Gas–Liquid Catalytic Hydrogenation Reaction in Small Catalyst Channel

Wei Liu, Shantanu Roy, and Xiaodong Fu
Corning Incorporated, Science and Technology Division, Corning, NY 14831

DOI 10.1002/aic.10547
Published online May 23, 2005 in Wiley InterScience (www.interscience.wiley.com).

A study is presented on the performance potential of gas–liquid–solid multiphase catalytic reactions in small-size structured catalyst/reactor channels. A hydrogenation reaction is performed over the Ni/alumina monolith catalyst module with a model feed consisting of styrene, 1-octene, and toluene. The gas/liquid feed stream is directly delivered into a single, representative channel of the multichannel monolith catalyst module to eliminate any flow distribution problem. The reaction tests are conducted with different channel sizes, wall structures, and feed compositions. The cocurrent downflow operation is compared to the cocurrent upflow. The olefin hydrogenation reaction is found to be severely limited by mass-transfer rates. Because of intensified mass transfer inside the small catalyst channel, substantial olefin conversion (>50%) is achieved even at unconventionally high LHSV (~2000 v/v/h). Liquid and gas superficial linear velocities were varied over a wide range (U_L = 1–50 cm/s, U_G = 1–2000 cm/s) to elucidate effects of possibly different flow regimes on the reaction performance. The mass-transfer rate constant of liquid reactant from bulk fluid onto the channel surface in a 1-mm reaction channel is found to be related to the flow conditions by a simple equation, ak_{LS} (1/s) = $0.094(U_L + 0.1U_G)^{0.788}$. The mass-transfer equation is useful for selection of suitable flow conditions for a given catalytic reaction rate. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 2285–2297, 2005

Keywords: multiphase reaction, gas/liquid; microreactor, minireactor, structured catalyst, structured reactor, monolith catalyst, monolith reactor, flow regime, hydrodynamics, mass transfer, hydrogenation

Introduction

Gas/liquid multiphase reactions over a solid catalyst have been used in a variety of processes in refining, petrochemical, chemical, biochemical, pharmaceutical, and environmental industries. For example, hydrogenation and hydrotreating processes represent one important category of gas–liquid–solid catalytic reactions for production of a number of refined products and chemical intermediates. Various reactor designs have been used in the commercial operation, such as trickle bed, fluidized bed, and slurry bed.

Improvements to those existing reactors have been incremental in nature. Recently, structured catalyst beds or reactors as well as other novel packed-bed configurations have been proposed as of high potential for significant improvement to three-phase catalytic processes, such as microreactors[1] and ministructured catalyst beds.[2] The structured catalyst/reactor is characterized with straight flow channels and a "flat" catalyst surface. The channel size is small enough to allow for efficient gas/liquid mixing and gas/liquid/catalyst contact to occur inside the channel. As one would expect, this kind of design is a step change away from the conventional catalyst pellet/particle-based bed that is characterized by randomness of the constituent pellets. In the structured catalyst bed, the channel wall

Current affiliation of S. Roy: Dept. of Chemical Engineering, Indian Institute of Technology, Delhi, New Delhi 110016, India.
Correspondence concerning this article should be addressed to W. Liu at LiuW@corning.com.

Table 1. Properties of NiO/Monolith Catalysts Tested in This Work

Catalyst No.	Catalyst Composition	Geometry Channel Size/Wall Thickness	BET Surface Area* (m^2/g)	Pore Volume* (cm^3/g)	Pore Diameter (nm)
Cat I	3.9 wt % NiO/30 wt % γ-alumina/cordierite	1 mm/0.18 mm-inert support**	36.4	0.10	9.6
Cat II	4.1 wt % NiO/30 wt % η-alumina/cordierite	1 mm/0.18 mm-inert support**	25.3	0.078	9.6
Cat III	9.18 wt % NiO/γ-alumina	1 mm/0.18 mm†	214	0.68	9.6
Cat IV	9.05 wt % NiO/γ-alumina	1 mm/0.71 mm†	217	0.50	5.6
Cat V	8.1 wt % NiO/γ-alumina	2 mm/0.71 mm†	187	0.46	7.6
Cat VI	1.96 wt % NiO/20 wt % η-alumina/cordierite	1 mm/0.18 mm-inert support**	8.9	0.037	3.1
Cat VII	11.0 wt % NiO/γ-alumina	1.5 mm/0.30 mm†	178	0.55	9.6

* Numbers are based on the total catalyst weight. For the washcoated catalyst, these numbers are much higher if normalized based on the net alumina weight.
**Thickness is only inert cordierite support. The catalyst coating thickness is about 20–100 μm varying along the perimeter. The closer to the corner, the thicker the coating is.
†Thickness is fully-catalyzed channel wall.

provides both catalyst support and confinement of the two-phase flow. Essentially, each catalyst channel itself works as an individual reactor unit. Thus, the catalyst design and reactor design become more integrated, which requires a change from the conventional thinking toward system design.

The low-pressure drop advantage of the structured catalyst/reactor is well recognized, although its performance advantage for the multiphase reaction needs to be demonstrated and better understood. The monolith catalyst module has been successfully used for gas-phase emission control, exploiting high geometric surface area, low pressure drop, and strong durability. The monolith catalyst of channel size as small as 0.5 mm is a proven materials technology. It is a natural choice to extend this type of structured catalyst material to the gas/liquid multiphase catalytic reaction process.

A considerable amount of exploratory reaction tests have been conducted to understand the application of monolith catalysts to gas/liquid (G/L) catalytic reactions, hydrogenation of nitro-compounds,[3] competitive hydrodesulfurization and hydrogenation,[4] glucose oxidation,[5] oxidation of acetic acid,[6] and olefin hydrogenation.[7] However, most reaction conversion data reported in the literature for monoliths have been generated in a recycle reactor operation and in a flow regime that is characterized by high liquid linear velocity and low G/L ratio (often called Taylor flow regime), which is not typical of most practical processes. In addition, the gas/liquid distribution in the previous studies has not been reported so that the intrinsic performance of the monolith catalyst is difficult to assess. In this work, we perform steady-state reaction tests over a wide range of flow conditions in a single monolith catalyst channel.

Understanding the single-channel reaction performance is critical to assess the potential advantage of the structured catalyst bed compared to conventional packed beds. Even in the single channel, the reaction conversion is affected by four groups of parameters and process variables: catalyst properties (X_{Catalyst}), reaction conditions ($X_{\text{Conditions}}$), channel geometry parameters (X_{Geometry}), flow conditions (X_{Flow}). For the structured catalyst bed, channel opening, catalyst layer thickness, and channel shape are all independent design parameters to achieve the most efficient reaction performance. Flow conditions and channel geometries are unique attributes of the structured catalyst bed. A systematic modeling analysis on potential impact of some geometry parameters on the reaction rate was presented in a recent publication.[8] In this work, we particularly address the effect of flow conditions on reaction performance.

Understanding effects of flow conditions is essential to both laboratory-scale reaction tests and commercial implementation. One has to be certain that the catalyst is effectively used under the laboratory testing conditions for that test to be "representative" of catalytic performance under commercial conditions. Compared to the conventional reactor technologies, there is little experience and knowledge about scale-up of the structured catalyst/reactor system. Because of the fundamental differences in flow characteristics between the structured bed and packed pellet bed, the flow conditions inside the channel are expected to have a significant impact on reaction performance. For example, if the liquid fluid vertically flows down through a channel, the surface wetting or liquid coverage of the catalyst surface is directly related to the liquid flux or liquid superficial linear velocity. This is an effect that could be, in principle, modulated in a structured catalyst reactor/system, but one does not have the same freedom in the operation of a packed pellet bed.

Experimental Methods

Catalyst properties

Two types of monolith catalyst supports were prepared and used in this work: the washcoated and the extruded. Basic channel parameters and catalyst properties are listed in Table 1. The washcoated support was prepared by applying a layer of mesoporous γ-alumina onto inert cordierite substrate. The cordierite substrate has low porosity, macropores, and little BET (Brunauer–Emmett–Teller) surface area. The washcoating gives a dense and uniform structure on the channel wall surface, and also makes the square channel corner more rounded. Cat I and Cat II have a washcoated layer similar to the automotive catalytic converter, whereas Cat VI was prepared in house with a different type of alumina precursor material at lower alumina loading. The γ-alumina was converted into η-alumina by calcining the γ-alumina washcoated monolith at 1000°C in air for 4 h. The washcoated monolith has a channel density of $60N/cm^2$ [or 400 channels per square inch (cpsi)], where N is the number of channels. The inert wall thickness is 0.18 mm (7 mil), whereas the alumina coating thickness is

about 20–80 μm. A thicker alumina layer is found in corner areas of the square channel.

The extruded monolith was prepared by directly extruding alumina precursor material into the monolith form. The extruded γ-alumina monolith has a high BET surface area and mesopore structure just like the typical γ-alumina catalyst support. The alumina monolith of different channel size and wall thickness was prepared to study the channel geometry effect. The monolith catalyst module size used in this work is 1 cm (diameter) $\times$ 15 or 30 cm (length). The monolith module used for the reaction testing was carefully selected to ensure its mechanical integrity.

The monolith support was catalyzed with an impregnation method. The procedure consists of (1) fully immersing the monolith support in a 2 M nickel nitrate solution, (2) taking the monolith module out of the solution, (3) draining and blowing out excessive solution on external surface of the monolith, (4) drying the wetted module in air at 100°C for about 16 h, and (5) calcining the dried module in air at 400°C for 2 h. Special care must be given to the catalyst preparation process to achieve uniform metal deposition along the wall thickness in both radial and axial directions.

Reaction setup and procedure

Selective hydrogenation is an important catalytic process for production of a number of chemicals. A model feedstock composed of styrene, 1-octene, and toluene was prepared with ACS-grade chemicals and pure hydrogen was used as gas reactant. The reaction temperature and pressure were typically 60°C and 15 bar, respectively. Under present conditions, the following reactions proceed on the Ni/alumina catalyst

$$\text{Styrene (L)} + \text{H}_2\text{ (G)} \rightarrow \text{Ethyl benzene (L)} \quad (1)$$

$$\text{1-Octene (L)} + \text{H}_2\text{ (G)} \rightarrow \textit{n}\text{-Octane (L)} \quad (2)$$

$$\text{Toluene (L)} + 3\text{H}_2\text{ (G)} \rightarrow \text{Methylcyclohexane (L)} \quad (3)$$

$$\text{1-Octene (L)} \rightarrow \text{Iso-octene (L)} \quad (4)$$

Hydrogenation reactions of styrene, 1-octene, and toluene are parallel gas–liquid catalytic reactions under the same conditions. Although the toluene saturation conversion level was low ($<$1.5 wt %), its conversion product methylcyclohexane was measurable by gas chromatography (GC) analysis. Isomerization of 1-octene was also observed, although its conversion level was insignificant compared to the hydrogenation reactions. In this work, all hydrogenation conversion numbers are calculated based on the product formation.

The experimental tests and thermodynamic calculations showed that the above reactions are not limited by the thermodynamic equilibrium under present conditions.

Reaction tests are conducted by directly delivering gas and liquid fluid streams into the 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. On the other hand, no single gas/liquid distributor can be found that is effective for a wide range of flow conditions. A single, representative channel is isolated from the others by plugging the top and bottom openings of all remaining channels with inorganic cement. A feed-delivery tube is cemented onto the test channel. The whole monolith catalyst module is housed inside a stainless steel reactor tube for pressure containment. As constructed, the central, open reaction channel represents the lowest pressure drop route for fluid flow. Cold-flow testing confirmed that there was no detectable 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 flow straight through the central reaction channel. As a result, active mass-transfer processes and catalytic reactions are confined inside the isolated reaction channel.

Details about the reactor setup can be found in the literature.[2] The reactor apparatus was pressure tested and purged with argon gas before the reaction. The as-prepared NiO/alumina catalyst was reduced in hydrogen flow under 15 bar by ramping the reactor temperature from room temperature to 400°C at a rate of 2°C/min and maintaining the system at 400°C for 10 h. Then, the reactor was cooled to 60°C and liquid feed was introduced once the temperature was stabilized. Unless specifically noted, the reactor was operated in cocurrent downflow mode. The reaction product stream exited the reactor tube and was allowed to cool. The liquid was separated from the gas and collected for analysis by GC. Material balance of the liquid feed/product was typically conserved within 97–101%.

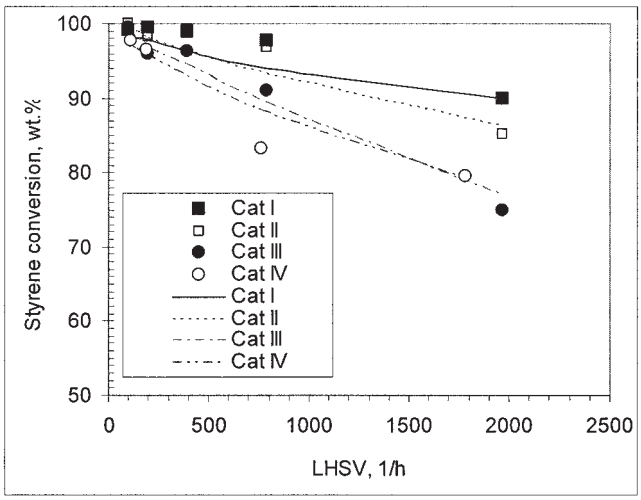
The whole reactor system was constructed in such a way so as to minimize the static liquid holdup. Because of the small catalyst channel volume (0.3–1.2 cm^3 only) and high liquid feed rate (1–30 cm^3/min), the reactor showed a rapid response to any condition change. Under steady-state operation, the reaction typically stabilized within a few hours, depending on the feed flow rate. However, a longer stabilization time was generally needed during start-up. It was found that trace amounts of oxygen and oxygenates in the feed could cause significant catalyst deactivation. A difference in the level of these contaminates in different batches of feedstock could result in erratic activity. Installation of an oxygen scrubber in the feed line eliminated this source of variation.

Several inlet and outlet configurations were examined for introduction and discharge of the reacting fluid into and out of the monolith channel. The consistent results were obtained with the present setup.

In this work, the reaction conversion was measured under steady-state reaction conditions in once-through mode. For clarity, space velocity and both liquid and gas superficial linear velocities are calculated based on the open channel only unless specially noted

$$\text{LHSV} = \frac{F_L}{V_C} \quad (5)$$

$$U_L = \frac{F_L}{A_C} \quad (6)$$



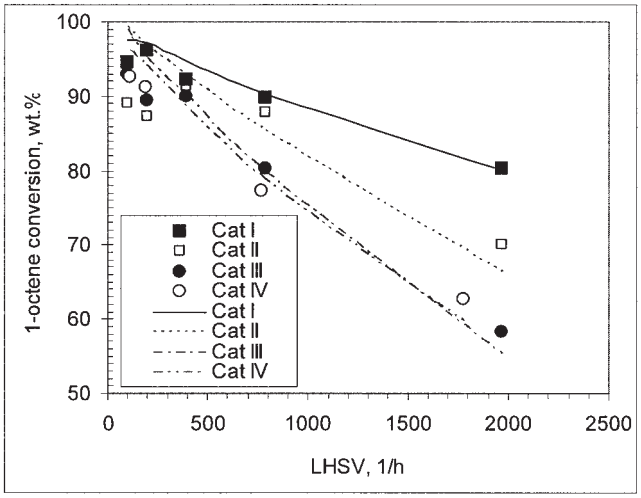


Figure 1. Hydrogenation conversion over structured catalyst of 1-mm-channel opening with different catalyst layer structure.

Pressure: 15 bar; feed H_2/oil ratio: 50 NL/L; reaction temperature: 61°C; liquid feed: 0.5% styrene, 0.5% 1-octene, 99% toluene.

$$U_G = F_G A_C \frac{T_R}{T_0} \frac{1}{P_R} \tag{7}$$

Results

Effect of catalyst wall structure

Figure 1 shows variations of styrene and 1-octene conversion over different catalysts with liquid-hourly-space velocity (LHSV) under constant temperature, pressure, and feed H_2/oil ratio. The liquid feed for this experiment consists of 0.5 wt % styrene, 0.5 wt % 1-octene, and 99% toluene. The catalyst bed volume is fixed and the LHSV variation is obtained by changing the liquid feed rate. Styrene conversion is always higher than that of 1-octene under the same conditions, but the two reaction conversions follow a similar trend. The four monolith catalysts tested here have similar channel openings (~1-mm square) but different catalyst wall structures. Channel walls of Cat I and Cat II constitute a washcoated catalyst layer on the inert ceramic support, whereas the whole channel wall of Cat III and Cat IV is made of Ni/γ-alumina catalyst. Conversion through all catalyst channels decreases with increasing LHSV. The conversions over Cat III and Cat IV are similar, even though the catalyst thickness differs by fourfold. Cat I and Cat II appear a little more active than Cat III and Cat IV, even though they contain only a thin layer of catalyst coating. These results indicate that the olefin hydrogenation under present conditions seems to occur on the external surface of the catalyst layer. The hydrogenation activity is likely dominated by the properties of external catalyst surface (shape, microstructure, and nanostructure) rather than by the catalyst mass (or thickness). The SEM and N_2 adsorption analysis showed that the pore size and texture of the washcoated γ-alumina are similar to those of the extruded ones. Unlike the extruded monoliths (Cat III and Cat IV), corners of the square channel are rounded after washcoating. The channel shape is a significant factor affecting the reaction rate and the rounded channel shape enhances the multiphase reaction activity over the square shape. The channel shape effect has been dealt with at length in a recent publication.[9]

The Thiele modulus was estimated to be a fairly large number for the olefin hydrogenation reaction over the present Ni/alumina catalyst, based on some kinetics tests in this work and an earlier work.[2] The catalytic reaction occurs in the outermost region of the catalyst layer. Even for the washcoated catalyst used in this work, the coating is thick enough so that the observed reaction rate is not limited by the catalyst mass. Detailed analysis of Thiele modulus and effectiveness factor for the monolith catalyst structure can be found in an earlier work.[9]

Thus, the olefin hydrogenation reaction serves as a good model-reaction system for the study of the effect of external mass transfer on the reaction performance. The lines in the figure are simulated conversions based on the model to be discussed later. The high one-pass olefin conversion observed in the present experiment suggests that the hydrogenation activity could be significantly underestimated in a recycle reactor operation as used in previous literature studies. For the recycle reactor operation, a differential reactor model, that is, small one-pass conversion through the catalyst bed was explicitly or implicitly assumed.[8]

Effect of channel size

Channel size is an important design parameter for a structured catalyst/reactor. Knowing the impact of reducing channel size on the reaction performance is necessary to assess the potential advantage of conducting multiphase reactions inside small-sized channels. Three extruded Ni/γ-alumina monolith catalysts of channel size 2, 1.5, and 1 mm, are compared for the hydrogenation reaction. These three catalyst modules were made of the same material precursors and have the same square channel shape. Although the catalyst wall thickness is different, it does not affect the conversion based on the above results. The extruded monolith has a uniform wall structure, which is difficult to achieve with the washcoated surface. Thus, a clean comparison of the channel size effect is possible by use of extruded modules. As shown in Figure 2, at the same LHSV, the 1-mm channel gives a higher conversion than the 2- and 1.5-mm reaction channel for both styrene and 1-octene. The

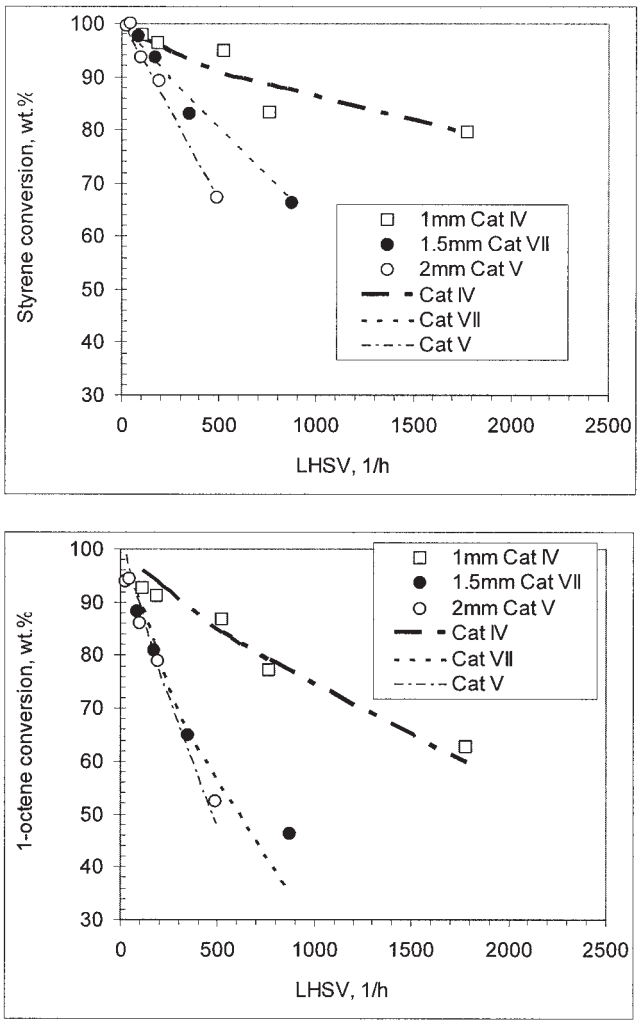


Figure 2. Hydrogenation conversion over structured catalyst of different channel size.

Pressure: 15 bar; feed H_2/oil ratio: 50 NL/L; reaction temperature: 61°C; liquid feed: 0.5% styrene, 0.5% 1-octene, 99% toluene.

1.5-mm channel gives slightly higher conversion than the 2-mm channel.

Because of the constraints of the reactor apparatus, the 2- and 1.5-mm channels could not be tested at a higher LHSV. Their behavior at higher LHSV can be projected with the model simulation.

Cocurrent downflow vs. upflow

Cocurrent downflow is an operation mode for most commercial packed-bed reactors. Comparative studies of cocurrent upflow vs. cocurrent downflow for packed-bed reactors are reported in the literature.[10-13] Perceived advantages for the upflow were higher selectivity, higher catalyst life, and better catalyst utilization. In the cocurrent upflow, the catalyst tends to be fully "wetted." For the catalyst pellet-packed reactors, however, catalyst pellets could be suspended and the catalyst bed could possibly become expanded in upflow operation.

For reactions inside small channels, there is little information about the flow mode effect (that is, upflow vs. downflow effects). The bubble slug flow or Taylor flow pattern may be created more perfectly in upflow than in downflow.[14] In the present work, the same catalyst module is tested in both cocurrent downflow and upflow configurations. In the cold-flow visualization, a train of gas bubbles emerge out of the reaction channel and dye tracer injected into the liquid feed passes right through the reaction channel. There was no observable leakage or bypass of the liquid tracer from the reaction channel. Effects of flow mode on the reaction conversion inside a 1-mm reaction channel are shown in Figure 3. The conversion decreases with increasing LHSV. Under the same reaction conditions, however, the conversion in the cocurrent downflow operation is consistently higher than that in the cocurrent upflow. For both flow modes, the conversion decreases as the feed H_2/oil ratio is reduced from 50 to 5 NL/L.

The flow direction effect is further tested with the 2-mm-size catalyst channel. The downflow is compared to the upflow in Figure 4. Similar to what is observed with the 1-mm channel, the cocurrent downflow operation yields an olefin conversion that is consistently higher than that in the cocurrent upflow operation.

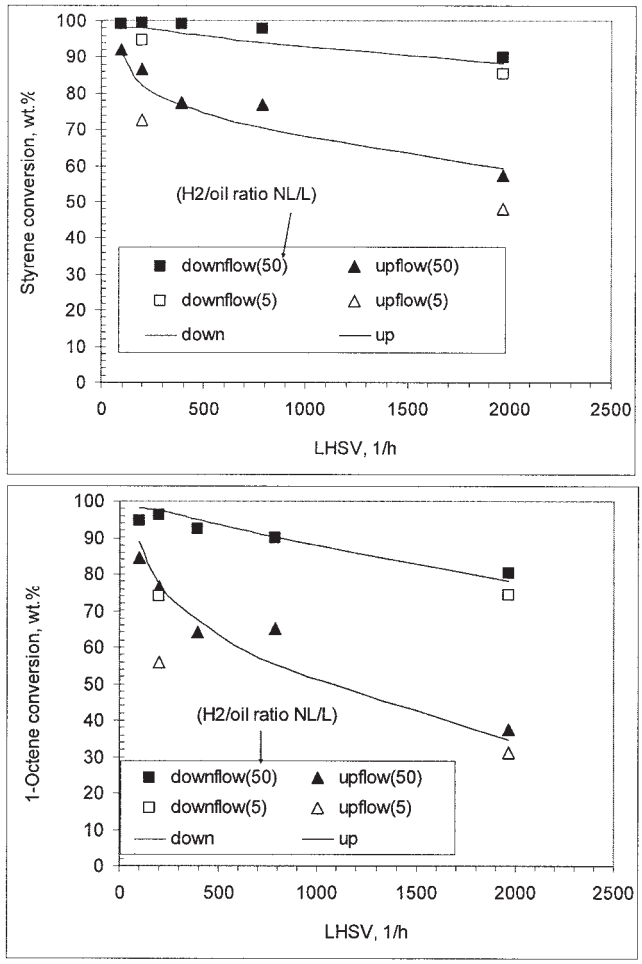


Figure 3. Cocurrent downflow vs. upflow operation in a 1-mm square channel (Cat I).

Reaction conditions: 15 bar, 61°C; liquid feed: 0.5% styrene, 0.5% 1-octene, 99% toluene.

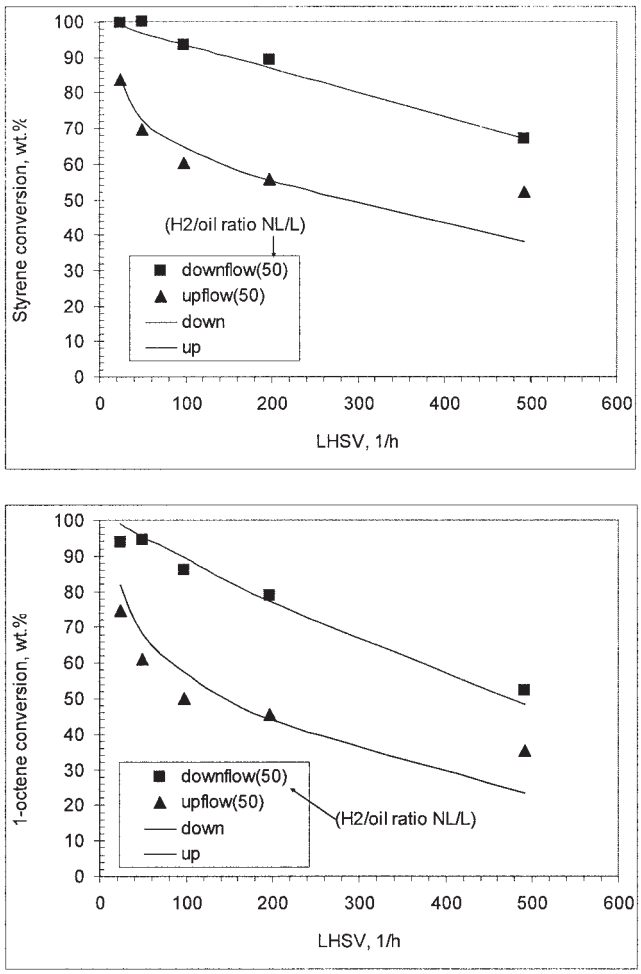


Figure 4. Comparison of cocurrent downflow to upflow operation in a 2-mm square channel (Cat V).

Reaction conditions: 15 bar, 61°C; liquid feed: 0.5% styrene, 0.5% 1-octene, 99% toluene.

Parametric studies of reaction conditions

Based on the previous results, a washcoated monolith catalyst module of 1-mm channel size was selected for parametric studies in the cocurrent downflow operation. The reaction tests are conducted with different liquid feed compositions, pressures, and temperatures. Stability of the reaction system was monitored during a 13-day test period. There was a rapid drop in hydrogenation conversion at the beginning of the reactor run. It is known that the fresh catalyst surface requires a certain time to reach a stable steady state under the reaction conditions. After the catalyst was stabilized, the parametric tests were conducted over a period of about 200 h. At the end of run, the catalyst was tested under the same condition as used in the start-up. There was no apparent change in styrene conversion, whereas 1-octene conversion slightly decreased. However, toluene saturation conversion declined significantly, although the conversion was small ($<$0.4 wt %). This can be explained by noting that the toluene saturation requires more active catalyst sites, whereas the more active site is more susceptible to deactivation. During the process, we found that different amounts of oxygenate impurities may have existed in different bottles of styrene chemical. A scrubber had to be used to maintain the catalyst stability and obtain consistent results.

Figure 5 shows the olefin conversion vs. the feed composition under constant reaction conditions. In this series of tests, styrene and 1-octene content in the liquid feed are varied proportionally, that is, the ratio of the styrene to the 1-octene in the feed is held nearly constant. Both styrene and 1-octene conversion decline with increasing olefin content in the feed. Such a variation is observed at different LHSV. It appears from these observations that the hydrogenation reaction is inhibited by the feed olefin content.

The effect of reactor pressure on the conversion is tested with feedstock containing a high level and low level of olefin (5/5% and 0.5/0.5%, respectively). As the pressure is raised from 7.5 to 25 bar (Figure 6), styrene conversion remains approximately constant, whereas the 1-octene conversion slightly increases and the toluene conversion increases dramatically. This kind of trend is observed with two sets of experimental conditions of different feed compositions. The feedstock containing a higher level of olefins demands more hydrogen than the feedstock containing a lower level of olefins. Because the olefin hydrogenation reaction occurs primarily on the external catalyst surface, the present observations suggest that the mass transfer of bulk hydrogen onto the channel wall surface may not be a rate-limiting step. The olefin hydrogenation seems to be more limited by mass transfer of liquid reactant onto the catalyst surface. Toluene saturation represents a case where the liquid reactant is abundant and the reaction rate is determined by the concentration of hydrogen reactant on the catalyst surface. Hydrogen concentration in the liquid phase increases with the reactor pressure. As a result, the toluene saturation conversion increases with the reactor pressure.

The effect of reaction temperature on the conversion rate was briefly tested. To attain a quantitative assessment about impact of temperature on different reactions, a first-order apparent rate constant is calculated based on the measured conversion:

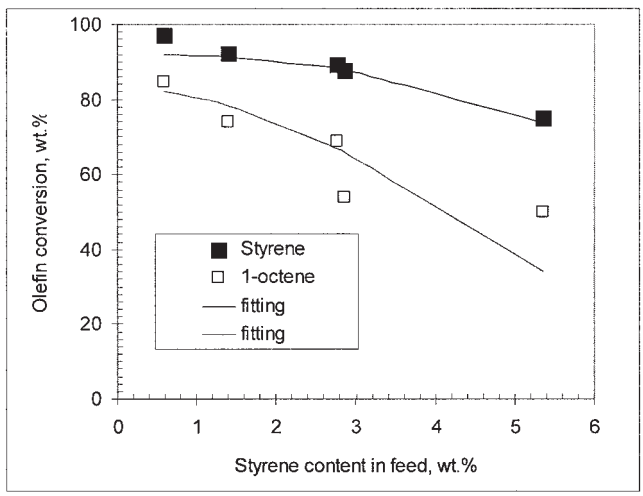
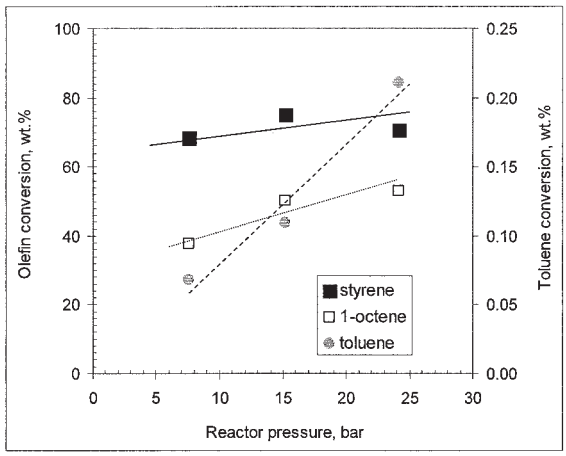
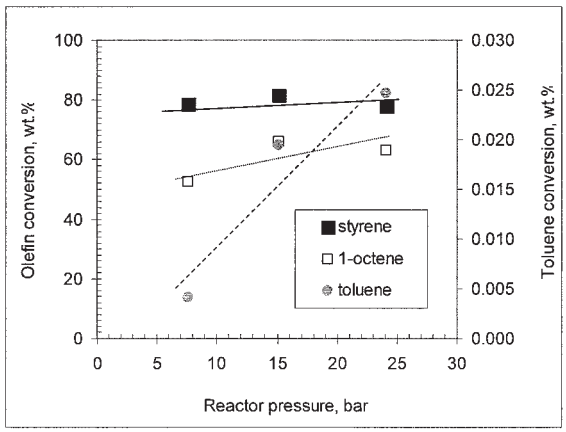


Figure 5. Effect of styrene content in feed on conversion inside in a 1-mm channel (Cat VI).

Reaction conditions: 15 bar, 61°C; feed H_2/oil ratio: 50 NL/L, U_L = 6.7 cm/s; liquid feed: styrene, 1-octene, toluene, [styrene]/[1-octene] = 1.0.



(a) U_L = 6.7cm/s and feedstock of 5 wt% styrene/5 w% 1-octene/90% toluene



(b) U_L = 16.7cm/s and feedstock of 0.5% styrene/0.5 wt. % 1-octene/99% toluene

Figure 6. Effect of reactor pressure on conversion inside 1-mm square.

Lines here are for visual guide and not the simulated results; Cat VI; reaction conditions: feed H_2/oil ratio = 50 NL/L, temperature = 61°C.

$$k_{app} = -\ln(1-x)\frac{\text{LHSV}}{3600} \tag{8}$$

Arrhenius plots for styrene, 1-octene, and toluene hydrogenation are shown in Figure 7. The toluene saturation rate is about three orders of magnitude lower than the olefin hydrogenation. The apparent activation energy for styrene, 1-octene, and toluene conversion is about 15, 20, and 65 kJ/mol, respectively. The olefin hydrogenation conversion is not very sensitive to reaction temperature, whereas toluene conversion increases rapidly with temperature. Because the main focus of this work is with respect to flow conditions, most reaction tests are conducted at reaction temperatures around 60°C.

Effects of flow conditions

In the previous reaction tests, the monolith catalyst module loaded in the reactor is fixed in its length, whereas the liquid feed flow rate is used as an operation variable. As a result, liquid superficial linear velocity (U_L) is varied concomitantly with LHSV. To decouple the flow condition effects, the monolith catalyst modules of two different lengths were tested under the same flow conditions. A diluted feedstock containing 0.5% styrene and 0.5% 1-octene in toluene is used to minimize the exothermic effect. Variation of olefin conversion with space contact time at different flow conditions is plotted in Figure 8. As expected, the conversion increases with the space contact time. The flow conditions have a significant influence on the conversion. At the same space contact time (that is, same LHSV), higher conversion is obtained under higher liquid superficial linear velocity. At the same space contact time and same liquid superficial linear velocity, higher conversion is obtained at higher gas/oil ratios.

To further elucidate the impact of flow conditions, the reaction tests are conducted over a wide range of liquid flow rate and H_2/oil ratio. The catalyst volume is fixed in this set of experiments. The space velocity and liquid linear velocity is changed at the same time by varying the liquid feed flow rate. Figure 9 shows that at a given LHSV, 1-octene conversion generally increases with feed H_2/oil ratio. Styrene conversion follows a trend similar to that of 1-octene. Under constant temperature, pressure, and liquid space velocity, varying H_2 gas flow results in a change of flow conditions inside the channel.

From results shown in Figures 1–8, we know that styrene hydrogenation activity is higher than 1-octene hydrogenation. It would be interesting to assess the impact of the flow condition on the relative conversion of styrene to 1-octene, that is, selectivity for parallel hydrogenation reactions. All 1-octene conversion data under various flow conditions are plotted against styrene conversion under the same condition in Figure 10. A clear correlation between the two hydrogenation reactions is shown. The result suggests that the relative hydrogenation rate of styrene to 1-octene is dominated by the reaction kinetics. The flow condition has a similar influence on these parallel reactions of different reaction rates.

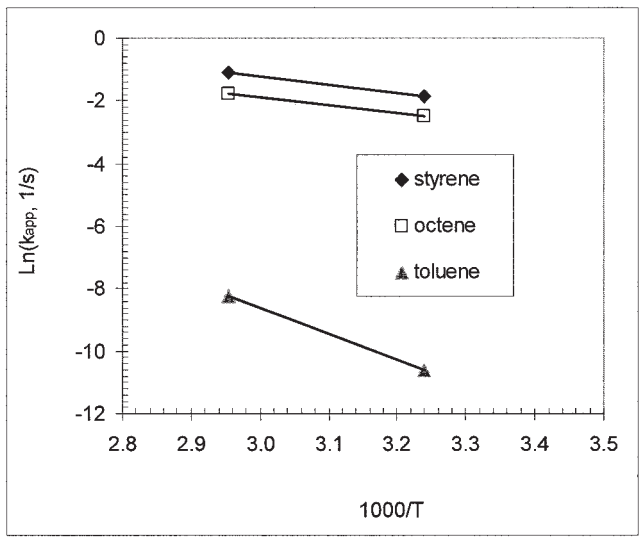
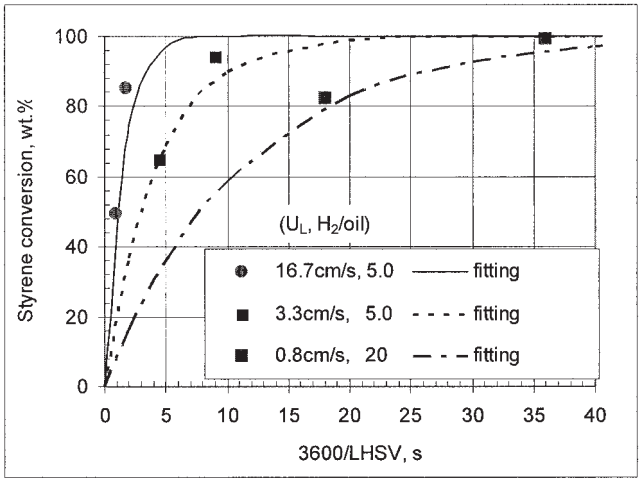


Figure 7. Effect of reactor temperature on observed reaction activity (Cat VI).

Reaction conditions: 15 bar; feed H_2/oil ratio: 50 NL/L, U_L = 6.7 cm/s; feed composition: 5 wt % styrene, 5 wt % 1-octene, and 90% toluene.



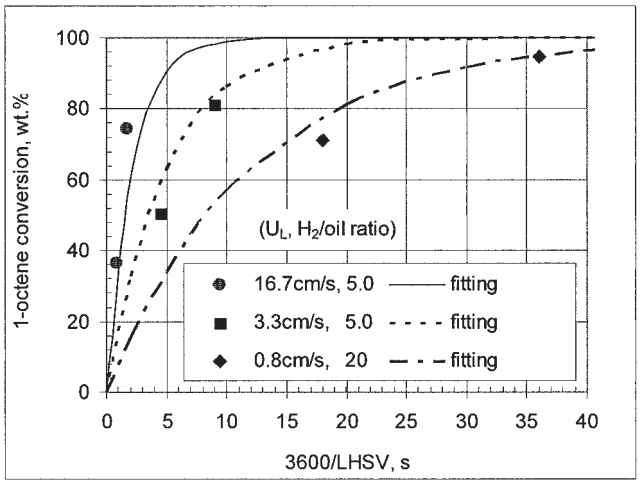


Figure 8. Variation of conversion with space contact time under constant flow conditions inside 1-mm square channel (Cat I).

Reaction conditions: 15 bar, 61°C; liquid feed: 0.5 wt % styrene, 0.5 wt % 1-octene, 99 wt % toluene.

Discussion

A simplified reactor model

Fundamental understanding of multiphase catalytic reactions inside single catalyst channels is essential for the design of a monolithic catalyst/reactor and for the design of a structured catalyst in general.

Obviously, for a catalytic reaction to occur, liquid reactant (A), gas reactant (B), and catalyst site have to be brought into intimate contact. These are, however, three immiscible phases. In actual multiphase-reaction processes of any reactor scale, several elemental mass-transfer steps are involved in addition to the catalyst surface reaction. According to established reaction engineering analyses, these steps include:

For Liquid Reactant

Bulk fluid → catalyst external surface →

inside catalyst pore

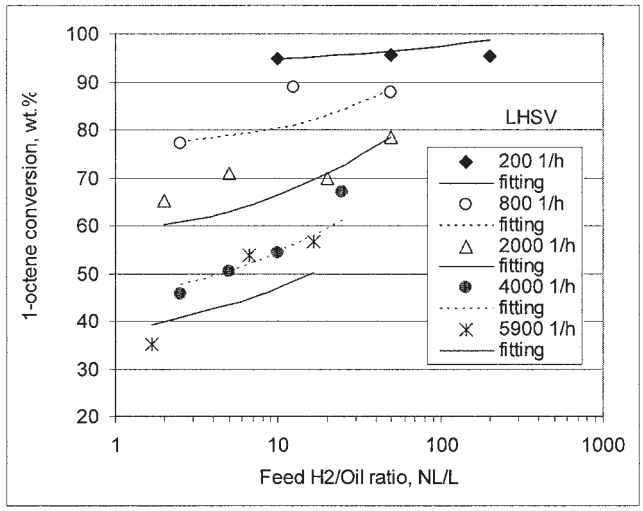


Figure 9. Variation of conversion with feed H_2/oil ratio at constant LHSV (Cat I).

Reaction conditions: 15 bar, 61°C; liquid feed: 0.5 wt % styrene, 0.5 wt % 1-octene, 99 wt % toluene.

For Gas Reactant

Bulk gas phase → liquid phase →

catalyst external surface → inside catalyst pore

For the olefin hydrogenation reaction over the Ni/alumina catalyst in this work, the experimental results and theoretical analysis show that the catalytic reaction mostly occurs on the outermost surface layer of the catalyzed wall. The monolith catalyst modules all provide sufficient thickness that the reaction is not limited by the catalyst mass or by the catalyst thickness. Thus, the olefin hydrogenation provides a good measurement of impact of mass transfer on to the catalyst

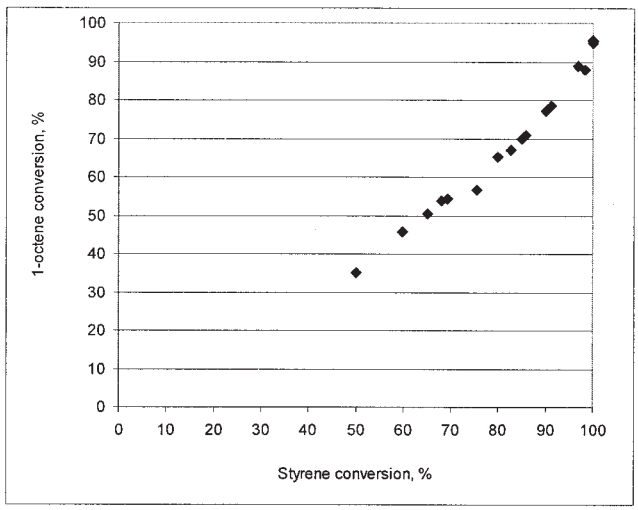


Figure 10. Correlation of styrene conversion with 1-octene conversion (Cat I).

Reaction conditions: 15 bar, 61°C; liquid feed: 0.5 wt % styrene, 0.5 wt % 1-octene, 99 wt % toluene.

external surface. An appropriate model is sought to decouple the reaction kinetics and external mass transfer, and rationalize the experimental data.

There are several possible flow patterns/regimes[15-18] for gas/liquid two-phase flow inside small channels: falling film, dispersed gas bubble inside the liquid fluid, slug flow with a train of gas bubble and liquid segment (or Taylor flow), annular flow. In the early work by Satterfield and Özel,[19] a slug flow was observed inside a 2-mm glass tube at $U_L > 1.7$ cm/s and found to be independent of gas velocity. The flow pattern would transform into annular flow when U_L is reduced. Two-phase flow inside 1-mm capillary tubes in the range of high liquid and gas linear velocities was studied by Triplett et al.[18] Pertinent to the multiphase catalytic reaction application, much of the hydrodynamic characterization has been centered on the Taylor flow regime.[20,21] The ^{1}H magnetic resonance imaging (MRI) technique was used to visualize liquid falling film at low liquid linear velocity inside 2-mm ceramic monolith channels in a countercurrent operation.[22] Slug flow patterns were revealed inside ceramic monolith channels under the Taylor flow conditions in the cocurrent flow.[23]

However, a complete map of two-phase flow patterns covering the flow conditions used in this work has not been found in the open literature, particularly at low liquid linear velocity (~0.5–5 cm/s) and high gas/liquid ratio (~1–100). These happen to be the conditions of interest for existing commercial reactor application. In addition to the flow conditions (flow rates and fluid properties), we believe that surface properties of the channel wall play a large role in determining the flow regime/pattern for gas/liquid flow inside small channels. This is something that is not elucidated in flow visualization studies conducted in glass channels. The surface tension and microstructure of the channel wall would have a strong influence on the liquid adhesion and its motion dynamics along the wall surface.

Without explicitly exploring the multiphase flow structure in the channels, a simplified, one-dimensional reactor model is proposed here to analyze the experimental data. The major assumptions are as follows:

(1) Mass transfer of liquid reactant from bulk fluid onto catalyst surface is a rate-determining step under *all* flow conditions tested in this work.

The rationale for this assumption is that the gas/liquid is mixed well inside the small channel, the amount of hydrogen in the channel is generally much more than the stoichiometric, and the surface will be more starved of liquid-phase reactant rather than the hydrogen. The conversion data at different reactor pressures, as illustrated in Figure 6, provide some supporting evidence.

(2) Isothermal catalyst bed.

This assumption is reasonable for the reaction tests with the liquid feed containing low levels of the olefin reactant. For the feed containing high levels of the olefin and high feed flow rate, the exothermic reaction can result in a substantial amount of temperature increase.

(3) Langmuir-type reaction kinetics for liquid reactant on the catalyst surface

$$r_i = \frac{k_i K_i C_i}{1 + \sum_i K_i C_i} \tag{9}$$

This kinetics equation is consistent with the literature model and is confirmed in a separate work.

(4) Effects of the catalyst properties and hydrogen concentration on the catalyst surface are factored into the rate constant, k_i

$$k_i = k_{i,S} C_{\mathrm{H2},S} \tag{10}$$

Assumptions 3 and 4 basically treat the porous catalyst layer as a "super surface." The rate constant would be affected by channel shape and size, coating uniformity, and the pore-diffusion and reaction.

(5) Plug flow pattern.

A mass balance of the liquid reactant i along the flow direction results in

$$-U_L \frac{dC_{i,B}}{dz} = a k_{LS} (C_{i,B} - C_{i,S}) \tag{11}$$

$$a k_{LS} (C_{i,B} - C_{i,S}) = \frac{k_i K_i C_i}{1 + \sum_i K_i C_i} \tag{12}$$

An analytical solution to the above equations could not be found. Numerical integration was conducted to obtain the conversion of liquid reactant.

The adsorption equilibrium constant K_i is derived by fitting the experimental data generated with different feed compositions under constant reaction conditions (such as Figure 5). The resulting adsorption equilibrium constants for styrene and 1-octene at 60°C is 5.0 and 0.5%$^{-1}$, respectively. Styrene adsorbs on the Ni/alumina catalyst much more strongly than does 1-octene. These K_i numbers are used in the following simulations.

Mass-transfer equation

The effect of flow conditions on the conversion is clearly shown in this work (Figures 8 and 9). The mass-transfer coefficient needs to be determined to apply the above model equations to various flow conditions. Gas–liquid and liquid–solid mass transfers inside small channels in the Taylor flow regime were the focus of studies reported by Bercic,[14] Bercic and Pintar,[24] and Kreutzer et al.[25] Both gas–liquid and liquid–solid mass-transfer constants were found to increase with the liquid velocity. However, those authors correlated the mass-transfer constant with the gas slug length, which limits the correlation equation to only the slug flow pattern.

There might be different flow patterns in the channel when the liquid and gas superficial linear velocities are varied over a wide range. A fundamental mass-transfer model may be developed if the flow pattern or flow regime can be clearly identified. In this attempt, however, we encountered two problems. First, a complete map of the flow regime encompassing the flow conditions used in this work could not be obtained. Second, even if the flow pattern model is conceptually created, there are still too many unknown parameters for development of mass-transfer equations.

As far as the overall reaction performance is concerned, knowledge of individual flow regimes might not be all that necessary. To elucidate detailed elemental steps of gas/liquid/

solid contact, however, we think that further study of flow patterns over a wide range of flow conditions is valuable.

Thus, we took a more practical and intuitive approach. We define the flow conditions based on liquid and gas superficial linear velocities, which can be calculated from the experimental conditions. Although the flow pattern or regime is unknown under each set of flow conditions, the basic feature for two-phase flow inside the small channel may be captured by a simple, empirical equation.

When the gas fluid and the liquid fluid are pushed through the channel, the liquid fluid tends to attach to the solid surface and form a liquid film, the gas fluid has to compete with the liquid fluid in the channel space. Solid surface coverage by the liquid and dynamic exchange of the liquid film with the bulk fluids is postulated to be a dominant factor for two-phase flow in the small-sized channels. Under constant gas/liquid ratio, increasing the liquid velocity would result in high coverage of the catalyzed channel surface by the dynamic liquid film and would enhance the mass transfer between the bulk fluids and the film. Under constant liquid linear velocity, increasing the G/L ratio would reduce the liquid film thickness and enhance the external mass transfer. Thus, the liquid mass-transfer rate constant should be correlated to the liquid and gas superficial linear velocities reflecting the above trends. Several expressions were evaluated, although the following equation is found to give the best-fitting result

$$ak_{LS} = \alpha(U_L + \beta U_g)^{\gamma} \tag{13}$$

The above correlation bears analogy to the classical mass-transfer correlation for gas/solid or liquid/solid fixed beds,[26] indicating the positive scaling of Sherwood (Sh) number with Reynolds (Re) number

$$\mathrm{Sh} \propto \mathrm{Re}^{\gamma} \tag{14}$$

Under present reaction conditions, the range of single-phase Re number inside the channel for liquid and gas is 5 to 10,000 and 5 to 200, respectively.

For gas/solid mass transfer, over the range of $3 < \mathrm{Re} < 2000$, the recommended correlation is

$$\mathrm{Sh} \propto \mathrm{Re}^{0.641}$$

For liquid/solid mass transfer, the recommended correlation is

$$\mathrm{sh} \propto \mathrm{Re}^{0.69} \qquad \text{for } 55 < \mathrm{Re} < 1500$$

Table 2. Parameters for Mass Transfer Correlation (Figures 8 and 11)

Channel size, mm	1
U_L, cm/s	0.8 to 50
U_G, cm/s	1.3 to 1800
Parameter	
α	0.094
β	0.100
γ	0.788

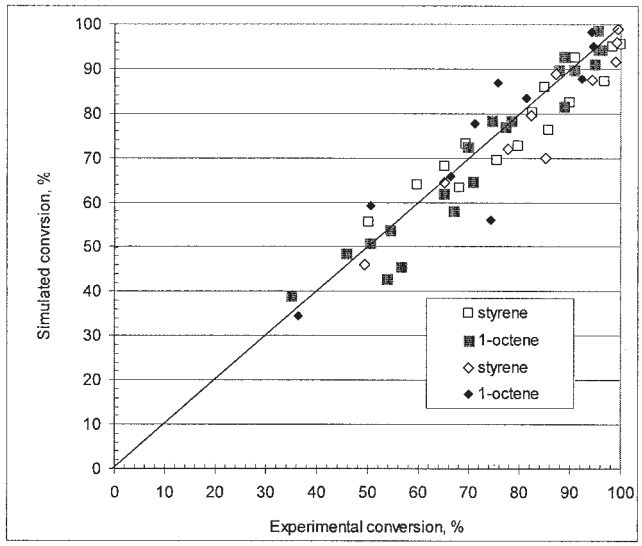


Figure 11. Parity plot of simulated conversion vs. measured conversion (Cat I).

Reaction conditions: 15 bar, 61°C; liquid feed: 0.5 wt % styrene, 0.5 wt % 1-octene, 99 wt % toluene.

$$\mathrm{Sh} \propto \mathrm{Re}^{0.33} \qquad \text{for } 0.0016 < \mathrm{Re} < 55$$

Intuitively, the G/L two-phase flow inside the small channel may be treated as a pseudo one-phase flow with a different weighing factor for the gas and liquid.

The above model equations are first tested with the experimental data of the 1-mm catalyst channel (Cat I) for the diluted olefin feed (as shown in Figures 8 and 9). The resulting parameters are listed in Table 2. The parameter γ, which represents the scaling of mass-transfer coefficient (Sherwood number) to Reynolds number, is found to have a value of about 0.79. This power order appears higher than that for either gas/solid or liquid/solid fixed beds. Such a correlation equation suggests that gas/liquid two-phase flow inside small channels is highly chaotic and dynamic (even at low superficial velocities) rather than steady laminar flows, causing enhanced mass transfer. A parity plot of experimental data vs. simulated data is shown in Figure 11. Some deviation from the experimental data is apparent. Given the wide range of flow conditions tested here and gross assumptions for the kinetics and reactor model (including the fact that we did not explicitly account for flow-regime transitions and impact thereof on the external mass transfer), we think that the present correlation captures salient features of the mass transfer inside small channels.

Regression parameters and limitation of the model

The above mass-transfer correlation and the reactor model are used to simulate all the experimental data generated in this work. The α parameter in Eq. 13 and rate constant k_i in Eq. 10 are adjusted when the model equations are applied to different catalyst channels. The lines shown in Figures 1 to 9 (except for Figure 7) are simulated results. In general, the model simulation shows a trend consistent with the experimental data, although a large degree of discrepancy exists for some data points.

Table 3. Regression Parameters for Different Channel Sizes (Figure 2)

	Cat IV 1 mm	Cat VII 1.5 mm	Cat V 2.0 mm
Geometric surface area, m^2/m^3	4000	2666	2000
Mass-transfer parameter			
α	0.090	0.082	0.078
β	0.100	0.100	0.100
γ	0.788	0.788	0.788
Kinetics constant			
Styrene, k_1	0.85	0.17	0.11
1-Octene, k_2	2.10	0.50	0.45

Regression parameters obtained for different channel sizes are listed in Table 3. Interestingly, the same correlation equation could be used. The mass-transfer parameter (α) slightly increases with decreasing channel size. The increment is less than what is expected from the increased geometric surface area (m^2/m^3). However, the apparent rate constant increases dramatically with decreasing channel size, more than the geometric surface area increment. Because the same catalyst is used, the large increase in the apparent rate constant is attributed to the enhanced hydrogen concentration on the catalyst surface. The results suggest that decreasing channel size disproportionately enhances the concentration of hydrogen on the catalyst surface. This can be explained by intensified gas/liquid mixing inside the smaller channel.

The cocurrent downflow and upflow are two typical operation modes for the multiphase reactor. At the same liquid flux and gas/liquid ratio, flow patterns/regimes under the upflow and downflow can be different. For the packed catalyst pellet bed, the reaction conversion in the upflow operation is typically not less than that in the downflow operation. In the upflow operation of pellet packed beds, presumably, the catalyst surface is better wetted by the liquid reactant, and the liquid holdup and residence time are increased, leading to higher volumetric activity. The significantly lower conversion obtained in the monolith catalyst channel with the upflow operation than that with the downflow operation (Figures 3 and 4) cannot be explained based on this argument.

Table 4 lists the regression parameters for the upflow vs. downflow operations. Both mass-transfer parameter (α) and apparent reaction rate constants (k_1 and k_2) associated with the downflow are higher than those with the upflow. Although the hydrogen mass-transfer step is not incorporated into the present reactor model, its impact is factored into the apparent rate constant (Eq. 10). Thus, the enhanced apparent rate constant in the downflow suggests high hydrogen concentration on the catalyst surface. The enhanced mass-transfer parameter may result from thinner liquid film in the downflow operation, thus offering less resistance for the bulk fluid to the catalyst surface.

Table 4. Regression Parameters for Upflow vs. Downflow (Figures 3 and 4)

	Cat V Down	Cat V Up	Cat I Down	Cat I Up
Mass-transfer parameter				
α	0.078	0.029	0.12	0.050
β	0.10	0.10	0.10	0.10
γ	0.79	0.79	0.79	0.79
Kinetics constant				
Styrene, k_1	0.11	0.06	2.2	0.70
1-Octene, k_2	0.45	0.20	5.0	0.99

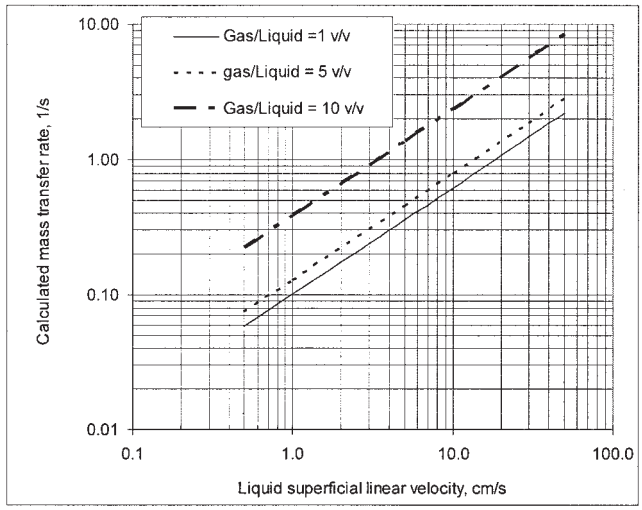


Figure 12. Mass-transfer rate constant for G/L cocurrent downflow in 1-mm channel calculated with correlation equation.

In the present work, the olefin conversion under constant LHSV is found to increase with feed H_2/oil ratio for both cocurrent upflow and cocurrent downflow operations. The feed H_2/oil ratio used was more than the stoichiometric requirement. Its impact results from hydrodynamics and mass transfer, which is not fully accounted for with the present model. The liquid residence time decreases with increasing gas/liquid ratio.[27] From the perspective of the residence time, the high H_2/oil ratio is not favorable to the reaction conversion. However, increasing hydrogen gas flow under constant liquid flow rate would reduce the thickness of the liquid film on the channel surface and enhance the external mass transfer of both liquid and gas reactant. The present results suggest that the enhanced mass transfer by increasing the gas/liquid ratio outweighs the reduced residence time of liquid reactant in terms of the impact to the reaction conversion.

Practical implication

Figure 12 shows the mass-transfer rate constant under various flow conditions, calculated with the correlation equation developed here, as a function of liquid superficial velocity and G/L ratio in the channel. The mass-transfer rate increases with the liquid superficial linear velocity and gas/liquid ratio. This plot is made to clarify two issues. First, a high gas/liquid ratio is actually beneficial to the mass transfer and it does not need to be limited to a narrow range for a certain flow pattern. Second, for a given catalytic reaction system, the multiphase reactor indeed needs to be operated above a certain liquid and/or gas linear velocity so that the reaction conversion is not limited by the external mass transfer. For example, to a kinetically slow reaction of first-order rate constant 0.001/s such as hydroprocessing reactions, the external mass transfer would have little impact on the conversion rate if the reactor is operated under such flow conditions that an external mass-transfer constant is $>0.05\ s^{-1}$. This mass-transfer number in Figure 12 corresponds to the liquid superficial linear velocity $\gtrsim$

0.5 cm/s and gas/liquid ratio > 1. To kinetically fast reactions, such as the olefin hydrogenation in this work, the multiphase reactor needs to be operated at sufficiently high liquid linear velocity and/or gas/liquid ratio to minimize limitation of the external mass transfer.

The mass-transfer number shown in Figure 12 for the 1-mm catalyst channel is significantly higher than the numbers reported in the literature for the packed-pellet bed and slurry reactors. The high mass-transfer rate and low pressure drop offered by structured catalysts make it possible to conduct kinetically fast multiphase reactions at unconventionally high LHSV. From Figure 8, we can see that under liquid linear velocity of 16.7 cm/s and feed H_2/oil ratio of 5, about 95% styrene conversion could be achieved at LHSV as high as 600 h^{-1}. A compact, highly efficient reactor may be built with the structured catalyst module for highly reactive multiphase processes.[28] The reactor size is so small that it could resemble a process pipeline. Such a type of reactor system is promising for purification and treatment of process streams by removing reactive species by catalytic reactions.

The present research aims to delineate the fundamental impact of reaction conditions within a single reaction channel. The practical reactor constitutes a number of reaction channels. The flow distribution would determine the effectiveness of a whole catalyst bed. The single-channel result sets an upper limit of the performance potential. The fundamental understanding from the single-channel study provides insight into the structured catalyst/reactor system. For example, because the flow conditions inside the channel have a substantial impact on the external mass transfer, the flow distribution among individual channels not only affects the liquid residence time distribution but also affects the actual reaction performance in individual channels (apparent rate constant).

Conclusions

An external mass-transfer correlation equation is developed over a wide range of flow conditions (U_L = 1–50 cm/s, U_G = 1–2000 cm/s), based on steady-state reaction conversion data. The correlation equation is tested with a catalyst channel size of 1 to 2 mm and with both cocurrent downflow and cocurrent upflow. The mass-transfer rate increases with liquid superficial linear velocity and gas/liquid ratio. The mass-transfer equation may be used to guide selection of suitable flow conditions for a given catalytic reaction rate.

The cocurrent downflow operation gives a higher reaction conversion than the cocurrent upflow. Dynamic mass transfer of both gas and liquid reactant onto the catalyst external surface is believed to be more important than the static liquid holdup and/or the catalyst wetting.

The olefin hydrogenation reaction is severely limited by both external and internal mass transfer. The high mass-transfer rate and low pressure drop offered by the structured catalyst channels make it possible to conduct multiphase catalytic reactions involving highly reactive species at unconventionally high LHSV (100–1000 h^{-1}).

Acknowledgments

The authors thank colleagues at Corning Incorporated, Matthew Morse for conducting the experiments, Kevin Brundage for the monolith catalyst extrusion, Drs. Tinghong Tao and Jimmie Williams for supplying washcoated monolith samples, and Drs. Thorsten Boger and Pierre Woehl for technical discussions.

Notation

ak_{LS} = mass-transfer rate constant of liquid to catalyst external surface
A_C = cross-sectional area of reaction channel
$C_{H2,S}$ = hydrogen concentration on catalyst surface
$C_{i,S}$ = concentration of liquid reactant i at catalyst surface
$C_{i,B}$ = concentration of liquid reactant i in bulk fluid
F_L = volumetric flow rate of liquid feed at room conditions
F_G = volumetric hydrogen gas flow rate at standard conditions
k_{app} = first-order apparent rate constant
k_i = mono-molecular rate constant of reactant i
k_1 = mono-molecular rate constant of styrene
k_2 = monomolecular rate constant of 1-octene
$k_{i,S}$ = bimolecular rate constant on catalyst surface
K_i = adsorption equilibrium constant of reactant i
K_1 = adsorption equilibrium constant of styrene
K_2 = adsorption equilibrium constant of 1-octene
LHSV = liquid-hourly-space velocity based on channel volume, v/v/h
r_i = reaction rate of reactant i based on channel volume
Re = Reynolds number
Sh = Sherwood number
T_0 = standard temperature, 293 K
T_R = reactor-bed temperature
P_R = reactor pressure
U_L = liquid superficial linear velocity
U_G = gas superficial linear velocity
V_C = volume of the reaction channel in which the reaction occurs
x = reaction conversion
z = reactor depth
α, β, γ = parameters

Literature Cited

1. Stankiewicz AI, Moulijn JA. Process intensification: Transforming chemical engineering. *Chem Eng Prog*. 2001;January:22-34.
2. Liu W. Mini-structured catalyst bed for gas–liquid–solid multiphase catalytic reaction. *AIChE J*. 2002;48:1519-1532.
3. Hatziantonlou V, Andersson B, Schöön N. Mass transfer and selectivity in liquid-phase hydrogenation of nitro-compounds in a monolithic catalyst reactor with segmented gas–liquid flow. *Ind Eng Chem Process Des Dev*. 1986;25:964-970.
4. Irandoust S, Gahney O. Competitive hydrodesulfurization and hydrogenation in a monolithic reactor. *AIChE J*. 1990;36:746-752.
5. Kawakami K, Kawasaki K, Shiraishi F, Kusunoki F. Performance of a honeycomb monolith reactor in a gas–liquid–solid three-phase system. *Ind Eng Chem Res*. 1989;28:394-400.
6. Klinghoffer AA, Cerro RL, Abraham MA. Catalytic wet oxidation of acetic acid using platinum on alumina monolith catalyst. *Catal Today*. 1998;40:59-71.
7. Smits HA, Stankiewicz A, Glasz HC, Fogl THA, Moulijn JA. Selective three-phase hydrogenation of unsaturated hydrocarbons in a monolithic reactor. *Chem Eng Sci*. 1996;51:3019-3025.
8. Roy S, Heibel AK, Liu W, Boger T. Design of monolithic catalysts for multiphase reactions. *Chem Eng Sci*. 2004;59:957-966.
9. Liu W, Roy S. Effect of channel shape on gas/liquid catalytic reaction performance in structured catalyst/reactor. *Chem Eng Sci*. 2004;59:4927-4939.
10. Ragaini V, Tine C. Upflow reactor for the selective hydrogenation of pyrolysis gasoline: A comparative study with respect to downflow. *Appl Catal*. 1984;10:43-51.
11. De Wind M, Plantenga FL, Heinerman JJJ. Upflow versus downflow testing of hydrotreating catalysts. *Appl Catal*. 1988;43:239-252.
12. Chander A, Kundu A, Bej SK, Dalai AK, Vohra DK. Hydrodynamic characteristics of cocurrent upflow and downflow of gas and liquid in a fixed bed reactor. *Fuel*. 2001;80:1043-1053.
13. Cheng Z, Yuan W. Influence of hydrodynamic parameters on performance of a multiphase fixed-bed reactor under phase transition. *Chem Eng Sci*. 2002;57:3407-3413.
14. Bercic G. Influence of operating conditions on the observed reaction rate in the single channel monolith reactor. *Catal Today*. 2001;69:147-152.

15. Mishima K, Hibiki T. Some characteristics of air–water two-phase flow in small diameter vertical tubes. *Int J Multiphase Flow*. 1986;22: 703.
16. Reinecke N, Mewes D. Flow regimes of two-phase flow in monolith catalyst. Proc of 5th World Congress on Chemical Engineering, San Diego, CA; 1996.
17. Mewes D, Loser T, Millies M. Modeling of two-phase flow in packings and monoliths. *Chem Eng Sci*. 1999;54:4729-4747.
18. Triplett KA, Ghiaasiaan SM, Abdel-Khalik SI, Sadowski DL. Gas–liquid two-phase flow in microchannels. Part I: Two-phase flow patterns. *Int J Multiphase Flow*. 1999;25:377-394.
19. Satterfield CN, Özel F. Some characteristic of two-phase flow in monolithic catalyst structures. *Ind Eng Chem Fundam*. 1977;16:61-67.
20. Thulasidas TC, Abraham MA, Cerro RL. Flow patterns in liquid slugs during bubble-train flow inside capillaries. *Chem Eng Sci*. 1997;52: 2947-2962.
21. Laborie S, Cabassud C, Durand-Bourlier L, Laine JM. Characterization of gas–liquid two-phase flow inside capillaries. *Chem Eng Sci*. 1999;54:5723-5735.
22. Heibel AK, Heiszwolf JJ, Kapteijn F, Moulijn JA. Influence of channel geometry on hydrodynamics and mass transfer in the monolith film flow reactor. *Catal Today*. 2001;69:153-163.
23. Mantle MD, Sederman AJ, Raymahasay S, Stitt EH, Winterbottom JM, Gladden JF. Dynamic MRI visualization of two-phase flow in a ceramic monolith. *AIChE J*. 2002;48:909-912.
24. Bercic G, Pintar A. The role of gas bubbles and liquid slug lengths on mass transport in the Taylor flow through capillaries. *Chem Eng Sci*. 1997;52:3709-3719.
25. Kreutzer MT, Du P, Heiszwolf JJ, Kapteijn F, Moulijn JA. Mass transfer characteristic of three-phase monolith reactors. *Chem Eng Sci*. 2001;56:6015-6023.
26. Satterfield CN. *Mass Transfer in Heterogeneous Catalysts*. Cambridge, MA: MIT Press; 1970 (reprinted 1977:78-82).
27. Patrick RH, Klindera T, Crynes LL, Cerro RL, Abraham MA. Residence time distribution in three-phase monolith reactor. *AIChE J*. 1995;41:649-657.
28. Liu W. *High-Throughput Selective Hydrogenation Process and Apparatus*. WO Patent No. 2002079125A1; 2002.

Manuscript received May 11, 2004, revision received Dec. 10, 2004, and final revision received Feb. 25, 2005.