600 \quad (20)$$

where χ is the one-pass conversion of the liquid reactant.

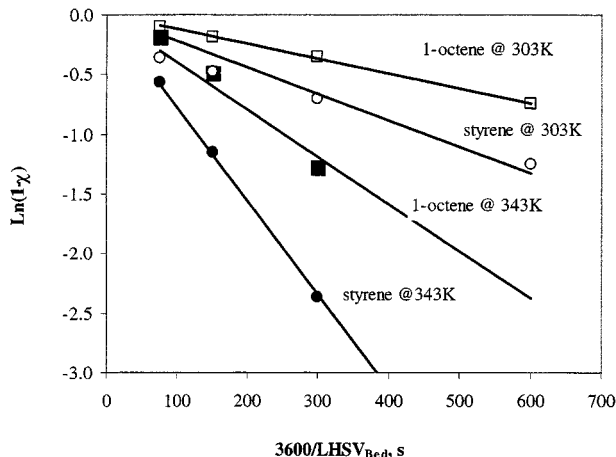


Figure 10. Effect of LHSV_{Bed} on olefin conversion over 3.2 mm Ni/alumina catalyst bead in trickle-bed testing.

Feed: 5% 1-octene/5% styrene/90% toluene; reaction condition: 15 bar, $\text{H}_2/\text{oil} = 50 \text{ NL/L}$; Catalyst: 10 wt. % NiO loading.

The apparent activation energy for the 3.2 mm catalyst bead is calculated as 32 kJ/mol for styrene and 29.3 kJ/mol for 1-octene. This result gives a strong indication that the olefin hydrogenation over the Ni catalyst may be limited by mass transfer inside the catalyst. Effect of the mass transfer on the olefin hydrogenation activity is further shown in Figure 11. At constant reaction conditions, the apparent rate constant increases with a decrease of the particle size. These results clearly show that olefin hydrogenation rate over the Ni catalyst in the trickle-bed operation is limited by mass transfer into the catalyst pore. For a reaction affected by the pore diffusion, increasing the activity by reducing the catalyst particle size is an obvious approach to improve the reactor per-

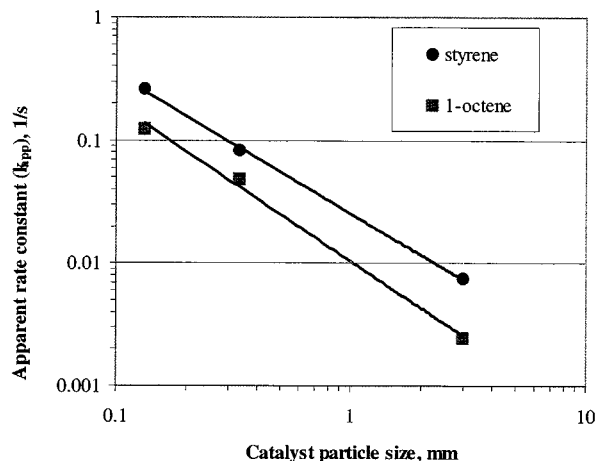


Figure 11. Effect of particle size on olefin hydrogenation activity on the basis of LHSV_{Bed} in trickle-bed testing.

Feed: 5% 1-octene/5% styrene/90% toluene; reaction condition: 15 bar, $\text{H}_2/\text{oil} = 50 \text{ NL/L}$, 333 K; Catalyst: crushed 3.2 mm NiO/alumina catalyst bead.

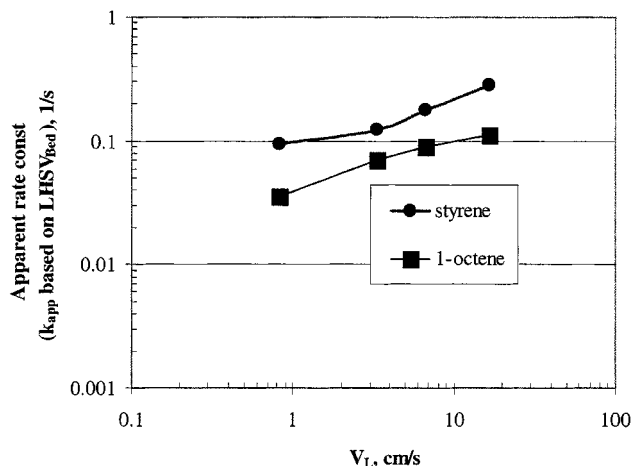


Figure 12. Effect of liquid superficial linear velocity inside channel on olefin hydrogenation activity inside ministructured reaction channel.

Feed: 5% 1-octene/5% styrene/90% toluene; Reaction condition: 15 bar, H_2 /oil = 50 NL/L, 333 K; Mini-reactor channel (Figure 2): 1.0 mm square x 30 cm long, 4 wt. % NiO loading, $\sim 70 \mu\text{m}$ catalyst layer on 400 cpsi cordierite monolith substrate.

formance. However, particle-size reduction is limited by a pressure drop across the catalyst bed, since the pressure drop drastically increases with decreasing particle size.

Olefin hydrogenation reaction in the ministructured reactor was systematically investigated by use of the washcoated Ni/alumina monolith catalyst, as shown in Figure 2. A layer of Ni/alumina catalyst at $70 \mu\text{m}$ thickness on average was uniformly deposited onto channel walls of a 400 cpsi cordierite monolith support. The ministructured reaction channel opening is 1 mm square. Figure 12 shows the apparent rate constant for the hydrogenation reaction in the minireaction channel. The rate constant is calculated using Eq. 20 with $LHSV_{\text{Bed}}$, based on the total channel volume, that is, open channel volume + whole channel wall volume. Since the reaction occurs only inside the testing channel, the other side of the catalyst layer may not participate in the reaction. Thus, this activity is a fairly conservative estimate. The rate constant increases with superficial liquid linear velocity inside the channel, which suggests that the reaction is also affected by liquid mass transfer from the bulk onto the catalyst surface. Comparing Figure 12 to Figure 11, we can see that under the same reaction conditions, the rate constant of the minireactor is much higher than the 3.2 mm catalyst bead in the laboratory trickle-bed testing, and is comparable to the crushed catalyst particle. It is noted that the trickle bed contains about 60% of the catalyst volume, while the ministructured bed for this test contains only about 10% of the catalyst volume. These experimental results are strong evidence to support the proposal that the catalyst in the trickle-bed operation is significantly underutilized, and that a dramatic improvement is feasible by use of the ministructured catalyst bed.

In the above testing of the ministructured reactor, liquid feed rate was varied, while the channel length was fixed. As a result, the liquid linear velocity and space velocity were

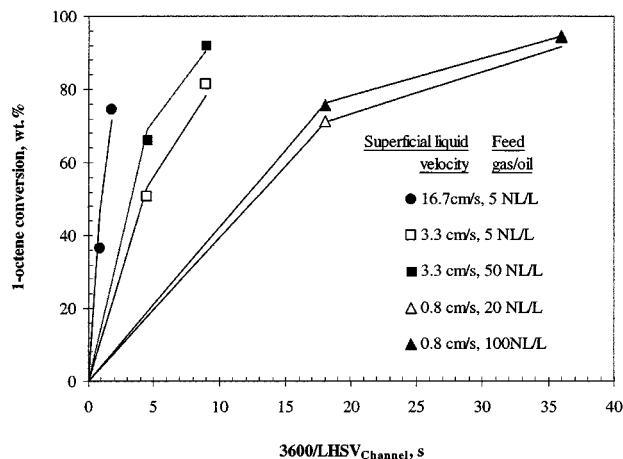


Figure 13. Effect of space contact time on 1-octene conversion under constant flow conditions inside ministructured reaction channel.

Feed: 0.5% 1-octene/0.5% styrene/99% toluene; Reaction condition: 15 bar, 333 K; Mini-reactor channel (Figure 2): 1.0 mm square x 15 or 30 cm long, 4 wt. % NiO loading, $\sim 70 \mu\text{m}$ catalyst layer on 400 cpsi cordierite monolith substrate.

changed at the same time and the effect of flow conditions such as liquid linear velocity on the activity was not explicitly shown. There was a concern about the data interpretation and the flow regime inside the channel. In general, it is expected that a certain channel length is needed to have a two-phase flow fully developed, so there might have been some possibility that the ministructured reactor was operated under transient flow conditions. To clarify these issues, a new set of experiments was conducted with the ministructured reactor of a different length. The conversion data were obtained at different LHSV under constant gas/liquid ratio and liquid linear velocity. Figure 13 shows variations of 1-octene conversions with channel volume-based LHSV under various flow conditions. $3600/LHSV$ is space contact time in seconds. At constant liquid linear velocity, the conversion increases with the contact time, which is in line with the basic principle. The two data points for each set of flow conditions are well regressed with a first-order kinetics. To achieve a certain conversion level, a shorter space contact time is needed when the reactor is operated at a higher liquid linear velocity. Such experimental data clearly shows the effect of flow conditions on the conversion. The flow condition inside the channel is indeed an important controlling factor for the ministructured bed as proposed in the previous fundamental analysis.

It is worthwhile to note that about 90% 1-octene conversion is obtained at a space contact time of 10 s or $LHSV_{\text{channel}} = 360 \text{ L/h}$ when the reactor is operated at 3.33 cm/s of liquid linear velocity and a 50 NL/L of H_2 /oil ratio. Such a large one-pass conversion is unprecedented given the exceptionally high space velocity used, which again demonstrates the exceptional high hydrogenation activity inside the ministructured catalyst channel. Only 1-octene conversions are plotted in Figure 13, because the same trend is found for the styrene conversion.

Gas and liquid two-phase flow inside a mini-structured channel may occur in various flow regimes such as falling film, annular flow, bubbling flow, slug flow, or others. Most of the hydrodynamic studies for two-phase flow inside the small tube in a dimension close to the channel opening of the mini-structured bed are conducted in a capillary glass with air/water. In the early work by Satterfield and Özel (1977), a slug flow was observed inside a 2 mm glass tube at V_L greater than 1.7 cm/s, independent of gas velocity, and the flow pattern would transform into annular flow when the V_L is reduced. Recently, Triplett et al. (1999) reported a systematic study of two-phase flow inside capillary tubes of millimeter size in the range of high liquid and gas linear velocities. Unfortunately, complete two-phase flow mapping under flow conditions of present interest, V_L from 0.1 to 10 cm/s and V_G from 1 to 100 cm/s, could not be found in the open literature yet. In addition, how to translate the air/water hydrodynamics into the hydrogen/hydrocarbon system, and how the flow pattern is affected by the wall surface properties are still open questions that need to be resolved in order to understand what the flow pattern would be inside a catalyst reaction channel.

The present objective is to assess the feasibility of a mini-structured bed under flow conditions that the author thinks would be relevant to most practical applications. From the above studies, we know that the olefin hydrogenation mostly occurs on the external surface of the Ni/alumina catalyst. This reaction system is a good measure of mass transfer from bulk fluid onto the catalyst surface. Thus, effect of flow conditions on the olefin conversion is further studied with the mini-structured catalyst module made of 400 cpsi Ni/alumina wash-coated cordierite monolith. Reaction testing was conducted with a feed consisting of styrene, 1-octene, and toluene over a wide range of liquid linear velocity and H_2 /oil ratio. It was found that the styrene conversion strongly correlates with the 1-octene regardless of reaction conditions. This observation suggests that the intrinsic kinetics of different hydrogenation reactions is not affected by the flow condition. In other words, effect of the flow condition or hydrodynamics on the relative activity of styrene to 1-octene is insignificant. Thus, only apparent activity for hydrogenation of 1-octene is plotted in Figure 14. This activity is based on $LHSV_{channel}$ and can be converted into $LHSV_{Bed}$ -based activity by multiplying 0.54. A general trend is observed that the hydrogenation activity increases with increasing feed H_2 /oil ratio and increases with increasing liquid linear velocity. The wide range of flow conditions used in this testing encompasses various possible flow regimes, annular, slug, and so on. The apparent activity is determined by the intrinsic reaction rate constant and mass-transfer coefficient, as illustrated by the model Eq. 8. Decoupling these factors will be reported in the future study. Since the volumetric mass-transfer coefficient has to be greater than the apparent rate constant, the high apparent activity obtained under all flow conditions tested here indicates that the mass-transfer rate within the mini-structured reaction channel would be high enough to meet the requirement of most reaction systems.

Experimental Result and Discussion of Aromatic Saturation

Olefin hydrogenation is known as a kinetically fast reaction. The exceptionally high activity previously shown for the

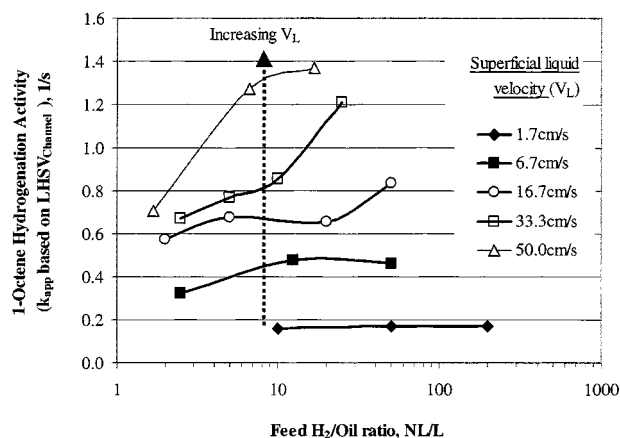
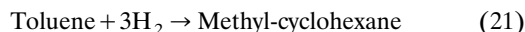


Figure 14. 1-octene hydrogenation activity under various flow conditions inside mini-structured reaction channel.

Feed: 0.5% 1-octene/0.5% styrene/99% toluene; Reaction condition: 15 bar, 333 K; Mini-reactor channel (Figure 2): 1.0 mm square x 15 or 30 cm long, 4 wt. % NiO loading, ~ 70 μ m catalyst layer on 400 cpsi cordierite monolith substrate.

olefin hydrogenation suggests excellent liquid/catalyst contacting and rapid overall mass-transfer rates of gas and liquid reactants inside the mini-structured catalyst channel. However, catalytic activity for one class of reactions cannot be readily extrapolated to other types of reactions. Thus, hydrogenation of toluene in a mini-structured reactor is used as a second model reaction to study the behavior of systems having kinetics slower than the olefin hydrogenation



The study of toluene hydrogenation is relevant to commercial processes involving mono-aromatic hydrogenation. Nickel on γ -alumina catalyst is used for toluene hydrogenation. Performances of mini-structured reactors made of Ni/ γ -alumina monolith catalysts of different channel sizes are compared in Figure 15. Different from the washcoated catalyst used for the olefin hydrogenation, the channel wall for toluene hydrogenation is fully catalyzed. Each catalyst module was prepared by the same procedure with the same precursor material, and both catalyst modules have square channel geometry. Catalyst wall thickness is about the same for both, but the channel opening is about 1.0 mm for the 200-cpsi reactor and 2.0 mm for the 100-cpsi. Thus, when liquid feed passes through each of the two reactor channels at the same flow rate, the $LHSV_{channel}$ differs by a factor of four.

Figure 15 shows conversion vs. temperature data for the 1 mm and 2 mm reaction channel operating at $LHSV_{channel}$ of 650 h^{-1} and 98 h^{-1} , respectively. Under the same reactor pressure and the same H_2 /oil ratio, with the same feed, comparable or higher conversion occurs inside the 1 mm-channel even though it is operating at 6.5 times higher $LHSV$ than the 2 mm-reaction channel. Therefore, catalytic activity inside the 1 mm-catalyst channel is at least 6.5 times that of the 2 mm-channel. The same materials and procedure were used in preparation of the two catalysts, which resulted in the same NiO loading. With the similar catalyst wall thickness, the cat-

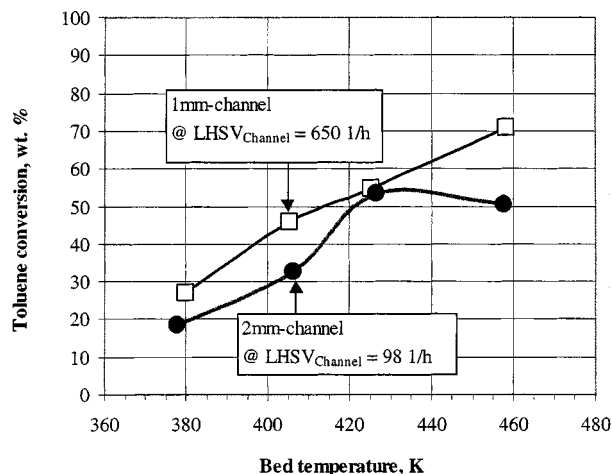


Figure 15. Toluene conversion in minireactor channels of a different opening.

Catalyst: 9 wt. % NiO/ γ -alumina monolith support (Figure 3); Feed: 5.0 wt. % toluene/methyl-cyclohexane; Reaction condition: 15 bar, H_2 /Oil of 50 NL/L, $V_L = 0.8$ cm/s for 2 mm-channel and $V_L = 5.5$ cm/s for 1 mm-channel; 1 mm-channel (200 cpsi): 1.0 mm square x 30 cm long, 0.7 mm wall thickness; 2 mm-channel (100 cpsi): 2.0 mm square x 30 cm long, 0.7 mm wall thickness.

alyst effectiveness factor should be similar. Geometric surface area for the 1 mm-channel is only two times that for the 2 mm-channel, which cannot explain the large activity difference. This is the reason why a fudge factor θ_{LS} is introduced into Eq. 6 for the L/S interfacial reaction model. It is emphasized that the external surface in the mini-structured system should not be assumed to be uniform implicitly. Although the liquid/catalyst contacting in the structured system is generally better than in the randomly packed pellet bed, full utilization of the catalyst surface in the structured system still depends on the hydrodynamics inside the channel, as well as the L/S surface dynamics. For the mini-structured system proposed in this article, the channel opening is close to the capillary length of the liquid fluid. As the channel opening decreases, the surface tension becomes increasingly significant. As a result, the surface wetting/de-wetting dynamics may play a significant role in the two-phase reaction process. The present testing result suggests that within the range of mini-structured systems, smaller channel sizes are generally preferred and decreasing the channel size may result in an activity increase that is disproportionately higher than an increase in the geometric surface area.

It is difficult to compare the mini-structured reactor activity to the packed catalyst pellet reported in the literature because of uncertainty and variation in the catalyst properties and reaction conditions. Thus, a comparative test was conducted in this work by using the same catalyst material and the same reaction condition. Two monolith catalyst modules used for this series of experiments have the same channel opening of 1 mm, but different wall thickness. One module has a wall thickness of 0.18 mm, while another one is 0.7 mm thick. The channel wall is fully catalyzed as evidenced by X-ray probe analysis. The Ni/ γ -alumina monolith catalyst module was crushed into 74-177 μ m particles. The activity of the crushed catalyst particles was measured in the trickle-bed re-

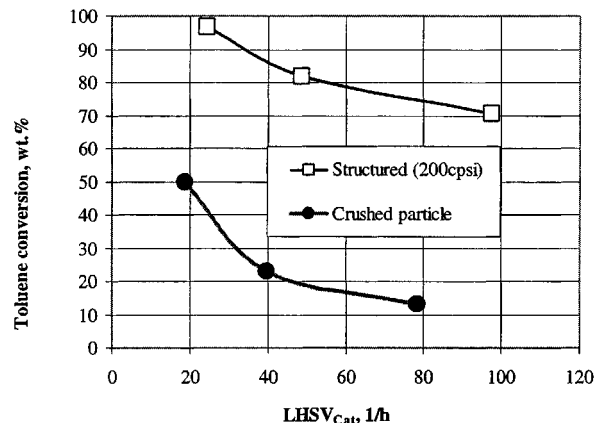
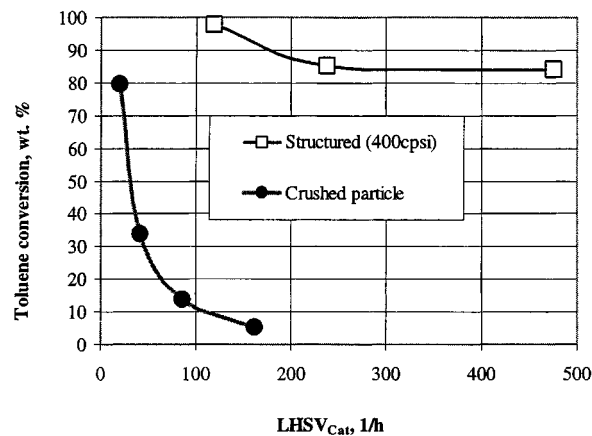


Figure 16. Effect of catalyst volume-based LHSV on toluene conversion over the same NiO/ γ -alumina catalyst in a different bed structure.

Catalyst: NiO/ γ -alumina monolith (Figure 3); Feed 1.0 wt. % toluene/methyl-cyclohexane; Reaction condition: 15 bar, 373 K, H_2 /Oil of 50 NL/L; Crushed particle size: 74-177 μ m; 400 cpsi mini-structure: 1.0 mm square, 0.18 mm thick; 200 cpsi mini-structure: 1.0 mm square, 0.70 mm thick.

actor with SiC particles as the diluting material. In Figure 16, catalytic activities of the mini-structured reaction system are compared with the respective crushed particles in the trickle flow operation under the same reaction temperature, pressure, and feed H_2 /ratio. In these comparisons, toluene conversion is plotted vs. a liquid hourly space velocity based on the Ni/ γ -alumina catalyst volume. For the mini-structured reaction channel, this volume is that of the catalyst wall that surrounds the reaction channel as shown in Figure 9. The volume of the crushed particle system is calculated based on the total bed weight and the Ni/ γ -alumina catalyst density. Figure 16 shows that at the same LHSV_{cat}, toluene conversion inside the mini-structured channel is significantly higher than in the bed of crushed catalyst particles. The size of the crushed catalyst particles (74-177 μ m), is smaller than the catalyst wall thickness. Thus, the large activity difference cannot be explained by the catalyst effectiveness factor. It is the better catalyst utilization that makes the catalyst in the structured form appear more active than in the crushed particle form.

Although the two structured catalyst modules were made of the same catalytic material and are of the same channel opening, they behave differently in the catalytic performance. Toluene conversion over the 200-cpsi structured catalyst steadily declines with increasing $LHSV_{Cat}$, while the same kind of trend is not shown by the 400-cpsi structured catalyst. For this structured system, the conversion changes little as $LHSV_{Cat}$ is increased from 230 to 460 h^{-1} . It is not clear presently why the two structured catalysts of different thickness can behave so differently. These experimental results suggest that the physics and reaction process actually occurring inside the channel could be very complicated. Wetting and de-wetting dynamics, partial and full wetting, all these liquid/solid surface phenomena can possibly affect the reaction performance. Thus, further study of the ministructured reactor system is necessary to fully understand and explore its potential as the next generation of multiphase reactor technology.

Concluding Remarks

The ministructured reactor concept is introduced and shown in this article to achieve significant improvements relative to trickle-bed reactors for gas/liquid two-phase catalytic reactions through structuring the catalyst bed at the particle level. The size of the ministructure open channel ranges from 0.5 to 5 mm, which are values that are comparable to the randomly oriented void openings in packed-bed reactors. The uniform orientation of the structured reactor is presumed to be the important difference between the performance of these systems and trickle beds. In the ministructured reactor, the catalyst bed is divided into a number of essentially independent reaction channels with catalytic walls. These can be made in many of the catalyst support materials used today in conventional catalytic processing.

Feasibility and performance of the ministructured reactor is demonstrated by conducting single-channel reaction testing with two different types of reactions, olefin hydrogenation, and toluene saturation. Gas and liquid feeds are directly injected into the ministructured catalyst channel to eliminate any maldistribution problem. A dramatic activity improvement was observed for both of these reactions compared to the trickle beds. The size of the improvement is larger than that predicted by differences in the geometric surface area of the catalysts. The testing results support a key premise of the ministructured reactor, that catalyst particles in randomly packed fixed-bed reactors are significantly underutilized. The large activity improvement with the ministructured catalyst bed results from much better contact of gas, liquid, and solid phases in the reactor channels.

It is proposed that the ministructured reactor system be studied by decoupling a single-channel performance and gas/liquid distribution factor because of its unique structure. The single-channel performance comprises the fundamental, while the gas/liquid distribution determines its practicality. Many controlling factors can affect the channel performance. In addition to reaction conditions (temperature, pressure), flow conditions inside the channel and channel geometries are important and unique features for the ministructured system. Since the channel opening is similar to the capillary length of the liquid fluid, liquid/solid surface phenomena may

also play a significant role. The experimental results show that the ministructured reactor is effective under the flow conditions within the range of most commercial gas/liquid catalytic operations, such as trickle-bed reactors. A systematic study of the ministructured system in every aspect is proposed to fully understand and develop its potential as the next generation of multiphase reactor technology.

Acknowledgment

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Notation

- A_{bed} = overall bed cross-sectional area for flow passage
- A_i = cross-sectional area of i th channel
- $C_{A,S}$ = concentration of reactant A at catalyst outer surface
- $C_{A,B}$ = concentration of reactant A in bulk fluid
- $C_{B,W}$ = kinetically-averaged concentration of reactant B inside catalyst wall
- D_{eff} = effective diffusivity of reactant A in the catalyst pore
- F_{feed} = volumetric flow rate of liquid feed at feed condition
- k_{LS} = liquid/solid mass-transfer constant
- k_V = mono-molecular rate constant based on catalyst volume
- k_S = bi-molecular rate constant based on catalyst volume
- $k_{app,bed}$ = observed rate constant based on bed volume
- k_{app} = apparent first-order rate constant
- $LHSV$ = liquid-hourly-space-velocity
- $LHSV_{Cat}$ = liquid-hourly-space-velocity relative to catalyst volume
- $LHSV_{Channel}$ = liquid-hourly-space-velocity relative to channel volume
- $LHSV_{bed}$ = liquid-hourly-space-velocity relative to catalyst bed volume
- l_W = catalyst wall thickness
- l_C = square channel opening
- $SA_{channel}$ = cross-sectional area of reaction channel
- V_{Cat} = volume of catalyst material that is exposed to liquid reactant
- $V_{channel}$ = volume of reaction channel in which the reaction occurs
- V_{Bed} = total volume of packed bed, catalyst volume plus the void space
- V_L = superficial liquid linear velocity
- V_G = superficial gas linear velocity
- $V_{L,avg}$ = average superficial liquid linear velocity
- $V_{G,avg}$ = average superficial gas linear velocity
- $V_{L,i}$ = superficial liquid linear velocity in i th channel
- $V_{G,i}$ = superficial gas linear velocity in i th channel
- X_{Flow} = flow condition variables
- $X_{Geometry}$ = channel geometry variables
- $X_{Reaction}$ = reaction condition variables
- $X_{Flow,i}$ = flow condition variables in i th channel
- $X_{Geometry,i}$ = channel geometry variables in i th channel
- $X_{Reaction,avg}$ = average reaction condition variables in bed
- z = reactor depth
- χ = conversion of liquid reactant
- χ_C = conversion of liquid reactant through individual channel
- χ_{Bed} = conversion of liquid reactant through structured bed
- δ_{MR} = characteristic reaction length
- ϕ = Thiele modulus of the reaction inside the catalyst wall
- η_W = effectiveness factor of catalyst wall
- η_{Bed} = G/L distribution factor
- θ_{LS} = fraction of channel surface involved in reaction process

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