

### 3

## Principles and Guidelines for Selection of Microstructured Devices for Mixing and Reaction

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### 3.1

#### Introduction

Microreaction technology is a promising tool for process intensification and for speed-up in process development. A long list of possible benefits due to the use of microstructured devices has been published [1, 2]. However, apart from these promising prospects, this technology is still very new. In some situations, the possibilities and benefits may lead to the decision to give microreaction technology a try. There are numerous problematic reactions that have not been solved satisfactorily for a long time, and the microreactor might be able to solve these finally. Various different microreactors now known and reactors with different principles, different materials and so on are available. But what is the best microreactor for a specific reaction to be carried out?

This chapter will not give an answer to this question. There are too many influencing variables that determine which reactor is the best, and these variables are not only of chemical or chemical engineering but also of economic and infrastructural nature. The microreactor with the best chemical performance in the laboratory is not automatically the best one to bring the reaction to production. Possibly a time-consuming formulation of an up-scaling concept is necessary or the possibility of using an existing infrastructure has to be considered. Such factors are specific from case to case and sometimes it may be more beneficial to use the second-best reactor in the laboratory, but have easier access to implementation in production.

Hence in this chapter some general issues will be discussed that can be important when choosing a microreactor. Common aspects of microreactor properties will be shown to give hints as to which of them may be important for a particular problem and which not.

The chapter is divided into three parts according to different possible combinations of contacted phases: liquid–liquid, liquid–gas and gas–solid. Other phase

combinations are not discussed in detail, but are partially addressed in one of the three parts.

## 3.2

### Liquid–Liquid Reactions

#### 3.2.1

##### Introductory Remarks

A variety of microreactors for liquid–liquid reactions are available and have been described in literature. The adopted throughputs start from below the  $\text{mL h}^{-1}$  level for analytical purposes. Micromixers for laboratory-scale process development or organic synthesis can handle flows from  $\text{mL h}^{-1}$  to  $\text{L h}^{-1}$ . For the range from above  $10 \text{ L h}^{-1}$  up to tens of  $\text{m}^3 \text{ h}^{-1}$  microstructured mixers are also available and some are already in production use.

This section gives a short outline of topics that can be important when selecting a microstructured device for the purpose of performing liquid–liquid reactions. It is aimed mainly at workers using such devices in the laboratory, but also gives some remarks that can be important for later implementation in production surroundings.

#### 3.2.2

##### Classification of Microreactors – Phase-contacting Principles

There are many different ways to contact liquid phases. The most important are serial or parallel multilamination, chaotic flow configurations and colliding jets. An extensive outline of different mixing principles and more detailed descriptions can be found in a paper by Hessel *et al.* [3].

- *Parallel multilamination.* Multilamination means that the microstructure generates micro-sized lamellae and contacts the lamellae in an alternating way. In mixers with parallel multilamination this happens for all lamellae at the same time. This means that all interfaces formed between the mixed liquids along the mixing channel have the same age and therefore the same reaction progress.
- *Serial multilamination.* Split and recombine mixers generate the lamellae sequentially. Therefore the interfaces formed between the lamellae do not have the same age. Consequentially the reaction progress at the end of the mixing channel is unequally distributed, which is intrinsic to the mixing principle. Definitely an advantage of this kind of mixers is that the lamellae-generating microstructure has much larger dimensions than the lamellae themselves, which makes such mixers robust.
- *Colliding jets.* High-velocity liquid jets are collided, which leads to fast chaotic mixing. The collision can be performed by different flow configurations. This mixing principle can be a good alternative for fast particle-producing reactions that cannot be handled in other micromixers.

## 3.2.3

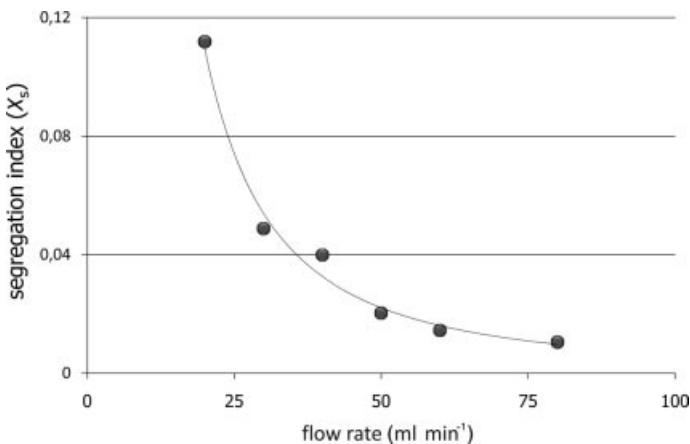
**Criteria for Reactor Selection**

It is not possible to give definitive selection advices for the most diverse area of liquid–liquid reactions. The necessities and requirements for different chemical applications are too different to be able to recommend a special reactor for a given reaction. Even for the same reaction it is possible that different reactors can be better suited, depending on the framework requirements. The following section therefore just presents critical issues that have to be considered separately for different cases.

**3.2.3.1 Process Parameters (Temperature, Pressure, Throughput)**

The pressure loss of the microstructured device in the range of the applied throughput is an important piece of information. It affects the selection of the surrounding plant equipment such as pumps or tubing. Usually a higher pressure loss can be handled easily on the laboratory scale, but usually it is not wanted on the pilot or production scale. On these scales typically required pressure drops are below 5 bar.

Microreactors or -mixers can be used with certain ranges of throughput. The throughput determines the pressure drop and therefore the energy consumption for the mixing process. The selection of a larger device that can be handled at the lower end of the throughput range and therefore at lower pressure loss suggests itself. However, this suggestion must be treated with caution. Usually microreactors give a better mixing quality at higher flow rates (Figure 3.1 [4]). This means that higher relative pressure drops are necessary to achieve good mixing quality. In practice, the decision will be guided by what quality is necessary and what pressure drop is possible.



**Figure 3.1** Mixing quality (segregation index) versus flow rate for a StarLam 30 with an adapted foil stack for low throughputs [4].

### 3.2.3.2 Mixing Performance

Of course, the mixing quality is a very important parameter for microstructured liquid–liquid reactors. There are some approaches to characterize the mixing quality of such devices. Up to now, the most important method for characterizing the mixing quality of micromixers is the Villermaux–Dushman reaction [5]. This is a two-reaction system with a fast and a very fast reaction, which has been adapted for use with microstructured mixers. The better the mixing, the less product of the slower reaction is formed. This product ( $I_3^-$ ) is easily detected by UV spectroscopy.

This method yields a factor called the segregation index ( $X_s$ ), which describes the extent of micromixing and is specific to the device. The smaller the segregation index, the better is the mixing quality. The segregation index of stirred vessels was determined as being in the range 0.1–0.01 [6]. The indices for micromixers are well below this range in most cases (Figure 3.1).

Segregation indices have been reported for a number of available microstructured mixers (Table 3.1) [57, 8, 9]. However, so far it has not been common to provide this information in specification data sheets for microreactors. The determination of  $X_s$  is well described but often the results vary depending on the experimenter. Therefore, it is not always advisable to compare results from different sources.

The Villermaux–Dushman method has also been adapted to use with viscous media [10], but only a few data have been published in this field so far. Of course, the mixing of more viscous liquids leads to a higher segregation index. The replacement of one of the mixing partners of 1 mPa s with a 50 mPa s liquid, for example, raises the segregation index from 0.001 to 0.003 [11].

Another important issue is the mixing time. pH-induced chromogenic reactions can be used to determine the time needed to achieve complete mixing [8].

Engler *et al.* [12] presented a dimensionless number (mixer efficiency,  $ME_{II}$ ) to compare different micromixers. This number consists only of primary mixer attributes such as mass flow rate  $\dot{m}$ , mixing time  $t_m$ , dynamic viscosity  $\eta$ , hydraulic diameter  $d_h$  or pressure loss  $\Delta P$ . It describes the mixer by the means of the necessary effort (such as pressure drop) to achieve a certain effect (short mixing time) with consideration of the throughput (mass flow rate):

$$ME_{II} := \frac{\dot{m}^2}{\eta d_h^2 \Delta P t_m} \quad (3.1)$$

**Table 3.1** Micromixers with determined segregation index from the literature.

Mixer	Provider	Ref.
SIMM	IMM	[5]
Triangular interdigital micromixer	Mikroglas	
Caterpillar micromixer	IMM	
T-mixer	Bohlender	
StarLam 300	IMM	[7]
StarLam 30, 300, 3000	IMM	[9]

Up to now there is no common consent regarding the use of one number to describe the mixing performance, so it is difficult to obtain comparable data for mixers from different distributors.

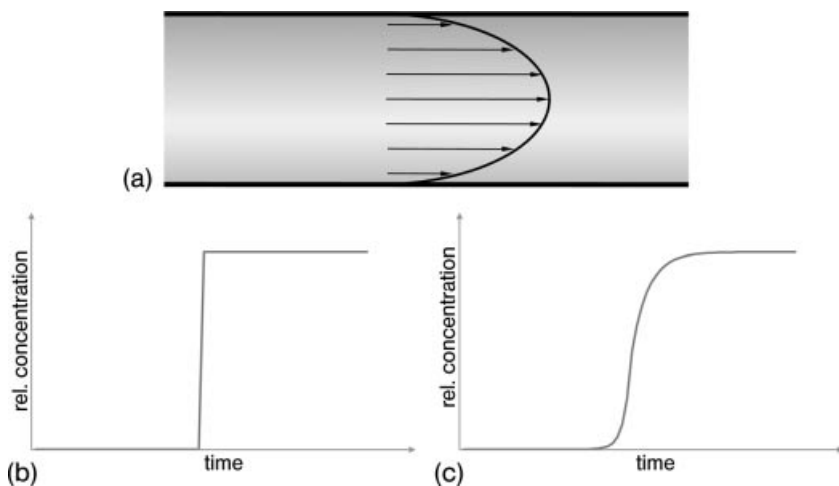
### 3.2.3.3 Residence Time Distribution

Residence time distribution can be an important issue in the selection process. Microreactors usually operate at Reynolds numbers lower than 200. In this regime, laminar flow prevails and mass transfer is dominated by molecular diffusion. An injected substance in the channel will dissipate caused by the flow profile in the channel. Hence the input signal will be broadened until it reaches the exit of the channel (Figure 3.2). The extent of such a distribution depends on the channel design. In microchannels the mixing process can then be described by the Fourier number (no axial diffusion, dominating radial diffusion  $D_r$ ). A high Fourier  $Fo$  number leads to a narrow residence time distribution:

$$Fo_d = \frac{t_{\text{mean}} D_r}{d^2} \quad (3.2)$$

A smaller channel diameter leads to a narrower distribution. However, the channel cross-section diameter is limited by pressure loss, fabrication method and other practical aspects (plugging, etc.). A narrow distribution can also be achieved through longer channels (higher mean residence time).

The residence time should be as short as possible so as to have the same reaction time for each reactant volume element. There are many applications where this can be important or at least must be taken into consideration. One example is high-throughput experimenting at low chemical consumption in the same microstructure. The residence time distribution affects the time that has to elapse between two



**Figure 3.2** (a) Velocity profile in a microchannel and concentration at (b) the inlet and (c) the outlet of the microchannel.

experiments before the analytics can start. A broad residence time distribution means a longer waiting time and therefore higher chemical consumption. For applications with higher mass flow in chemical or process development, this issue is not that important in respect of chemical consumption, but it also has to be taken into consideration in the process of project planning for evaluating waiting times to sampling or product taking.

A broad residence time distribution and the associated varying reaction times in the solution can also have negative effects on the product distribution. This is especially true for fast multi-step reactions, which need a very definite reaction time for the first step. This second step can also be a precipitation or a quench (chemical or thermal).

#### 3.2.3.4 Ability for Scale-up or Scale-out

Microreactors are already in use at mass flows up to some  $\text{m}^3 \text{h}^{-1}$  [13, 14]. There are already a couple of industrial production plants with microreactors reported [15–17] and a lot more are estimated to be in operation, as reported by Hessel *et al.* [18].

Especially in chemical and process development it can be of particular interest to use a microreactor, which has a known strategy for scale-up or scale-out. There are different strategies for increasing the throughput from the laboratory-scale to pilot- or production-scale (Figure 3.3).

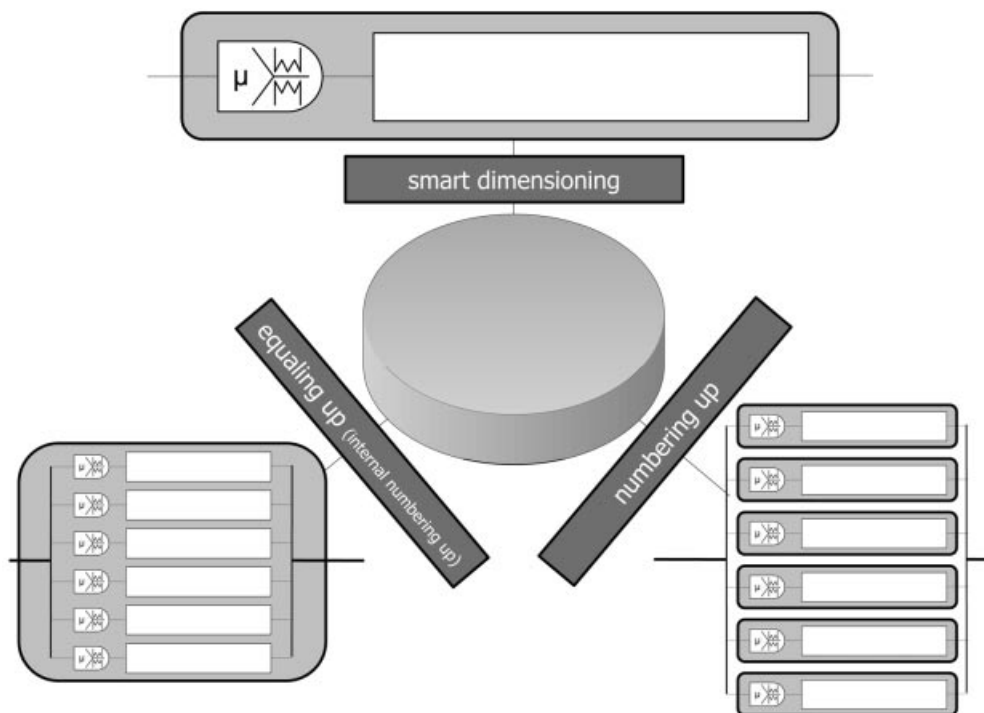


Figure 3.3 Methods for scaling up to higher mass flows.

- *Scaling – smart dimensioning.* The simplest way to achieve a higher mass flow is to increase the size of the microstructured device. This leads also to an increase in the characteristic length of the device and, as most advantages of microreactors are based on very small characteristic lengths, the positive effects of microstructured devices will decrease. For some micromixers this approach has been chosen, as for the StarLam family. A smart increase in inner dimensions leads to a higher throughput with little loss of mixing quality.
- *Numbering-up.* Another approach to increase the mass flow is to raise the number of devices and parallelize them. One problem with this approach is the equal distribution of the flow across all devices. A second and more serious problem is the measurement and control of the devices. A numbering-up factor of 1000 will lead to 1000 sensors to be monitored and controlled. Both problems are solvable but especially the second one is expensive.
- *Equaling (internal numbering-up).* This approach realizes a higher mass flow by increasing the number of microstructures in a single device. So the number of devices is kept low and therefore the control effort is small. The characteristic lengths of the microstructures and therefore the microspecific advantages are unchanged. The only serious problem remaining is the internal equal flow distribution across all microchannels.

#### 3.2.3.5 Usability

Of course, the functional capability is most important for a microreactor, but the usability in practical operation should also be taken in consideration.

The possibility of easily cleaning a microstructured device is essential for any development use on the laboratory scale. During the process development of chemical reactions, it is necessary to go to extreme conditions, at which dissociation or polymerization of educts and/or products takes place. Often this is connected with fouling in the reactor, which sometimes cannot be easily cleaned by rinsing. Then it is most important to have an easy, time-saving way to open the reactor and to clean the structure.

The same is true for microreactors in production use. Even with the obligatory use of filter cartridges the microstructure is susceptible to plugging. Moreover, it will be necessary to monitor the actual condition of the microstructure at periodic intervals. Such maintenance steps should be possible with the lowest expenditure of time possible.

#### 3.2.3.6 Reactor Material

A wide range of materials are available for microreactors, so it is possible to choose a suitable material for most chemical applications. The most important property for liquid–liquid applications is chemical and/or mechanical corrosion resistance. Corrosion in microstructured devices is certainly a problem and needs special attention. Corrosion rates of 1 or 0.1 mm yr<sup>-1</sup> may be resistant concerning standard reaction vessels or pipes, but may cause significant changes to the behavior of microstructures with dimensions of 0.1 mm or even below. Up to now no common

design rules or regulations dealing with corrosion in microstructured devices exist. Hence it is necessary to check carefully the resistance of the materials for every reactant that will be used.

Temperature and pressure resistance are another important issue. These properties can be handled in a common way. Temperature resistance and thermal properties are known for possible materials. Concerning the pressure resistance, there exist norms and directives such as the Pressure Equipment Directive (PED) 97/23/EG or AD-Merkblätter. Usually microreactors are exempt from these directives because of their small active volumes, but although not obligatory they are often used as guidelines for the construction and installation of such devices.

The widest used materials in microreaction technology are, of course, metals. Metals provide good thermal and pressure resistance. There are different, known methods to manufacture the microstructure such as mechanical micromachining, laser micromachining, wet chemical etching and selective laser melting. An outline of different manufacturing methods for metal microstructures was published by Brandner *et al.* [19]. The chemical resistance of metals varies, but for a wide range of applications suitable metals can be found. Usually metal microreactors are made of stainless steel such as 1.4401 or 1.4571. However, any reactor manufactured from stainless steel is often also available with more chemically resistant alloys, such as Hastelloy, or even noble metals such as titanium.

Other widespread materials for microreactors include glass and polymers. Polymers have lower thermal, chemical and mechanical resistance than metals. But there is a great advantage in producing microstructured devices from polymers that are cheap and available in large amounts using molding, hot embossing or polymer laser micromachining.

Glass has a high chemical resistance and high resistivity at higher temperatures. Additionally, the transparency of glass makes it possible to use it for analytical or photochemical applications. Photolithography is mainly used to manufacture the microstructures. Laser patterning and sandblasting are other manufacturing methods.

Ceramics are a very interesting material for reactions with corrosive chemicals that cannot be handled in metal reactors, owing to their high chemical, thermal and mechanical resistance [20].

#### 3.2.4

##### **Liquid–Solid Reactions**

Whereas the handling of solids in the input streams of micromixers is a hardly solvable problem, many particle-forming liquid–liquid reactions are carried out in micromixers. Precipitation reactions benefit from controllable conditions in microstructures. Usually particles with higher quality and better controllable properties in comparison with batch reactions can be achieved [21, 22].

Precipitations can be carried out stably in microstructured mixers, as the formation of the solid takes place in the residence time tube and no particles come in contact with the microstructure. Nevertheless, plugging can occur due to backflow into or leak-flow between the supply channels. The cause of backflows can be



pulsation of the pumps or an uneven flow distribution in the microchannels. Precipitation reactions have been carried out not only on the laboratory scale but also on the pilot scale [23].

### 3.3

#### Gas-Liquid Reactions

##### 3.3.1

###### Introductory Remarks

This section gives a short overview of gas-liquid and gas-liquid-solid microreactors, providing information for the correct choice of a proper microreactor for particular industrial problems and technical background information behind the reactors.

##### 3.3.2

###### Classification of Microreactors – Phase-contacting Principles

Basically, there are two possibilities for bringing two phases into contact. The first (Type A) is to keep both fluid phases continuous in order to create a defined interface. Consequently, the reactor should embody microstructures that generate two stable continuous phases with a preferably high exchange area. The second possibility (Type B) is to disperse one phase into the other by using a suitable inlet or a micromixer upstream of the reactor section. The goal to create an exchange area is also a dominant aspect for this type.

###### 3.3.2.1 Continuous-Continuous Phase (Type A)

Both phases feed the microreactor with separated streams. To guarantee no dispersion, the regions of both flows can never be the same. Hence both phases enter the reactor separately, come into contact while streaming in their own region and are withdrawn separately at the reactor outlet.

The principal challenge concerning the reactor design is to guarantee the stable flow of both phases, which are never dispersed into each other, while perpetuating a preferably high constant exchange area interface between them [24].

**Momentum Transport** The liquid film profile and its thickness  $\delta$  depend on the flow rate, the surface tension (liquid, gas and reaction plate material property) and on the channel dimensions (width, depth, length, diameter, etc.), which determine the interfacial area. In mesh reactors, the meniscus stability (depending on the surface tension and pore geometry) plays a certain role. We encounter the following parameters:

- $Re$  (Reynolds number) =  $(\rho dU)/\mu \approx 0.01-10$
- $Fr$  (Froude number; only for vertical arrangements) =  $\sqrt{(U^2/Lg)} \approx 10^{-2}-10^{-3}$
- $Ca$  (Capillary number) =  $(\mu U)/\gamma$
- $We$  (Weber number) =  $(dU^2)/\gamma$

- $Bo$  (Bond number) =  $(\rho g d^2)/\gamma$
- $Bo^*$  (Bodenstein number):  $Pe_{ax} = Bo^*(d/L) = (Ud)/D_{ax}$  (depending on  $Pe' = ReSc$ ).

**Heat and Mass Transfer** Using the film theory, both phenomena mainly depend on the film and gas stream thickness and the type of reaction. Other parameters are the interfacial area, the residence time and the axial dispersion. Good mass and heat transport presume a good flow equipartition in the channels. In mesh reactors the mesh open area determines the interfacial area. Mass transfer coefficients  $k_L^* a$  from 3 to  $8 \text{ L s}^{-1}$  and higher values in catalytic systems can be achieved [25].

**Advantages** One advantage of this contacting concept is the facile phase separation, as the phases are never intermixed. The greatest benefit is the fact that the defined geometry of the phase flow regions assure a well-defined known interface, whereas the second type (Type B) features an interface size distribution since bubble or droplet size can never be equal over all fluid particles. The single-phase distribution, as it is achieved easily compared with the multiphase distribution, is another advantage of this type. This last point also facilitates the internal numbering-up concept, where many microchannels are located parallel in order to feed the reactor with higher throughput.

**Disadvantages** Nevertheless, one major disadvantage concerns the realization of phase separation along the complete apparatus. Therefore, to prevent phase intermixing, special measures have to be taken, with the consequence of a higher technical expenditure of the reactor.

### 3.3.2.2 Disperse–Continuous Phase (Type B)

These reactors normally consist of a microchannel or even a larger sized tube, where both phases stream in the form of a multiphase flow in the same encasing.

**Momentum transport** The flow patterns mainly depend on the velocities of both phases, the surface tension (liquid, gas and reaction plate material properties) and on the channel dimensions (width, depth, length, diameter, etc.). We encounter the following parameters:

- $Ca$  (capillary number) =  $(\mu U)/\gamma \approx 10^{-3}$
- $Re$  (Reynolds number) =  $(\rho d U)/\mu \approx 10^{-3}$
- $Fr$  (Froude number; only for vertical arrangements)
- $We$  (Weber number) =  $(\mu d U^2)/\gamma \approx 10^{-6}$
- $Bo$  (Bond number) =  $(\rho g d^2)/\gamma \approx 10^{-4}$
- $Bo^*$  (Bodenstein number):  $Pe_{ax} = Bo^*(d/L) = (Ud)/D_{ax} \approx 2-7$  (depending on  $Pe' = ReSc$ ).

**Heat and Mass Transfer** The flow pattern, that is to say the fluid particle shape and dimensions, and the film thickness play a dominant role concerning these transport phenomena due to their importance for the determination of the size of the interfacial area. In bubbly and foam flow it can be characterized by the interfacial

area depending on the Weber number, which contains the gas velocity. Hence generally increasing the gas velocity means an increase in the interfacial area while the residence time decreases. For the highest conversion an optimal combination between then two variables has to be found. Marangoni effects may occur in presence of trace impurities and may have an influence. Mass transfer coefficients  $k_L \cdot a$  from 0.04 to 0.3 L s<sup>-1</sup> and from 3 to 15 L s<sup>-1</sup> in catalytic systems can be achieved [25–30].

**Advantages** One major advantage of this type is related to the relatively low technical expenditure for the phase dispersion.

**Disadvantages** Since flow patterns are not well known for these new systems, they will be identified, documented and furthermore controlled. A slight disadvantage is the phase separation as the phases are totally intermixed. Another weak aspect concerns the particle size distribution, which can be rather broad, and the fact that mixed flow patterns may occur. Consequently, the engagement of the exchange area is definitely complicated and intricate. In microchannels even drying-out phenomena may occur, which is attributed to the maldistribution of the phases in the encasings. The equidistribution of the phases presents one of the greatest challenges for engineers in device development fields for both types. The internal numbering-up concept is undoubtedly more complicated to realize for this type than for Type A.

### 3.3.3

#### Criteria for Reactor Selection

The detailed knowledge of the fluid system and the kinetics of the reaction which will be performed constitute the precondition for the selection of the appropriate microreactor. The criteria for the selection and the diverse parameters depend strongly on this knowledge. The following parameters have to be identified and embraced.

##### 3.3.3.1 Process Parameters (Temperature, Pressure, Throughput)

The throughput mainly substantiates the choice of the microreactor and the surrounding plant equipment. Nevertheless, microreactors with gas-liquid contacting are only available on the laboratory- or pilot-scale, but recent research projects have focused on the development of production-scale reactors. The process temperature and pressure are other criteria for the selection which can be identified and lead directly to the material choice of the reactor. Due to the high corrosion probability in chemical reactions, it is sometimes convenient to choose ceramic or glass reactors in place of metallic reactors, in spite of the high ductility of metals. Microreactors made of highly alloyed steels or metals are associated with relative higher costs, but are more reliable when operating with high pressures or temperatures. On the basis of the lower material mass of microreactors, the costs of highly alloyed metals do not constitute issues compared with conventional apparatus technology. Partial currents, temperature and pressure in microstructures are part of an appropriate information system which in many cases are not available since sensors cannot be integrated in

the devices [31]. For the purpose of the identification of overheating in the presence of an explosive regime in compressible flows with chemical reactions, such sensors would be very useful for the measurement of temperature [32].

#### 3.3.3.2 Reaction and Fluid Properties

The fluid properties and the type of reaction determine the mass transfer resistance and in consequence the regime in which the process is recommended to be accomplished. A good alternative between the bubble or droplet regime is the continuous flow regime, where both phases remain continuous, in order to constitute a large interfacial area and a lower pressure drop. Generally, in single-phase flow the pressure drop is lower than in multi-phase flow (e.g. Jasmin effect). Increasing the amount of bubbles per unit channel length results in an increase in the pressure drop. The residence time is important to consider with respect to the kinetics of the desired reaction, which should be carried out in a microstructured device. Although there are fluids which show the same behavior on the microscale as on the macroscale, the size and choice of the microstructure play a dominant role for different fluids. In contrast to the macroscale, capillary forces, pressure drop and fouling have to be dealt with. In the case that the driving power of the fluid is low and the microstructure is very small, capillary forces can involve problems. Choosing a microreactor with higher structure dimensions may diminish these problems and pressure drop issues. When dealing with some fluids, fouling may occur and further this leads to clogging of the microstructure. This happens when a fluid is moving at insufficient speed, and sedimentation of particles is the consequence, mostly found in dead volumes, narrow bends and holes. The handler can use filters upstream of the device, before or at least after the pump, or may modify the surface with protective layers or integrate mechanical energy (ultrasound, pulsed flow, etc.). Regarding fouling, users have to consider choosing reactors where cold or hot spots can be barred for this application. The knowledge of the whole kinetic reaction process, as said before, constitutes a precondition in order to prevent overheating. The use of sensors can deliver data from the inside of the process, so that the design can be trimmed to fit the process demands and avoid “hot spots”.

#### 3.3.3.3 Reactor Material

The availability of the materials for microreactors ranges from metals to glass and ceramics, silicon and others. Basically, the material choice depends on the chemical reaction and the mixtures of fluid substances. The following three properties have to be taken into account.

**Temperature and Pressure** As in conventional apparatus technology, the calculation of the temperature and pressure resistance can be leaned against the existing norms and directives as the Pressure Equipment Directive (PED) 97/23/EG or AD-2000 Regelwerk, although microreactors typically are exempt from these directives because of their small active volumes. This is due to the absence of guidelines for the construction and installation of such devices. However, if technically relevant throughputs, as on the production scale, for instance, are to be obtained, the hold-up (active

volume) is of such an order that the rules apply. Some approaches for microreactor norms are just being framed, even though the demand on research methods in micro process engineering still remains very high. Typical temperature resistance limits can be specified: polymers, such as PEEK, resist temperatures up to 300 °C and applications in ceramic reactors could be accomplished at temperatures up to 800–1000 °C. Depending on the alloy, metallic microreactors resist temperatures up to 1500 °C; however, the maximum process temperature is usually constrained by the gasket material. Glass (FOTURAN) shows good heat resistance up to 750 °C [31]. Pressures up to 15 bar and temperatures up to 200 °C are the common process limits for glasses. Together with their good chemical, optical and electrical properties, glass and ceramic microreactors are suitable for a huge variety of chemical applications.

**Corrosion** One major difference between the macro- and microscales is the corrosion behavior. A device material suitable for the macroscale might not be applicable for the microscale. Even if the corrosiveness of the fluids has not changed, the rate may be too high for microdevices. Corrosion rates for conventional apparatus, concerning macroscopic vessels, tubes and fittings with dimensions greater than 1 mm, range from 0.1 mm yr<sup>-1</sup> (resistant) to >3.0 mm yr<sup>-1</sup>. In contrast, microstructures often do not exceed 100 μm. Consequently, these rates do not hold any longer. Furthermore, no regulations have been established by private or public institutions which deal with proper “micro corrosion rates”. In order to prevent damage, the handler should choose a reactor material that is definitely resistant, as a first approximation, followed by careful experiments with the expected conditions that have to be undertaken.

**Flow and Transport Performance** The material of the reaction plate and the surface integrity have a large impact on the performance of the flow by means of the interfacial tension (triple line). In consequence, liquids act differently when choosing different reactor plates. Hydrophilic channel materials are surfaced-oxidized silicon, silicon compounds and stainless steel. Channels made of polymers or nickel are wetted in a hydrophobic way. The wetting characteristics play a dominant role in emulsification technology. Thus, an appropriate combination of channel material, liquid phase and surfactants has to be selected to optimize the transport processes. It might be mandatory to insulate the reaction plate or the whole reactor thermally or electrically. In the extreme case, the complete device has to be decoupled from the rest of the process equipment to achieve the correct performance. In particular for the thermal behavior, the correct material is essential. For longer connecting tubes or residence time modules, a heat bath is recommended to guarantee a constant temperature. Electrical insulation gains importance when using explosive mixtures or disturbances of integrated sensors. Electrokinetic flow or electro-osmosis applications make several demands on the material.

#### 3.3.3.4 Affordability, Reliability and Sustainability

Reliability embraces fouling and safety of microreactors. Fouling is referred to in the section above. The latter term encompasses safety against overpressure, overheating

and detonation. Another section above dealt with pressure and temperature matters. Detonation safety is one of the most delicate aspects in micro process engineering. In microstructures, the dimensions normally are below the extinction length or quench distance of many fast reactions, which is about 1 mm. The mechanisms are thermal quenching by the wall heat conduction and quenching of the radicals by kinetic effects where the mean free path  $\lambda$  of the molecules does not exceed the channel dimensions. It has been reported [32] that coupled heat and mass transfer and the reaction kinetics are a self-organized system that exhibits flame length and periodicity. The Maximum Experimental Safe Gap (MESG), for instance, in microstructures is a fluid system property and should be investigated for the application and other safety aspects such as explosion limits, extinction clearances for flames and maximum oxygen concentration. Concerning the thermal stability, users have to ensure that the temperature of the process in the chosen microreactor does not exceed the onset temperature and that the energy required for decomposition can never be reached. Concerning the affordability, safety, simplicity and maintainability, well-defined geometries with respect to fouling and handling should be taken into account when choosing microreactors. Users have to get a clear picture of the benefit and the favored added value of the upgraded system. Sustainability aspects of the whole microreactor and plant must always be considered.

#### 3.3.3.5 Ability for Scale-up or Scale-out

Scaling-up dispersed-phase systems is more complicated than it is for continuous-phase systems. This is due to the interfacial forces which let the phases coalesce rapidly. Generally, when the characteristic size of a system decreases, the surface tension, described by  $Ca$  (capillary number),  $Bo$  (Bond number) and  $We$  (Weber number), becomes more important. The maintenance of perfect equipartition of the liquid phase has to be taken into consideration when increasing the characteristic length. Manifold channels have to be of a large diameter compared with the diameter of the reaction channels, so that the pressure drop across the reaction channels is significantly higher than in the manifold channels. For both systems the equaling-up concept (scale-out), which is the multiplication of the channel or reaction plates, can be accomplished if a phase supply system is developed which ensures good equipartition.

#### 3.3.4

#### Microreactors for Gas–Liquid Contacting

Tables 3.2 and 3.3 summarize microreactors from the literature and purchasable ones ordered by the classification introduced above (see Section 3.3.2). There are additional comments to the reactors to give an idea of the mode of operation.

In Table 3.4, a compilation of gas–liquid reactions from the literature that were carried out in different microstructured reactors is presented. This table not only shows which reactions were carried out in which reactors, but also whether these reactions have been successful or not.

**Table 3.2** Purchasable microreactors for gas/liquid contacting.

Microreactor	Company	Comment
<i>Continuous gas/continuous liquid-phase contactors (Type A)</i>		
Falling Film Microreactor (FFMR) A thin film is created by a liquid feed flowing down a microstructured vertical plate driven by gravitational force. The microstructure guarantees a stable film at low flow rates	IMM          Mikroglas Velocys	It contains a reaction plate of stainless steel which generates the very thin liquid film and a structured heat exchanger copper plate, housed in a stainless-steel enclosure. The structures on both plates are parallel microchannels. The liquid enters the microchannel device via a large bore that is connected to a microchannel plate via a slit. The slit serves for equipartition of the many parallel streams, which are collected again via another slit at the bottom of the plate, leaving the device by a bore afterwards. The gas enters a large gas chamber, positioned above the channel section, via a bore and a diffuser and leaves via the same type of conduit. A co-flow and counter-flow guidance is possible. It can be equipped with an inspection window, which allows a visual check of the quality of the film formation and identification of flow maldistribution. Hence photochemical gas-liquid contacting can be performed
<i>Continuous liquid/disperse gas-phase contactors (Type B)</i>		
Slug and annular patterns, bubbly flows and foams		
One of the simplest systems to generate multiphase flows is to use micromixers, followed by a tube for the multiphase stream. The diameter of the reaction channel downstream of the mixing section is sufficiently large that the small bubbles, generated in the mixing section, pack together in the reaction channel resulting in foam flows. In principle, any type of liquid-liquid mixer can be applied for gas-liquid mixing also, which has already been accomplished by different researchers at IMM and Microinnova Eng. GmbH, Interdigital micromixers, Star Laminator, other micromixers		

(Continued)

Table 3.2 (Continued)

Microreactor	Company	Comment
Microbubble column	IMM	Bubbles are guided in microchannels through a continuous liquid medium. Slug flow pattern and Taylor bubbles (large range of stability), bubbly flow (limited stability) and spray flow and annular flow patterns can be observed in microbubble columns. The microbubble column consists of a four-piece housing. Two main pieces carry the mixing unit, which comprises an interdigital feed structure with very different hydraulic diameters for the gas and liquid feed and the channel plate. Separate gas and liquid films enter in one reaction microchannel each, which is on a separate reaction plate. This generates a specific flow pattern, depending on the gas and liquid velocities. The microchannel plate can be encompassed by one or two heat exchanger plates for cooling or heating

#### *Catalytic gas–liquid–solid microreactors*

For catalytic reactions many multiphase microreactors contain catalysts coated on walls, incorporated in thin nonporous films or in packed beds

Catalytic falling film microreactor	IMM	The catalysts are incorporated as thin porous films or as particles on alumina-coated plates
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### 3.4

#### Catalytic Gas-phase Reactions

##### 3.4.1

##### Introductory Remarks

Catalytic gas-phase reactions represent the most investigated type of reaction in microstructured devices. Several gas-phase reactions have been carried out in microreactors so far, for instance oxidations, hydrogenations, dehydrogenations and halogenations.

This section starts with a classification of phase-contacting principles according to the type of catalytic bed. Advantages and disadvantages of the reactor types are explained, followed by a discussion of criteria for reactor selection and an overview of purchasable microreactors for catalytic gas-phase reactions.



**Table 3.3** Non-purchasable microreactors for gas–liquid contacting.

Type	Comments
<i>Continuous gas/continuous liquid-phase contactors (Type A)</i>	
(Partly) overlapping-channel microreactor [33–35]	There are two immiscible phases each flowing in separate adjacent micro channels, only having a small, stable fluid interface. This flow configuration is accomplished with one microchannel each in two plates which are connected to a reactor sandwich. The position of these channels is such that their open channel sides do not completely overlap, but are displayed to result in partial overlap, covering more of the open area than releasing it as conduit. A numbering-up concept was developed successfully with 120 parallel micro channels also
Mesh microreactor [36, 37]	A mesh structure is implemented to separate the planar chambers which contain two fluids. The mesh has a large open interface area, while the mesh to wall distances can be set to 80–140 $\mu\text{m}$ , so that the volumes of the chambers are about 100 $\mu\text{L}$ . The cavities have a width of 1–10 $\mu\text{m}$ and a length to width ratio of 1:1. This design allows high volumetric mass transfer stabilizing the gas/liquid interface of about 2000 $\text{m}^2 \text{m}^{-3}$ referred to the liquid
<i>Continuous liquid/disperse gas-phase contactors (Type B)</i>	
<b>Slug and annular patterns, bubbly flows and foams</b>	
Segmented (Taylor) flow reactor [38–41]	In the simplest form, the gas and liquid phases are merged into each other in a single channel. Although a variety of flow patterns can be generated, the segmented or Taylor bubble pattern is mostly preferred. These reactors have many similarities with the catalytic monolith reactors
Dual-microchannel chip reactor [42, 43]	This consists of two parallel microchannels which are separated by a wall. In front of the channel section a hole is located for the liquid feed which is followed by two holes for the gas feed
Single-/three-channel thin-film microreactor [44, 45]	The reactor, which was initially made as a single-microchannel version and later as numbered-up three-microchannel version, was developed specially for fluorination reactions
Modular multi-plate stack reactor [46–48]	This modular reactor concept was developed for flexibility, ease of handling and fast change of parameters. It contains five assembly groups, which are microstructured platelets, a cylindrical inner housing, two diffusers and a cylindrical outer shell with a flange. The reactor module can be equipped with a fixed-bed catalyst or with a stack of microstructured wafers

*(Continued)*

Table 3.3 (Continued)

Type	Comments
Microchannel reactor in disk housing [49]	A pair of iron plates coated with Pd catalysts is inserted in disk-type holders
Photochemical single-channel chip microreactor [50]	A liquid inlet port splits into two liquid streams, which are merged with a third channel. The latter is connected to a second port for gas feed, in such way that the two liquid streams encompass the gas stream. This section is followed by a serpentine channel passage, which ends in a third outlet port. The channel material is made of glass
Fork-like chip micromixer – tube reactor and other micromixers	This split–recombine type of reactor has fork-like segments which are machined on a silicon plate by micromachining. As in other micromixers, this mixing unit is connected to conventional tube for residence time enhancement reasons
<i>Catalytic gas–liquid–solid microreactors</i>	
Multiphase packed-bed or trickle-bed microreactor [29, 30]	Standard porous catalysts are incorporated in silicon–glass microfabricated reactors consisting of a microfluidic distribution manifold, a single microchannel reactor or a microchannel array and a 25- $\mu\text{m}$ microfilter. The fluid streams come into contact via a series of interleaved high aspect ratio inlet channels. Perpendicular to these channels, a 400- $\mu\text{m}$ wide channel is used to deliver catalysts as a slurry to the reaction channel and contains two ports to allow cross-flow of the slurry. High maldistribution, pressure drop and large heat losses may occur
Wall-coated microchannel reactor [48, 51]	A reactor which incorporates either a conventional packed bed or a stack of microstructured wafers with Pd catalysts is used

### 3.4.2

#### Classification of Microreactors – Phase-contacting Principles

Several principles have been developed for contacting gas and catalyst in microreactors. They are based on the form of the catalyst, so the classification of phase-contacting principles here is made according to the type of catalytic bed. A schematic overview of the principles is shown in Figure 3.4.

##### 3.4.2.1 Packed-bed Microreactors

Packed-bed microreactors are prepared by filling catalyst powder into the microchannels of the reactor. Since this is the easiest and fastest way for the incorporation of the catalyst, this type of microreactor is frequently used for catalyst screening [82]. Another advantage over other types of catalytic beds is the possibility of using

traditional and optimized catalysts [83]. However, there are also some drawbacks of packed-bed microreactors. The pressure drop is fairly high compared with catalytic wall and catalytic bed microreactors. In addition, it is necessary to apply the catalyst evenly to every reactor channel to avoid maldistribution, which, in turn, has a strong influence on product yield and selectivity. Particularly in the case of small gas flows, temperature gradients can occur, which cause hot spots in the catalytic bed [84]. Although these effects can be reduced to an approximately isothermal operation of the microreactor, the drawbacks of the high pressure drop and wide residence time distribution have to be considered anyway.

#### 3.4.2.2 Catalytic Wall Microreactors

This type of microreactor was developed in order to avoid the high pressure drops that occur in packed-bed reactors. The catalyst is deposited on the reactor wall by several techniques. This offers the advantage of low pressure drop and temperature gradients which leads to the absence of transport limitations [85]. As the geometric surface of the microchannels is not sufficient to perform catalytic reactions, several steps are necessary to enhance the specific surface area, for instance by chemical treatment or deposition of porous catalyst supports [86]. These treatments are often complex and time consuming and therefore they represent the prime disadvantage of this contacting principle. Nevertheless, this type of microreactor is currently the most commonly used for catalyst testing and for the production of chemicals by gas-phase reactions.

#### 3.4.2.3 Catalytic Bed Microreactors

To combine the advantages of packed-bed and catalytic wall microreactors, catalytic bed microreactors were proposed recently. In this novel reactor design, the catalyst is applied on metallic filaments or wires which are incorporated in a microreactor, leading to a low pressure drop and a narrow residence time distribution [87–89]. By insertion of metallic wires a uniform gas distribution and a reduced risk of temperature gradients is obtained. However, similarly to catalytic wall microreactors, an increase in the specific surface area of the grid or wire is required. In addition to metallic wires and grids, modified ceramic tapes can also be used as a catalyst support [90].

### 3.4.3

#### Criteria for Reactor Selection

Several parameters have to be considered when choosing a microreactor, mainly depending on the reaction which is to be performed. Information about the reaction conditions such as temperature or pressure is fundamental, in addition to the required chemical resistance of the reactor material. The selection of a microreactor for a given problem also includes considerations about the desired handling and performance of the reactor. For instance, in the case of catalyst testing, the deposition and incorporation of the catalyst should be easy and time saving, since only the performance of different catalysts is compared. For the optimization of a gas–solid reaction, different features, such as optimal distribution of the catalyst material, are needed.

Table 3.4 Compilation of gas-liquid reactions that have been carried out in different microreactors

Application	Microreactors									
	FFMR <sup>1</sup>	FFMR <sup>2</sup>	MBC <sup>1</sup>	MCR	SCR	PBMR	MMR	MM		
Fluorination	(a)		+ [52, 53]	+ [44, 45, 54]						
	(b)		+ [52, 53, 55]	+ [43, 56, 57]						
	(c)			o [58, 59]						
Oxidation	(d)			+ [60]						
	(e)		+ [61]		+ [50]					
	(f)					+ [62]				
Chlorination	(g)		o [63]							
	(h)		+ [63-65]							
	(i)		+ [66]							
Sulfonation	(j)		+ [67]							
	(k)			- [49]						
	(l)		+ [67, 68]							
Hydrogenation	(m)			+ [69]		+ [29, 30]				
	(n)		o [70, 71]	+ [48, 72]						
	(o)					o [62]	o [36, 37]	+ [73-77]		
Special application	(p)							+ [64]		
	(q)		+ [64]	o [33]				+ [64]		
	(r)							+ [78, 79]		
	(s)									
	(t)		o [29]							
	(u)				+ [80]					
	(v)					+ [81]				

**Evaluation:**

+, Microreactor is recommended for this application

o, Experiments performed with indifferent conclusions or no experiments yet

–, No recommendation




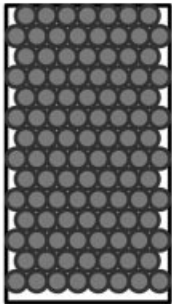
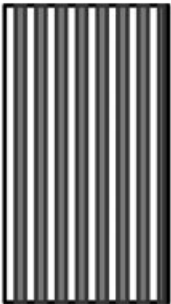
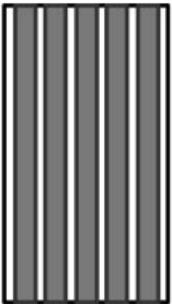
**Purchaser:**

<sup>1</sup>Institut für Mikrotechnik Mainz, <sup>2</sup>Mikroglas Chemtech GmbH

**Applications:**

Direct fluorination of aliphatics and non-C moieties  
 Direct fluorination of benzenoid aromatics  
 Direct fluorination of heterocyclic aromatics  
 Oxidations of alcohols, diols and ketones with fluorine  
 Photo-oxidation of  $\alpha$ -terpinene and cyclopentadiene  
 Oxidation of benzyl alcohol to benzaldehyde  
 Homogeneously catalyzed oxidation of butyraldehyde  
 Oxidation of sulfite to sulfate  
 Photochlorination of aromatic isocyanates  
 Monochlorination of acetic acid (chlorination of  $\alpha$ -keto compounds)  
 Dechlorination of *p*-chlorophenol to phenol  
 Sulfonation of toluene  
 Cyclohexene hydrogenation (over Pt/Al<sub>2</sub>O<sub>3</sub>), dehydrogenation  
 Hydrogenation of *p*-nitrotoluene and nitrobenzene over Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub>  
 Heterogeneous hydrogenation of  $\alpha$ -methylstyrene  
 Asymmetric hydrogenation of cinnamic acid derivatives  
 Carbon dioxide absorption (acid–base reaction between carbon dioxide and sodium hydroxide)  
 Ammonia absorption (acid–base reaction between ammonia and Brønsted inorganic acids)  
 Particle synthesis with segmented gas–liquid flow  
 H<sub>2</sub>O<sub>2</sub> evaporation  
 Direct formation of H<sub>2</sub>O<sub>2</sub>  
 Methanol reforming

**Type of reactor:**  
 FFMR, falling film microreactor  
 PBMR, packed-bed microreactor  
 MM, micromixer  
 MBC, microbubble column  
 MMR, microstructured mesh reactor  
 SCR, single-channel reactor  
 MCR, multiple-channel reactor (dual channel, triple channel, ...)

	Packed bed	Catalytic wall	Catalytic bed
Top view			
Front view			
Advantages	-Catalyst incorporation -Residence time	-Pressure drop - no transport limitations	-Pressure drop - Residence time distribution
Dis-advantages	- Pressure drop - Residence time distribution	- Specific surface area - Catalyst deposition	- Specific surface area - Catalyst deposition

**Figure 3.4** Schematic view of the phase-contacting principles including the main advantages and disadvantages.

#### 3.4.3.1 Reactor Material

Purchasable microreactors are limited in their temperature and pressure resistance, depending mainly on the reactor material used and the fabrication of the reactor. Most metallic microreactors operate at a maximum temperature of 500 °C, whereas ceramic microreactors offer temperature resistance up to 1100 °C at ambient pressure and high chemical resistance. Metallic microreactors, in contrast, can withstand higher pressures generally. Further, it has to be considered whether the reactor material has any influence on the performance of the reaction, for instance unwanted catalytic activity. Normally most metallic microreactors can be provided in several materials.

#### 3.4.3.2 Control of Critical Parameters

Performance and optimization of reactions in microstructured devices requires information about the conditions inside the reactor, such as temperature and pressure. Therefore microreactor choice is also dependent on the data needed since sensors cannot be integrated in any device [91]. For reactions carried out near or in the explosive regime, the incorporation of a temperature sensor would be reasonable for rapid identification of overheating [83]. Additional knowledge, especially when reactions are optimized, of the situation inside the reactor may be useful for the explanation of the variable product selectivity and yield.

### 3.4.3.3 Pressure Drop

The pressure drop depends mainly of the type of catalytic bed, as described above. The highest pressure drops usually occur in packed-bed microreactors with axial flow design. A reduced pressure drop while maintaining catalytic area can be achieved by a cross-flow design packed-bed microreactor [82]. To keep pressure drops down, the use of catalytic wall and catalytic bed microreactors is recommended.

### 3.4.3.4 Reactor Handling

Metallic microreactors can usually be opened and closed easily by bolts. Thereby the reactor can withstand pressures up to 100 bar, which is advantageous compared with ceramic microreactors. Ceramic microreactors for catalyst screening also are not sealed permanently. They can be closed by pressing a plate on to the reactor housing. Sealing can be achieved by grinding and polishing of the surfaces. Ceramic microreactors for gas-phase reactions can be closed by ceramic clamps, which press the lid on to the housing. A drawback to consider here is that ceramic microreactors cannot be operated at pressures exceeding 1 bar due to the closing technique of the reactors [92].

### 3.4.3.5 Residence Time

This criterion is important to consider with respect to the kinetics of the desired reaction. Slow reactions require longer residence times in the reactor and not every reactor provides the same contact time of the gaseous educts with the catalyst. Packed-bed microreactors offer the longest residence times, since the gaseous molecules have to pass through a region of closely packed catalyst particles. Unfortunately, this also negatively effects the residence time distribution.

### 3.4.3.6 Catalyst Deposition and Characterization

Several methods for the incorporation of catalysts into microreactors exist, which differ in the phase-contacting principle. The easiest way is to fill in the catalyst and create a packed-bed microreactor. If catalytic bed or catalytic wall microreactors are used, several techniques for catalyst deposition are possible. These techniques are divided into the following parts. For catalysts based on oxide supports, pretreatment of the substrate by anodic or thermal oxidation [93, 94] and chemical treatment is necessary. Subsequently, coating methods based on a liquid phase such as a suspension, sol-gel [95], hybrid techniques between suspension and sol-gel [96], impregnation and electrochemical deposition methods can be used for catalyst deposition [97], in addition to chemical or physical vapor deposition [98] and flame spray deposition techniques [99]. A further method is the synthesis of zeolites on microstructures [100, 101]. Catalysts based on a carbon support can be deposited either on ceramic or on metallic surfaces, whereas carbon supports on metals have been little investigated so far [102].

Depending on the material of the microreactor, different methods of catalyst deposition are feasible. Most of the mentioned techniques are possible for metallic microreactors; especially sol-gel synthesis is very commonly used as a coating method. By the use of ceramic microreactors, several pretreatments such as anodic oxidation cannot be carried out; in turn the deposition of carbon supports has been

well investigated compared with metallic reactors. Further, the suspension method is widely used for ceramic microreactors [103], which also offers the possibility of using commercially available catalysts. Another factor to consider is the assembling of the reactor. Some catalyst deposition methods can be applied to preassembled microreactors by pipetting the liquid catalyst into the microreactor and removing excessive catalyst with air. Anodic oxidation of assembled microreactors is also possible by the use of a suitable electrode arrangement. However, compared with packed-bed microreactors, where commonly available catalysts can be used, catalyst deposition for catalytic wall and catalytic bed microreactors is more complicated and time consuming in any case. This has to be considered in the reactor selection.

Catalysts which are deposited on microchannels before assembling the reactor can be easily characterized by different methods [104, 105]. One important factor is the specific surface area of the catalyst, which is determined by nitrogen sorption and BET methods. X-ray diffraction measurements, scanning electron microscopy and secondary ion mass spectrometry are further methods used for catalyst characterization [106].

#### 3.4.4

##### **Purchasable Microreactors**

IMM provides two reactors for catalyst screening. The catalyst testing microreactor contains 10 microstructured plates made out of stainless steel, which can be coated on demand with various catalysts. Every plate is fed simultaneously by a sub-stream and the reactor can be operated serially or in parallel. The pressure stability of this reactor is 20 bar (100 bar at 400 °C) and a maximum temperature of 800 °C is possible. Microchannel plates with different channel geometries with specific surface areas around  $7300 \text{ m}^2 \text{ m}^{-3}$  are offered by IMM.

Another reactor for fast catalyst testing is a modular microstructured device with up to 10 catalysts applied on titer plates. An advantage of this reactor is the composition of various modules such as flow distribution, reaction heat exchange and gas sampling, which can be interconnected in different ways. The reactor can be operated at maximum pressure and temperature of 30 bar and 600 °C in the reaction module, and flow rates up to  $10 \text{ mL min}^{-1}$  are possible. Catalyst deposition can be carried out very rapidly by a sputtering method or by washcoating, which has already been tested for the oxidation of methane [107, 108].

Reactors for the performance of gas-phase reactions manufactured by IMM are the gas-phase microreactor, a gas-phase microreactor including a mixing unit and a catalyst microburner.

The gas-phase microreactor can be used on the laboratory scale under maximum conditions of 3 bar and 500 °C. It is made up of a stack of stainless-steel microstructured plates that are arranged for counter-flow or co-current flow practice. Already tested applications of this reactor include the dehydration of 2-propanol [109].

A gas-phase microreactor with an included mixing unit is also offered by IMM, especially for the performance of reactions in the explosive regime. It consists of two recesses, each filled with a stack of microstructured platelets for premixing of gases



and reaction. Reaction conditions up to 50 bar (at 500 °C) and 600 °C have already been tested successfully. The catalyst plates provide a specific surface area of  $12\,700\text{ m}^2\text{ m}^{-3}$ . The reactor has been applied to, for example, the preparation of ethylene oxide [110].

The catalyst microburner is usable for testing all kinds of heterogeneous gas-phase reactions and offers the advantage of higher flow rates compared with the reactors above. External heating is effected by heating cartridges to a maximum operating temperature of 550 °C and pressure up to 5 bar.

A purchasable cross-flow heat exchanger for application in laboratory-, pilot- and production-scale plants was developed by FZK. By incorporation of a catalyst on the quadratic plates inside the heat exchanger, it can also be used as a catalytic wall reactor. Operating conditions up to 850 °C (stainless steel) and pressures of more than 100 bar are possible, and the specific inner surface area is up to  $30\,000\text{ m}^2\text{ m}^{-3}$ . The reactors can be obtained in many materials and three different sizes with a maximum flow of  $6500\text{ kg h}^{-1}$  (water). Therefore, the reactors can be adjusted for various processes, and all types of catalyst deposition techniques are possible [111]. This reactor has already been applied to the catalytic oxidation of  $\text{H}_2$  by Janicke *et al.* [112], for example.

Ceramic catalytic wall microreactors, made out of aluminum oxide, were developed by FZK. Their advantage is a high temperature resistance up to 1100 °C at ambient pressure high chemical resistance under corrosive conditions. These devices are mainly used for catalyst screening and process intensification since the modular assembly allows rapid adaptation to different fields of application. Temperature sensors can be integrated into the reactor to measure the catalyst temperature. Catalysts can be deposited by several techniques, for instance wet impregnation. Amongst others, the reactor was tested for oxidative methane coupling and partial oxidation of isoprene [92, 113].

Ehrfeld provides a cartridge reactor, including a heatable cartridge for the incorporation of a packed-bed catalyst filling and a temperature sensor. Characteristic fields of application are heterogeneously catalyzed gas-phase reactions up to temperatures of 200 °C and pressures around 30 bar (at 25 °C). The standard material is stainless steel; further materials can be supplied on request [114].

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