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Gas–Liquid-phase Reactions: Reduction

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Traditional chemical systems for use in chemical analyses, chemical synthesis and catalyst development are giving way to microchemical systems or “microreactors” that have good heat and mass transfer properties [1, 2], making them especially well suited to study exothermic and highly endothermic reactions [3]. With new methods of depositing a variety of catalyst materials being developed, more and more reactions are being studied in microreactors [4]. Hydrogenation and dehydrogenation are two classes of chemical reaction that are important to making products in everyday use. They are found in the production of petrochemicals, foods [5] and synthetic organic species [6], among many other products in everyday use. Most of these reactions use precious metals in heterogeneous catalysis where a solid phase provides a surface for reactions between fluids.

Heterogeneous catalysis provides the possibility to keep the solid catalyst from mixing with the fluid phases and also eliminates the need for separation and purification of products. Prototypical studies, such as that of the reaction of cyclohexene, have been carried out in the past few decades to understand mechanisms of catalysis over precious metals such as Pt, Pd and Au so that more complex reactions in this class could be understood and made more economical [7–9]. Such studies have been integral in understanding the influence of catalyst structure and activity on selectivity, conversion and stability of the reaction system [10]. Using these studies as a basis, a variety of hydrogenation and dehydrogenation reactions have been studied in microreactors to prove their suitability as tools for understanding catalysis in the chemical industry by maximizing information gained per unit space, per unit time. Additionally, these studies provide a proof of concept of microreaction technology as a competing platform for hydrogenation and dehydrogenation processing for production.

Hydrogenation and dehydrogenation reactions of many compounds, such as cyclohexene, common alkanes such as ethane, cyclohexane, aromatic compounds such as benzene, unsaturated compounds such as fatty oils and aldehydes, and their respective catalyst chemistries have been studied in microreactors. The combinatorial chemistry-style approach that has been popular in biomedical and pharmaceutical research has been extended to catalyst discovery in hydrogenation

and dehydrogenation reactions [11]. These studies have focused on investigating different catalyst materials and catalyst supports, in-depth catalyst characterization for application in hydrogenation reactions [12], selectivity of the reaction products, conversion and residence times. Compared with laboratory-scale fixed-bed reactors, microreactors used in such setups have demonstrated that complex catalyst studies can be done with minimum resources and the results of previous studies can be duplicated in microreactor setups and, in many cases, alternative strategies can be developed to improve on them.

10.1

Microreactor Configurations for Hydrogenation and Dehydrogenation Reactions

Process development or experimentation strategy for microreactors involves optimizing reactor design issues such as catalyst loading, operating temperature and pressure conditions and heat conductivity of reactor building material [13, 14], which is essential to ensure completion of reaction at desired output levels and time durations. Consequently, a number of reactor configurations, materials and fabrication strategies are possible and have been deployed for hydrogenation and dehydrogenation reactions, as outlined below.

10.1.1

Glass/Quartz Microreactors

Tubular “microreactors”, which are in reality mini- or millimeter-scale reactors, have been used to study these reactions. Tubular microreactors take the form of a fixed-bed reactor with various materials of construction. Chao *et al.* used a quartz tubular microreactor (5 μm i.d.) to compare oxidative dehydrogenation of ethane over vanadium- and magnesium-based catalysts of different preparations [15]. The catalysts were introduced in the middle of the reactor tube with quartz granules used to fill the space above the catalysts and quartz wool used to retain the packing. This quartz microreactor was placed in a tubular furnace with the catalyst bed held in a constant-temperature zone. After performing experiments to study selectivity and conversion on the catalysts, surface analysis of the catalyst materials was used to identify the best catalyst preparation method.

10.1.2

Metal/Alloy Microreactors

Microreactors have been made by machining of common metals such as stainless steel (SS) and specialty alloys such as Hastelloy [16] (a nickel-based alloy) to make falling film microreactors in which gas-liquid reactions were studied. Titanium and aluminum plates with micromachined channel areas have been used as microreactors in a closely packed setup for gas-phase heterogeneous catalyzed reactions [17] (Figure 10.1).

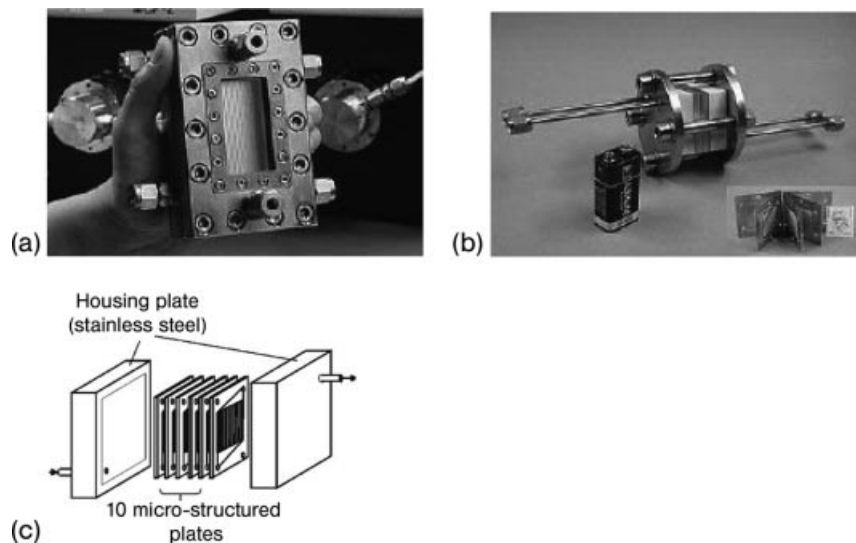


Figure 10.1 (a) SS falling-film microreactor for gas-liquid reactions [14], (b) catalyst-coated SS microchannel plates [14] and (c) catalyst-coated titanium microchannel plates, stacked together for gas-phase reactions in heterogeneous catalysis [17].

10.1.3

Silicon-based Microreactors

With advances in silicon microfabrication and semiconductor micromanufacturing technologies, various geometries of microreactors in silicon are feasible (Figure 10.2). Along with microchannels made in silicon and glass, other geometries such as membrane microreactors, fixed-bed microreactors and falling film microreactors have also been developed using silicon bulk and surface microfabrication techniques. Depending on the level of chemical compatibility with silicon, materials such as quartz, glass, polymers or a combination of these materials can be used instead to suit the needs of the particular reaction being carried out and reaction requirements [18].

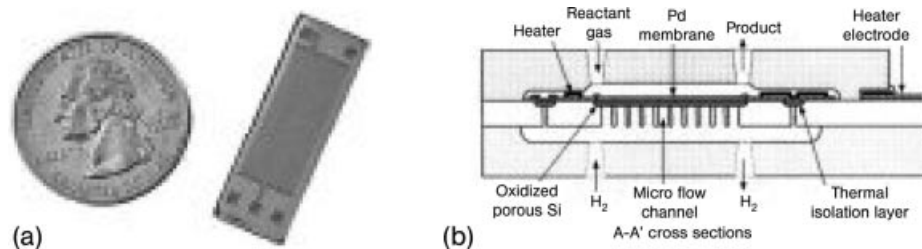


Figure 10.2 Silicon-based microreactors: (a) microchannel reactor [19] and (b) membrane microreactor [20].

10.1.4

Ceramic Microreactors

In addition to metals, silicon, glass and polymers that are commonly used in microchemical engineering, plastics and ceramics microfabrication techniques have also been implemented for microreactors for hydrogenation/dehydrogenation [21]. Where reactor material and corrosion phenomena become important, ceramic materials provide an interesting alternative because of their high thermal and chemical stability. A disadvantage with ceramic materials, however, is that due to their novel properties mass production techniques of micromolding and micro-patterning known for other materials cannot be conveniently extended to them and specific techniques are required. Senkan *et al.* have used non-porous ceramic silica slabs to make rectangular microchannels to study a library of Pt/Pd/In catalysts for catalytic dehydrogenation of cyclohexane [22].

10.2

Catalysts

Heterogeneous catalysis usually employs a solid-state catalyst surface over which liquid and/or gas phases are brought into contact using different contacting principles. A large number of important compounds are products of hydrogenation and dehydrogenation reactions using a large variety of catalysts. Since microreactors are fast gaining importance in the area of catalyst screening and development, placing the catalyst phase into the reactor setup has been investigated vigorously and various techniques have been developed for preparing such catalysts to be compatible with use in the new designs of microreactors possible with advances in micro-machining and microfabrication. Schimf *et al.* have studied different catalyst preparation methods for supported Au nanoparticles in selective hydrogenation of acrolein, crotonaldehyde and 1,3-butadiene using techniques of sol–gel, deposition–precipitation, impregnation, coprecipitation, incipient wetness, metal–organic CVD and dip coating [12]. With the help of structural and chemical analysis from XRD, XPS and related techniques, they were able to demonstrate the use of microreactors to screen a library of catalysts and catalyst support materials for the design of heterogeneous catalysis processes.

10.3

Gas-phase Hydrogenation Reactions

Heterogeneous catalytic hydrogenation and dehydrogenation reactions proceed in a pathway of elementary steps that involve mass transfer of reactant molecules to the catalyst surface, adsorption and migration of reactant molecules on the catalyst surface to active sites, reaction conversion to the product on catalyst surface and then desorption of product molecules from the catalyst surface. Microreactors in their various geometries have the potential for detailed studies of reactions for multiple

parameters, especially in cases where one of the elementary steps may normally dominate overall kinetics in an inconvenient fashion. For heterogeneously catalyzed gas-phase reactions, microchannel reactors are the preferred geometry due to the increase in the surface area of the empty reactor, narrow residence time distribution and good heat and mass transfer properties [18, 23].

A packed-bed reactor is commonly used for gas-phase reactions due to relatively low pressure drops and effective contacting; in the case of a micro-packed bed reactor, the catalyst can be introduced by filling channels with catalyst powder. To avoid pressure drops that may arise, the catalyst can be deposited in the form of thin films on the reactor/channel walls. Other modifications include using catalyst material in the form of wires that run along the length of the channel and the space between the wires serves as the microchannel pathway for the reactants [24]. In comparison with conventional laboratory-scale reactors, e.g. fixed-bed reactors, microchannel reactors have excellent heat transfer properties owing to their high surface area to volume ratio, which is helpful in carrying out catalysis tests isothermally.

Further gas-phase studies include the work of Maria *et al.*, who used an isothermal differential microreactor to study the dehydrogenation of cyclohexane and its methyl derivatives [25]. Ye *et al.* fabricated a Pd membrane microreactor from a silicon wafer using surface and bulk micromachining to study the hydrogenation of 1-butene [19]. A feed gas mixture of 1-butene, N_2 and Ar was passed through the membrane microreactor to observe the dependence of conversion and selectivity on the 1-butene flow rate. It was observed that at higher flow rates (or lower residence times), the conversion of 1-butene and selectivity to *n*-butane was suppressed.

Steinfeldt *et al.* used microchannel reactors to compare the gas-phase oxidative dehydrogenation reaction of propane to propene (C_3H_6) [17]. The microchannels were made of SS and titanium plates that were stacked tightly together in a graphite housing that provided the inlet and the outlet ports for the reactants and products. The plates had microchannels with different dimensions so as to give different reaction volumes for SS and Ti microchannels. Figure 10.3 shows the comparison between a laboratory-scale fixed-bed reactor and a microchannel reactor. Studies were

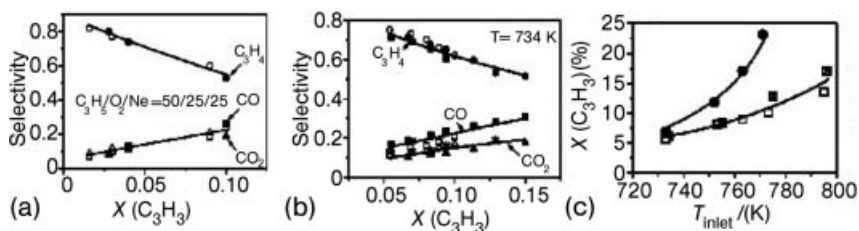


Figure 10.3 Product selectivity versus propane conversion at (a) 695 K and (b) 734 K and (c) propane conversion versus inlet temperature for laboratory-scale reactor and SS/Ti microreactors [17]. Laboratory-scale reactor, closed symbols; Ti microreactor, open symbols; SS microreactor, open symbols with dot.

carried out comparing microchannel reactors and laboratory-scale fixed-bed reactors for oxidative dehydrogenation of propane to propene over a redox catalyst as a model reaction. Figure 10.3a (reaction temperature 695 K) and Figure 10.3b (reaction temperature 734 K), show that microreactors were able to detect the small changes in product selectivity with increasing inlet temperature as also observed in the laboratory-scale reactor. Figure 10.3c shows that the SS microreactors provide higher levels of conversion than Ti microreactors, possibly due to SS material acting as a catalyst at higher temperatures, in contrast to Ti, which forms a thin, inert passivating layer of TiO_2 under these conditions.

Despite the difference in conversion due to material selection, these studies showed that although laboratory-scale reactors show higher conversion levels than microchannel-type reactors at a given inlet temperature, the laboratory-scale reactors suffer from axial temperature gradients that appear at higher temperatures and, as a result, catalytic yields differ. For increasing reaction temperatures, small differences in conversion and selectivity were observed between the microchannel and fixed-bed reactor and also within the microreactor types. It was also found that microchannel reactors were better suited to maintaining isothermal conditions for such an exothermic reaction even at high concentrations of reactants compared with the fixed-bed reactor. Axial temperature gradients in a fixed-bed reactor also became more pronounced when the reactant concentration was increased. Since it was difficult to measure temperature gradients in a microchannel, CFD simulations were performed, which showed that the SS microchannel reactors were better able to avoid axial temperature gradients because of higher rates of heat conduction through the channel walls.

Although the conversion levels for propane measured in both reactor types were approximately the same, detailed studies were possible with microchannel reactors with near isothermal operation and using a fraction of the resources of those needed for the fixed-bed reactor. The same reaction was studied by Sadykov *et al.* over metal-supported Pt-based monolithic catalysts in a microtubular reactor at short contact times [26]. Early studies have shown that the mechanism of dehydrogenation is based purely on surface Pt chemistry and this study was able to demonstrate that the conversion of propane and selectivity to propene was improved due to quenching of secondary products by Pt surface modification and conjugation with different promoters and feed tuning. CO_2 formation (trend 4 in Figure 10.4a) was significantly reduced by decreasing O_2 concentration and no carbon buildup or reactor deactivation was observed. Since very high propene selectivity (trend 1 in Figure 10.4a) was observed for promoted Pt systems compared with non-promoted Pt systems, the study was able to demonstrate the fact that the activity of catalyst monoliths is favored by the formation of metal–catalyst conjugates in the intermediate steps and also by reducing the O_2 concentration.

In a study by Yamamoto *et al.*, a simple microreactor was constructed by inserting an SS rod into a Pd membrane tubular reactor to investigate the effects of microchannel size on the dehydrogenation of cyclohexane to benzene [27, 28]. As shown in Figure 10.5b, it was found that at higher temperatures, increased surface area and a longer residence time for the reactants result in greater benzene production. For a

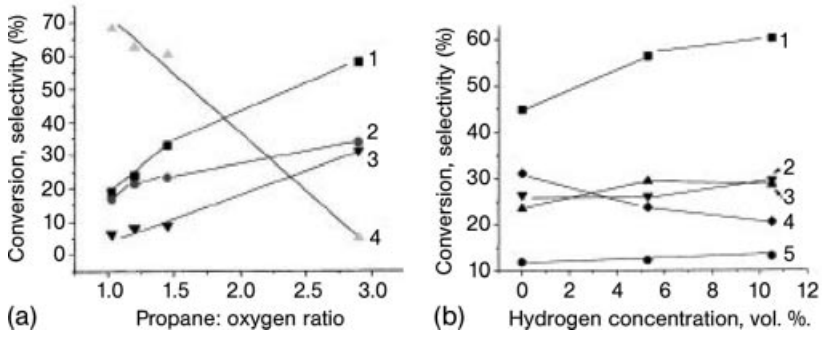
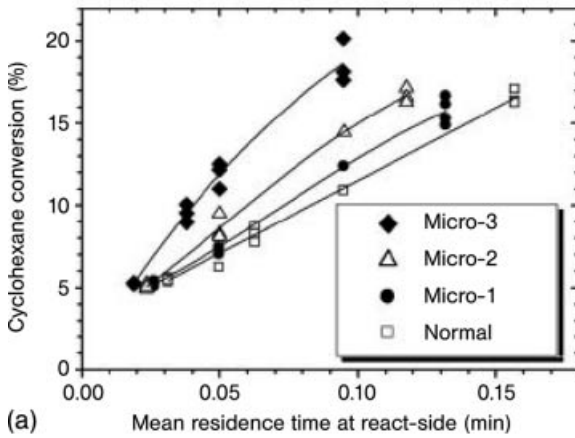
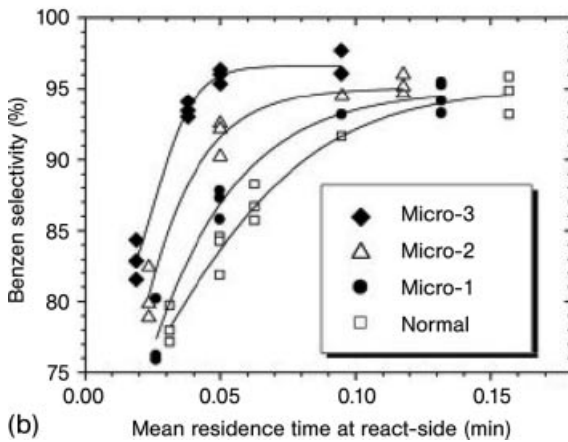


Figure 10.4 Dependence of propane conversion on (a) feed ratio and (b) H_2 concentration [26].



(a) Mean residence time at react-side (min)



(b) Mean residence time at react-side (min)

Figure 10.5 (a) Cyclohexene conversion and (b) benzene selectivity versus mean residence time [27].

given mass flow rate, when the catalyst surface area was increased by adding more microchannels within the same device volume, the conversion for reactant cyclohexene was observed to increase, thereby contributing to increased selectivity depending on the temperature. More importantly, it was observed that increased surface area of the catalyst maintained conversions at high levels at higher gas velocities as compared with a lower surface area of catalysts where conversions decrease significantly at higher velocities. By changing the flow rates of the reactant gases, namely cyclohexene and hydrogen, the conversion was observed to be a function of changing partial pressures. As the partial pressure of hydrogen is reduced in the feed stream, the reaction equilibrium shifts away from hydrogenation product and results in more benzene. On the other hand, when the hydrogen partial pressure is increased, the equilibrium shifts towards the hydrogenation product and more cyclohexane is produced.

Selectivity for benzene and cyclohexane was also studied as a function of variation of temperature. It was observed that although both benzene and cyclohexane were produced at room temperature, the selectivity to cyclohexane was almost 100% when the temperature reached about 50 °C.

In hydrogenation and dehydrogenation reactions of cyclohexene, which possesses one less single bond and two more hydrogen atoms than cyclohexane, different pathways may be followed depending on the catalyst and experimental conditions, hence it is widely studied for different catalyst chemistries. Surangalika *et al.* studied the hydrogenation and dehydrogenation of cyclohexene over a Pt layer as a catalyst in silicon-based microchannel microreactors [29]. The Pt catalyst was deposited in bulk micromachined silicon microchannels with the PVD method and gas-phase reactants were allowed inside the channels after making an anodic bond between silicon and a glass cover to make hermetic microchannels. The product stream was analyzed with a mass spectrometer for the reaction products and their concentrations to determine the conversion, selectivity and yield for given reaction conditions. Compared with earlier studies done in a laboratory-scale setup for catalyst studies, the results were in good agreement with the effect of temperature and channel geometry on conversion and selectivity. Two types of microchannel reactors were used, differing in the widths of the channels, i.e. 100 and 5 μm . Microreactors with 5 μm wide microchannels were able to provide a catalyst surface area that was 14 times greater than that with 100 μm wide microchannels.

The effect of increased surface area can be seen in Figure 10.6a, where cyclohexene conversion stabilized at higher levels for 5 μm than 100 μm wide microchannels. For reactions that are highly mass transfer limited, microreactors offer short diffusion paths to avoid this situation, resulting in much higher yields compared with conventional reactors. In most cases, it has been observed that the reactions exhibit reaction-limited behavior. Calculations show that microreactors most frequently operate in reaction-limited regimes even with reactions possessing relatively fast kinetics. As observed in Figure 10.7a, the hydrogenation product cyclohexane is the more favored product as the temperature continues to rise until about 130 °C, when the reaction shifts towards dehydrogenation and selectivity to benzene increases. This shift in selectivity at higher temperature is due to changing catalytic surface conditions, as shown in previous spectroscopic investigations of cyclohexene hydrogenation and

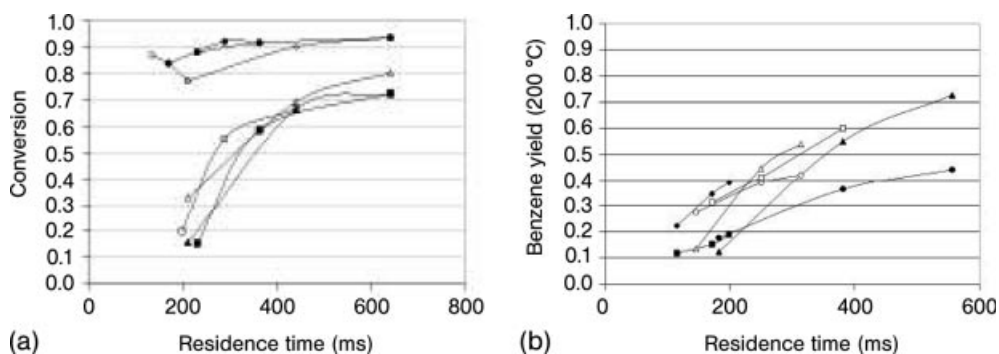


Figure 10.6 (a) Cyclohexene conversion and (b) benzene yield versus residence time.

dehydrogenation reactions with techniques such as X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy (AES) [8, 9, 30, 31]. It was found that these reactions proceeded by forming an intermediate with the solid catalyst surface involved. The double bond in the molecular structure of cyclohexene plays an important role in the formation of a bond with the Pt catalyst surface, most likely by donating its π -electron density to the metal atoms to form the intermediate species 1,3-cyclohexadiene (1,3-CHD) and 1,4-cyclohexadiene (1,4-CHD), which ultimately form cyclohexene and benzene, respectively. It is observed that at higher temperatures, the 1,3-intermediate is increasingly unstable and hence more of the 1,4- intermediate results in the formation of more benzene [32]. In addition to selectivity, it was also observed that the conversion suffers when the temperature rises above 130 °C. The decrease in conversion is likely due to the deactivation of the catalyst surface due to carbon deposition on the Pt, as verified by XPS.

It is important to note that most industrial-scale reactions operate in a mass transfer-limited mode where the rates of adsorption and desorption of reactants and products from the catalyst surface depend on the conditions of temperature, pressure

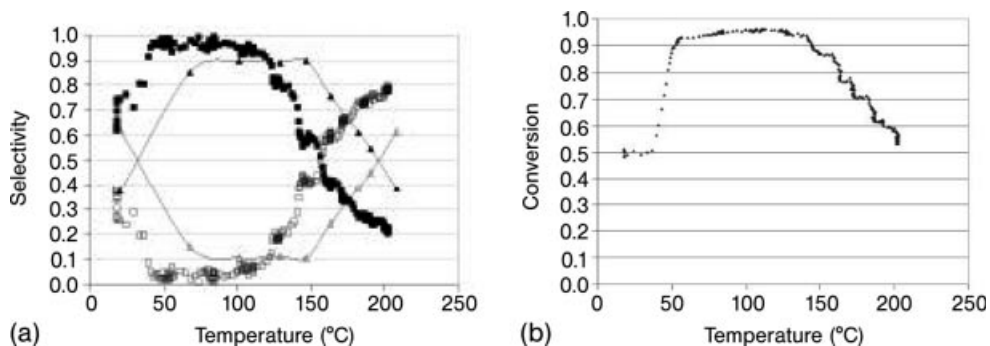


Figure 10.7 Effect of temperature on (a) cyclohexane (solid symbols) and benzene selectivity (open symbols) and (b) cyclohexene conversion.

and flow velocities employed. If the fluid velocities employed are not sufficiently high, the mass transfer of reactants to the catalyst surface will be slow, thus hindering the progress of reactions to completion with satisfactory yields and conversions. Thus high fluid velocities and, as a consequence, turbulent conditions, have to be employed in most cases to make the mass transfer to the catalyst faster. In contrast, microreactors operate in laminar conditions without the reaction being mass transfer limited, making the process more energy efficient and easier to simulate with better process control and higher yields. Microreactors are suitable for kinetically slow reactions where the external mass transfer (or fluid velocity) does not affect the progress of the reaction such that the reaction is carried out under proper flow conditions. In addition, the microreactors are also suitable for kinetically fast reactions where increasing the fluid velocities within the laminar flow regimes is found to be sufficient to maintain high reaction rates to completion.

10.4

Multiphase Hydrogenation Reactions

Multiphase catalytic reactions are of particular relevance in the field of microreactors. These reactions can be thought of as operating in a stepwise sequence, requiring the dissolution of gas into the liquid phase, the transport of the reactants throughout the bulk liquid to the catalyst support surface, the diffusion within the porous particle to the catalyst and finally reaction at the active sites. Transfer of gas into the liquid phase is often the limiting step. As in the case of gas-phase hydrogenations and dehydrogenations, the superior mass transfer performance of microreactors compared with conventional equipment arises from their inherently small characteristic dimensions. In the case of commercial-scale production, relief of mass transfer limitations would serve to de-bottleneck the system, allowing for higher production rates and further optimizations. Again, we focus our discussion at the laboratory scale, where the bulk of the current work on microreactors has been conducted. In this case, low transport resistances can be combined with other advantages characteristic of microreactors to produce powerful tools for isolation of intrinsic reaction kinetics, rapid screening of catalyst or chemical process miniaturization.

The surface area-to-volume ratios that promote high mass transfer rates for hydrogenation reactions, which are on the order of $20\,000\text{ m}^2\text{ m}^{-3}$ or more, are not uncommon, compared with $1000\text{ m}^2\text{ m}^{-3}$ for a conventional reactor. Laminar flow is typically affected by microgeometry, but because resistance to heat transfer displays a similar dependence on channel dimensions to mass transfer, overall heat transfer coefficient values for liquids are on the order of $10\,000\text{ W m}^{-2}\text{ K}^{-1}$, roughly one order of magnitude higher than in conventional heat exchangers [33]. As hydrogenation reaction rates are typically very sensitive to temperature, the overall heat transfer coefficient is important in promoting a uniform temperature throughout the device to prevent the formation of local temperature and concentration gradients, which can adversely affect product selectivity with undesired side-reactions. Therefore, when used in a laboratory setting, microreactors allow precise control of temperature. Short

residence times help further to suppress side-reactions common to some organic and selective alkene hydrogenations by limiting the exposure of fragile product species to the reactive environment. Methods of fabrication also make microreactor technology suitable for laboratory-scale use. The ability to fabricate multiple channels on a single microdevice, in a type of “lab-on-a-chip” arrangement, allows for economic screening of catalysts, including costly precious metal hydrogenation catalysts. Rhodium-based catalysts were investigated by de Bellefon *et al.* in microreactors for dynamic, high-throughput screening of gas–liquid hydrogenation reactions [34]. For reactions involving multiphase contact and mixing, Bellefon *et al.* used a single-channel helicoidal falling film microreactor to study gas–liquid asymmetric hydrogenation of mainly (*Z*)-methyl acetamidocinnamate over rhodium-based chiral complexes. A library of different transition metal molecular catalysts mixed with a library of chiral ligands was screened for given operating conditions of temperature and pressure, etc. [35]. Comparison with other traditional reactors revealed that the effects of very small changes in chiral ligands on catalyst activity were accurately detected using a fraction of the inventory of that used in traditional reactors.

The better control of reaction conditions suppresses side-reactions and reduces or avoids the need for complex separation and or purification systems. Formaldehyde has been produced traditionally by partial oxidation of methanol on Fe–Mo oxides or by oxidative dehydrogenation over Ag catalysts [36]. Water is a byproduct in both the reactions and needs to be removed to obtain pure formaldehyde. Direct dehydrogenation of methanol on solid Na compounds in a homogeneous phase has been studied and demonstrated as an alternative where water-free (anhydrous) formaldehyde is needed. This reaction has some limitations in that it is highly endothermic; thermodynamic equilibrium dictates that the reaction temperature be as high as 700 °C for equilibrium conversion higher than 95% and that the reaction product, formaldehyde, is unstable at such high temperatures and decomposes. Therefore, to obtain high yields of formaldehyde and avoid byproducts, the reaction conditions must be able to achieve fast interaction of the catalyst with the reaction gases, fast heating and uniform temperature control within the reactor, narrow residence time distribution and efficient and rapid quenching of the reactor outlet. It has been demonstrated by Maurer *et al.* that these conditions can be met by microreactor systems made of microchannels with the advantages of high surface area-to-volume ratio and about an order of magnitude higher heat transfer coefficients compared with conventional reactors [36]. The reaction was carried out in a microstructured mixer and micro-heat exchanger assembled together from specialty metal alloys to avoid undesired catalysis at high temperature from the reactor material itself. Although the reactor was unable to give consistent operation for durations longer than 30 min and significant coke formation was observed, the principle of reaction was successfully demonstrated with high conversion rates (>98%). The study also showed that proper mixing of the reactant gases with catalyst, shorter residence times and efficient heat exchange at the outlet will help avoid coke formation.

Essential to the use of microreactors as a laboratory tool for multiphase reactions is an investigation of the flow behavior in gas–liquid systems. Considerable work has been carried out in the area of two-phase flow within microchannels. Kreutzer *et al.*

presented a review of the various flow regimes that can emerge in multiphase flow [37]. At the extreme of high liquid and low gas velocities, bubble flow is characterized by liquid as the continuous phase, with bubbles of gas dispersed into a fully wetted channel. The opposite regime of annular flow occurs at high gas and low liquid velocities, where gas becomes the continuous phase and the liquid flows as a thin film along the channel walls. The intermediate regime is known as Taylor flow, where alternating segments (slugs) of gas and liquid travel down the channel. Salman *et al.* found that the volume of Taylor bubbles (slugs) formed is weakly dependent on the fluid properties, but strongly dependent on the relative gas and liquid flow rates [38]. Thus, the average lengths of the segments are approximately constant for a given set of inlet conditions, with gas segments increasing in size as the gas-to-liquid flow rate ratio increases. Further gradation can exist in the definition of flow regimes, with some authors presenting a churn flow regime between Taylor and annular flow. As the ratio of gas-to-liquid velocity is increased from Taylor flow, satellite bubbles appear in the liquid and disrupt the pattern of slugs, yielding a very chaotic flow pattern. The regimes of bubble, Taylor and annular flow are illustrated in Figure 10.8.

Wall effects can be significant for two-phase flow in microchannels, as demonstrated by Cubaud *et al.* using liquid surfactants [39]. Kreutzer *et al.* also noted that across a wide range of conditions in a microchannel, roughly defined as a channel having a diameter less than 5 mm, Taylor flow is the predominant regime. This is true because the viscous ($\sim\mu u/d$) and interfacial ($\sim\sigma/d$) stresses, inversely proportional to channel diameter, tend to dominate over inertial ($\sim\rho u^2$) and gravitational ($\sim\rho gH$) forces. In the context of a multiphase reaction, the preferential emergence of Taylor flow is advantageous with respect to gas-liquid mass transfer.

In reviews of mass transfer in two-phase flow in microchannels, Kreutzer and coworkers [40, 41] noted that the Taylor flow regime is typically associated with the best gas-liquid mass transport because of the no-slip condition at the channel walls. The velocity gradient within the liquid slug promotes a chaotic mixing effect. The resultant continual refreshing of the two-phase interface provides a high driving force

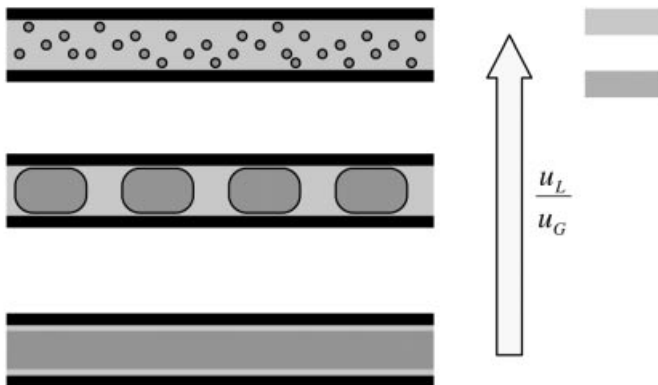


Figure 10.8 Illustration of gas-liquid flow.

for diffusion of gas into the liquid. For a given liquid holdup, Taylor flow with shorter liquid slugs will yield a higher mass transfer rate than flow with longer liquid slugs, as the shorter slugs exhibit a larger interfacial area and more intense mixing. This result was confirmed by Waelchli and von Rohr [42], who use micron-resolution particle velocimetry (μ PIV) to observe significant mixing at the slug interface, but negligible mass transport across the channel centerline. Note that because of the small channel diameter, the flow remains laminar, relegating any turbulence in the classical sense to the slugs themselves, rather than the entire channel. Yue *et al.* observed liquid mass transfer coefficients as high as 21 s^{-1} in Taylor microchannel flow, and a high interfacial area of $9000 \text{ m}^2 \text{ m}^{-3}$ [43]. Comparable values for a macro-scale stirred-tank reactor, where gravitational and inertial forces may induce non-Taylor flow regimes [44], are 0.1 s^{-1} and $1000 \text{ m}^2 \text{ m}^{-3}$.

Heiszwolf *et al.* studied the effect of slug length in Taylor flow on the mass transfer rate within the channel [40]. Across a range of liquid holdups from 0.40 to 0.85, they observed a unit cell length, defined as the total liquid plus gas slug length, of approximately four times the channel diameter. The gas-liquid mass transfer coefficient was found to increase with decreasing slug length, as shown in Figure 10.9, with ψ_{UC} representing the dimensionless unit cell length.

Across the entire range of liquid holdup, the authors observed a dimensionless slug length ranging from approximately two to ten times the channel diameter, with variations of up to 30% at high liquid holdup values due to the presence of large liquid slugs. Qian and Lawal used CFD simulations to study the non-uniformity of Taylor slug lengths using a T-junction microchannel [45]. They determined that as the gas or liquid flow velocity increases, the slug non-uniformity becomes more pronounced and thus mass and heat transfer behavior becomes more difficult to predict. Because the dimensionless slug length depends on the channel diameter, smaller channels exhibit shorter slugs and hence less variation in slug length. The authors proposed correlations for the dimensionless unit slug length, and also liquid and gas slug lengths, in the T-junction channel that can be used for estimating pressure drop and heat and mass transfer coefficients.

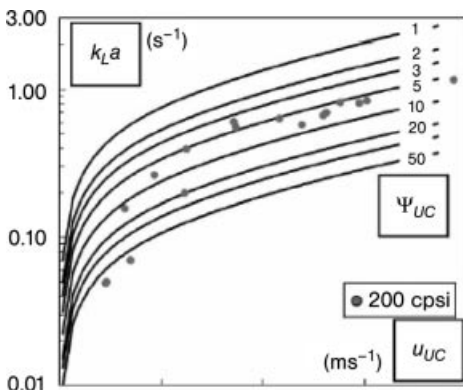


Figure 10.9 Gas-liquid mass transfer coefficient in Taylor flow [40].

The study of mass transfer in two-phase flow regimes, and in particular Taylor flow, can ultimately be used for the design of multiphase catalytic reaction systems. Examples of such reactions are found throughout the chemical industry, such as organic synthesis reactions for pharmaceutical compounds, selective hydrogenation of petrochemicals and in hydroprocessing for refining applications [46]. Rapid mass transfer from gas to liquid addresses the principal limitation of these types of reactions. Although considerably more work exists for two-phase flow patterns and mass transfer in microchannels, a growing number of researchers have extended these findings to multiphase reaction engineering in microreactors. Mass transfer rates for microchannel reactors have been shown to be significantly higher than those reported in the literature for conventional packed-bed and slurry reactors. With high mass transfer rates and low pressure drop possible due to microchannels and favorable catalyst structures, it is possible to conduct both kinetically slow and fast reactions at unconventionally low flow rates and high LHSV (liquid hourly space velocity, which takes into account the liquid volumetric flow rate relative to catalyst volume). When compared with conventional or laboratory-scale reactors, the space time yield (STY) and LHSV numbers were much higher for microreactors [23].

McGovern *et al.* investigated the two-phase behavior in a rectangular-shaped microchannel in the context of the hydrogenation of an organic nitro compound [47]. Such reactions are of interest in the production of pharmaceutical intermediates, which are largely carried out in batch stirred-tank reactors. Matrixes of silicon microfabricated structures trap catalyst particles within the channel. Due to the square channel geometry, a Taylor flow does not occur, at least in the strict definition above, but rather an intermittent chaotic flow termed transitional that is characterized by competition between gas and liquid phases. With regard to mass transfer, however, the benefits of this transitional flow regime are analogous to those of Taylor flow. First, the two-phase competition causes a periodic shearing of the gas-liquid pattern, offering a high driving force for gas-liquid diffusion. Second, liquid droplets are observed to form around individual catalyst "traps", creating regions with local interfacial area as high as $50\,000\text{ m}^2\text{ m}^{-3}$. Reaction experiments demonstrate that the highest conversion is achieved in the transitional regime owing to these mass transfer characteristics. From the reaction data, a gas-liquid mass transfer coefficient of 0.98 s^{-1} is calculated in the transitional regime, compared with one order of magnitude lower in the gas- or liquid-dominated regimes. These results still represent a mass transfer-limited reaction, but one in which the gas and liquid flow conditions can be adjusted to relieve this limit significantly. With respect to commercial-scale production, this type of reactor might be designed for high liquid throughput at a proportionately high gas rate so as to maintain the two-phase competition characteristic of the transitional flow regime.

A similar result was observed by Wang *et al.* in a microchannel used for reaction of hydrogen and oxygen to form hydrogen peroxide, which requires the presence of a liquid feed [48]. They found that Taylor flow enhances the mass transfer across the phase interface and yields the highest reaction conversion. The catalyst productivity was found to increase with the square root of the liquid flow rate, lending support to the assertion that the respective flow rates can be increased to maintain a favorable

regime for mass transfer and achieve maximum product throughput. The authors demonstrated this result in devices with two different types of catalyst structures. The first was a single-channel device with a coated layer of catalyst. The second was a multi-channel device with catalyst grown in a honeycomb structure to simulate a monolith reactor.

Kreutzer *et al.* investigated the hydrogenation of α -methylstyrene to cumene in monolith reactors of varying cell density [41]. They found that at low to moderate cell densities (200–400 cells per square inch) the reaction was mass transfer limited at temperatures above 393 K. At a cell density of 600 cpsi, however, the external mass-transfer rate was sufficiently high at temperatures above 413 K that the reaction was not fully mass transfer limited.

Nijhuis *et al.* also carried out the hydrogenation of α -methylstyrene in both a monolith and trickle bed reactor [49]. The monolith was 10 mm in diameter with a cell density of 400 cpsi, whereas the trickle bed was 47 mm in diameter. Both reactions were carried out in the Taylor flow regime. The catalyst productivity, defined as the rate of product formation per unit volume of catalyst, was found to be $6.2 \text{ mol m}^{-3} \text{ s}^{-1}$, compared with $4.6 \text{ mol m}^{-3} \text{ s}^{-1}$. To test the importance of Taylor flow in the reduction of mass transfer limitation and enhancement of the observed reaction rate, the researchers also carried out a “liquid-full” experiment, where only liquid presaturated with hydrogen was fed to the monolith. The catalyst productivity in this case was $1.5 \text{ mol m}^{-3} \text{ s}^{-1}$. This experiment clearly indicates that the mass transfer rate of hydrogen through the phase interface in Taylor flow is much faster than in the bulk liquid.

Losey and coworkers studied cyclohexene hydrogenation as a model reaction in a packed-bed microreactor incorporating standard porous catalysts in silicon–glass devices with a microfluidic distribution manifold and reactor area in the form of a single microchannel or as a group of 10 microchannels [50, 51]. An array of microfabricated columns was formed in the microchannel to simulate the effect of a packed column. These columns were made porous and then coated with catalyst. When the catalyst was incorporated in the form of a fixed bed with the help of a microfilter, the resulting surface area and reaction rate were comparable to those provided by a microcolumn packed-bed reactor. Because of the exothermic nature of hydrogenation reactions, the increased interfacial area was useful in heat dissipation. Along with the gain in mass transfer rates, microreactors showed an improvement in overall performance over conventional reactors in this study. Diaz *et al.* have studied cyclohexene reactions in a microreactor setup consisting of a small tube of Pyrex glass packed with the catalyst material supported in two different liquid phases [52]. The reactants were fed in both the pulse injection mode and continuous mode to compare the effects on conversion. It was found that microreactors are better suited than conventional reactors for pulse flow (or slug, segmented flow) of reactants because of the low hold-up volume and shorter response times. The pulse flow gives rise to liquid slugs that are uniformly separated by gas bubbles and provide the advantage of better radial mass transfer [14, 23].

Reports on multiphase flow studies in the literature support the view that in the intermittent or Taylor flow regime, interface shearing occurs at the gas–liquid

boundary that serves to enhance the mass transfer rate. Across a wide range of conditions, Taylor flow exists in microchannels due to the dominance of viscous rather than gravitational forces. The additional benefits offered by microreactors, such as a large surface area-to-volume ratio and the absence of temperature gradients, make such devices an ideal vehicle for catalytic reactions controlled by external mass transfer, such as hydrogenation. Process intensification and miniaturization efforts may ultimately find application for these systems as an alternative to conventional macroscale reactors.

10.5

Conclusion

Hydrogenation and dehydrogenation reactions have been the the subject of much work in the field of microchemical systems owing to the attractive transport properties and fabrication aspects of such devices. Both gas-phase and multi-phase as well as catalytic and non-catalytic reactions have been carried out, with applications as far-reaching as the pharmaceutical, chemical processing, energy, and food industries. The studies discussed in this chapter demonstrate the various benefits of microreactors as continuous processing devices, including enhanced effective reaction rate, improved selectivity, superior heat transfer and temperature uniformity, less potential for runaway reactions, and availability of advanced fabrication techniques.

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