3
Gas-phase Reactions

Gas-phase reactions, together with single-liquid-phase organic reactions, nowadays belong to the most frequently investigated processes in microstructured reactors. This is not only due to the economic and scientific impact of the corresponding investigations, it is also due to the good suitability of gas-phase reactions, from a process engineering point of view, to be carried out in micro reactors.

Wörz et al. [1] give a definition of processes suitable for micro reactors. Investigation of such processes is supposed to be advantageous that combine high reaction rates with large heat release, in particular when involving multiple phases. The first aspect holds for many gas-phase reactions, e.g., for some total or partial oxidations, proceeding in the millisecond regime at elevated temperatures. Concerning the second issue raised by Wörz et al., this also applies to most gas-phase reactions; usually they are carried out with catalyst contact, and hence involve two phases (gas/solid). Accordingly, since all criteria are fulfilled, gas-phase reactions seem to be particularly suited for chemical micro processing.

There is an additional point to be made about this type of processing. Many gas-phase processes are carried out in a continuous-flow manner on the macro scale, as industrial or laboratory-scale processes. Hence already the conventional processes resemble the flow sheets of micro-reactor processing, i.e. there is similarity between macro and micro processing. This is a fundamental difference from most liquid-phase reactions that are performed typically batch-wise, e.g. using stirred glass vessels in the laboratory or stirred steel tanks in industrial pilot or production plants.

It is worth while to go into the latter discussion a bit further. While micro reactors and technical reactors have similar ways of processing, they have distinctly different sorts of catalyst implementation. Conventional reactors typically rely on catalyst beds, either of fixed type, e.g. formed by pellets, or of fluidized type, e.g. formed by fine, agitated powders. Thin film coatings on reactor walls, which are widely used in chemical micro processing, are seldom found with conventional processes (although a few exceptions are known). In micro reactors, washcoats, which have wide use in automobile exhaust gas treatment, are deposited on the micro channel wall and serve as carriers for catalysts which are inserted by wet-chemical post-treatment, e.g. by impregnation via precursor solutions. In turn, powder and grain beds in micro channels are not very favorable as high pressure drops result, the laminar flow pattern is changed in a way more difficult to de-

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Volker Hessel, Steffen Hardt, Holger Löwe

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scribe by simulation, and it is difficult to generate these materials in a reliable manner. Nevertheless, the indisputable advantage of powders and beds is that conventional catalysts, without the need for post-processing, may be analysed in that way on the micro scale. Indeed, micro processing with powders inserted in micro channels has been described a few times in the literature.

Considering the major importance of catalysts, especially for gas-phase reactions, a separate section was allocated to the description of techniques for catalyst layer formation in micro channels and the respective analytical characterization (see Section 3.1).

3.1 Catalyst Coating in Micro Channels: Techniques and Analytical Characterization

With the increasing quest for chemical micro processing research on catalyzed gas-phase reactions, both the catalysts themselves and their carriers have become the focus of scientific investigations – on their preparation, morphology, porosity, composition, etc.

Catalysts and their carriers are provided in micro channels by various means and in various geometric forms. In a simple variant, the catalyst itself constitutes the micro-reactor construction material without need for any carrier [2–4]. In this case, however, the catalyst surface area equals that of the reactor wall and hence is comparatively low. Accordingly, applications are typically restricted to either fast reactions or processing at low flow rates for slow reactions (to enhance the residence time).

Methods specifically made for or adapted to the needs of a micro channel's coating are available. For this reason, more and more recent reports are concerned with catalyst/carrier layers with typical depths of 1–50 µm. There are objective arguments in favor of catalyst coatings; a very large variety with regard to porosity, material, composition, mass, shape and (crystal) structure is thereby possible. A disadvantage of such coatings was, however, their non-uniform geometric cross-sectional and longitudinal shape. This is mainly the consequence of the dominance of surface forces on the micro scale which can lead to a significant difference in profiles before and after coating. For instance, coatings in rectangular micro channels tend to have a U-shape; those in semi-circular channels often have a V-shape (Figure 3.1) [5]. In the latter case, meanwhile, advanced compositions of the slurry solution have been identified by which U-shaped catalyst layers in semi-circular micro channels result, which is desired here owing to their uniform layer thickness [6].

The placement of catalysts/carriers in micro channels can be done by various means. In a conventionally oriented variant, catalyst powders or small grains are inserted as mini fixed beds [7]. However, more specific catalyst arrangements are also known, originally designed for novel ways of processing at the macro scale, such as catalyst filaments [8], wires [9] and membranes (Figure 3.2) [10, 11].

Among the non-traditional routes for formation of catalyst and catalyst/carrier coatings, the most prominent way is the washcoat route followed by wet impregna-

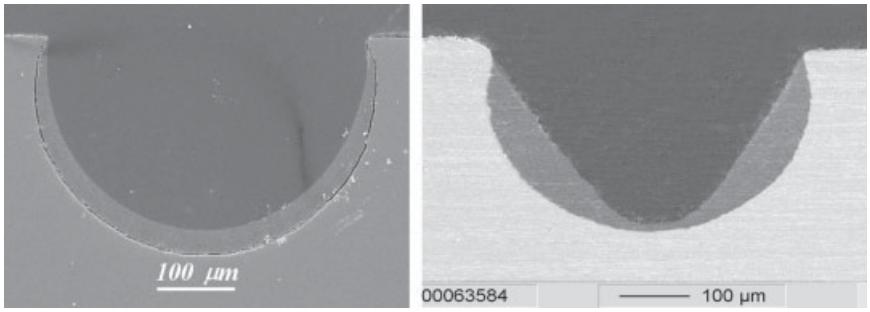

Figure 3.1 Cross section of micro channels coated with alumina washcoat exhibiting U- or V-shapes [6].

tion (see, e.g., [12–14]). Washcoats constitute an industrially accepted class of catalysts. Another class of industrially employed catalysts/carriers are created in micro reactors via the zeolite growth method [15–17]. Anodic oxidation is also widely used (see, e.g., [18]) to generate nano-porous oxide carrier layers, when aluminum reactors can be employed. Besides this, thin-film techniques such as CVD (see, e.g., [4]) and PVD, namely sputtering [11], serve for generating thin catalyst films. To complete this list of approaches towards catalyst and catalyst/carrier coatings, various other techniques have been tested, such as aerosol techniques [19], sol–gel techniques [20], an advanced plasma electrochemical process belonging to anodic spark deposition [21] and electrolysis [22].

Detailed descriptions of the procedures for the preparation of catalysts/carriers, for instance, have been given explicitly for washcoats (see, e.g., [5, 12, 14]) and for zeolite growth (see, e.g., [15–17]). For washcoats, a typical sequence of catalyst preparation steps is as follows (Figure 3.3) [6, 23]. The inlet and outlet chambers, encompassing the micro channel arrays on micro reactor plates, are protected with a thin polymer film. The suspension is deposited on the micro channel plate and the excess suspension is wiped off. Such a derived coating is dried at room temperature accompanied by shrinkage of the washcoat coating. Having cleaned the top parts of the micro channel fins, the dried washcoats are calcined typically at 500–600 °C to burn out the binder and to remove the protecting polymer film [12, 13]. Thereafter, the catalyst is brought into the washcoat by means of impregnation.

At present, very few comprehensive reports are devoted solely to catalyst/carrier coatings in micro channels, providing a deep insight in the subject and a detailed characterization of the coatings in terms of preparation, morphology, porosity, composition, etc. (see, e.g., [5]). However, an increasing number of reports concern the preparation of one sort of catalyst, e.g. for zeolites [15, 16, 24, 25]. The majority of these shorter reports provide also some basic characterization of the catalysts, with a focus on direct surface imaging, determining porosity and sometimes on cross-sectional profiles. In many further publications, SEM or other types of images of catalyst surfaces are found, most often before and from time to time after use [4,

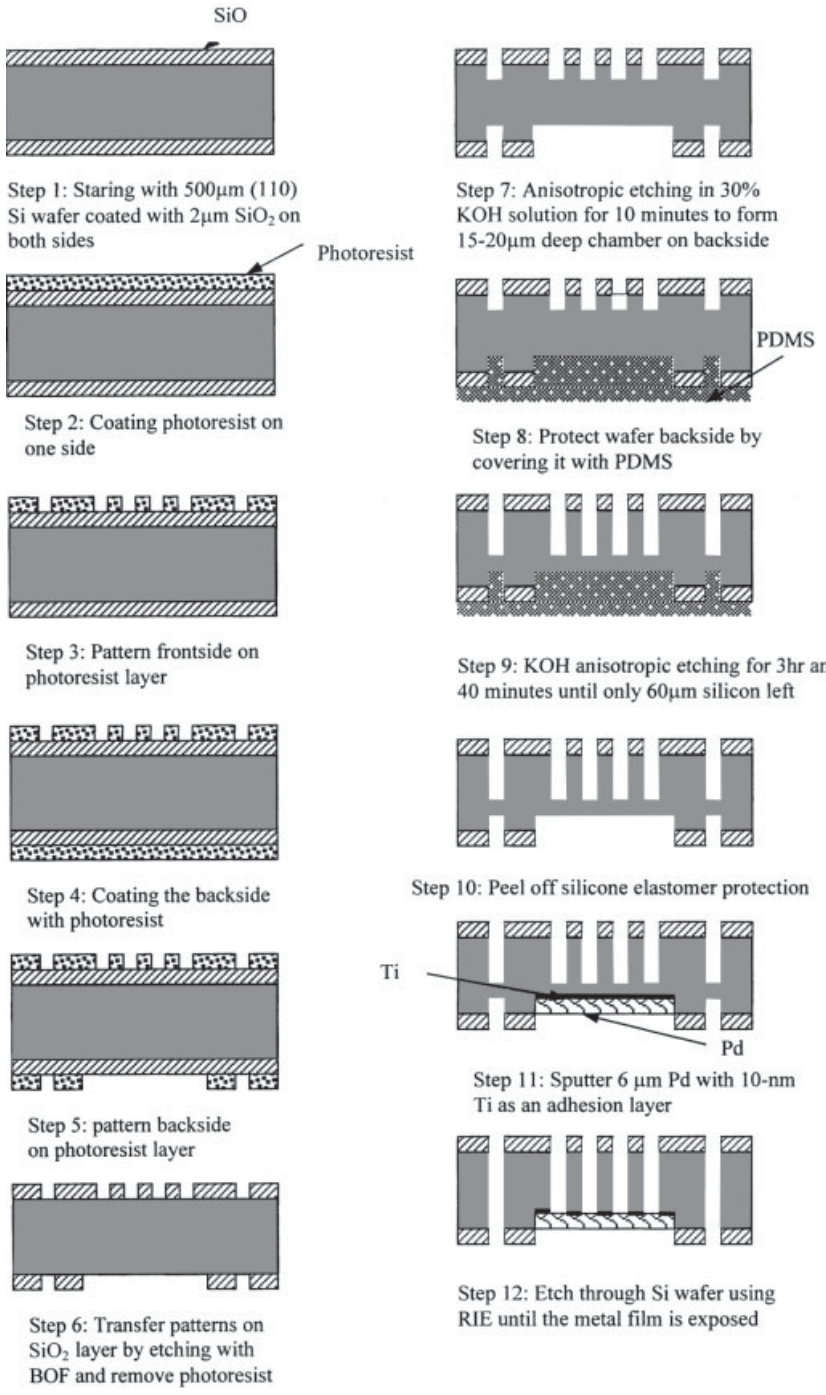

Figure 3.2 Flow chart for palladium membrane fabrication process [10].

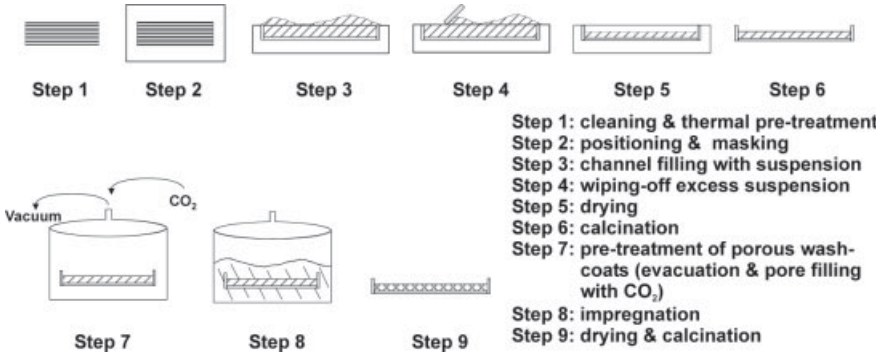

Figure 3.3 Typical preparation steps needed for preparing a washcoat layer in a micro channel [23].

26]. The few reports on surface and cross-sectional imaging often indicate that today's micro channel coatings have uneven profiles, in both semicircular and rectangular channels (see the discussion above). Further, the coating depth varies according to its position in the channel [19, 20, 27]. Recently, considerable progress has been made here [5]. Details on temperature profiles inside a catalyst under operation, another important feature, are rarely found, an exception being, e.g., the simulation of such profiles for an alumina layer [28].

3.2
Micro Reactors for Gas-phase Reactions

3.2.1
Housing-encased Single-platelet and Multi-platelet Stack Micro Reactors

One of the most frequently used micro reactor types relies on the use of microstructured platelets with multiple parallel channels, typically manufactured by methods other than routinely used for chip processing, encased in a housing [3, 4, 12, 13, 18, 28–39]. If more than one platelet is used, which is usually done to increase throughput, a stack-like arrangement is preferred for parallel feed. Such stacks are either welded directly from the outside [29, 30], are encompassed by a cover [3, 18, 31, 32, 37–39], have end caps with fluidic connectors [12, 13, 33] or are inserted into a recess of a housing, which is typically composed of two parts [4, 28, 34–36, 40–41].

Reversible sealing is achieved by seals, e.g. made of graphite or other materials, to achieve tightness between the plates and also between different functional fluidic elements on one plate [12, 13]. For achieving tightness in this way, compression of the housing is needed, usually done by screwing. In rare cases, specially polished surfaces are directly compressed without any seal. More often, the latter is used to seal stacks within a housing, omitting the individual seal between the platelets [4].

As an alternative to seals, irreversible bonding can be applied, e.g. by laser welding the surface of a microstructured stack [29, 30] or by diffusion bonding via vacuum compression of a microstructured stack [18, 37–39]. For better handling and fluid interconnection, diffusion-bonded stacks may be surrounded by a shell [18, 37–39]. Diffusion-bonded stacks typically are more compact. In addition, this interconnection technique is principally amenable to small-series production. Accordingly, it is seen as a proper way to realize future commercial, off-the-shelf micro reactors.

3.2.1.1 Reactor 1 [R 1]: Reactor Module with Different Multi-channel Micro Reactors

A complete reactor module was built, consisting of the actual micro reactor and an encasement that serves for temperature setting [28]. The latter consists of two parts, a furnace for setting the high temperature in the reactor inlet collection zone and in the reaction zone and a cooler for the outlet collection zone. The micro reactor has a housing with standard tube connections. An electric furnace serves for heating. Temperatures can be measured in the furnace, at the furnace/micro reactor border and in the outlet collection zone. For thermal insulation, a 2 mm ceramic

Reactor type	Multi-plate-stack micro reactor with outer module	Catalyst No. 1 material; formation	Pt, impregnated
Furnace material	Copper	Reactor No. 2: monolith channel diameter; length	500 µm; 9.0 mm
Cooler material	–	Cube No. 2 dimensions; material	10 mm × 10 mm × 9 mm; Pt
Micro reactor housing material	Nickel	Reactor No. 3: total number of reaction channels	49
Platelet material	Aluminum; Pt	Reaction channel No. 3 width; depth; length	280 µm; 140 µm; 9.0 mm
Temperature of cooler/furnace	–20 °C; max. 430 °C	Platelet No. 3 material; width; length	Aluminum, anodically oxidized 9.0 mm; 9.0 mm
Power input furnace	max. 185 W	Catalyst No. 3 material; formation	Pt, impregnated
Operating temperature	370 °C	Reactor No. 4: total number of reaction channels	20
Operating pressure	–	Reaction channel No. 4 diameter; length	145 µm; 6.5 mm
Reactor No. 1: platelet width; depth; length	4.34 mm; 0.3 mm; 7 mm	Platelet No. 4 width; length	6.5 mm; 6.5 mm
Platelet No. 1 material	Aluminum, anodically oxidized	Cooling channel No. 4 diameter; length	300 µm; 6.5 mm

ring is placed between furnace and cooler. The cooler removes heat from the reaction zone and quenches the reaction gas mixture. The reactor has three versions, each with a set of reaction channels of various dimensions. The first is a parallel-plate reactor, the second a monolith and the third a stack of microstructured platelets. A fourth reactor type is a combined reactor/heat exchanger which so far is only a concept study.

3.2.1.2 **Reactor 2 [R 2]: Steel Multi-plate-stack Reactor with Micro Mixer**

The reactor is a two-piece housing which is sealed by flat sealing by screws using graphite seals [4, 26, 40, 41]. The bottom piece contains two closely positioned square recesses made by die sinking, a μEDM process. In the recesses, stacks of platelets of micro channels, not connected and without seals, are inserted. The recesses are connected via a breakthrough that functions as diffusion zone to guarantee mixing of the reactant gas before entering the reaction zone (Figure 3.4). The stacks of platelets are compressed when screwing the top and bottom housing piece together. The inlet and outlet tubes are welded to the bottom piece of the housing.

The first recess contains a stack of mixer platelets made by a combination of laser-LIGA and electroforming. These platelets have curved micro channels that make a 90° fluidic turn. In order to have equal flows in each curved channels, different channel widths had to be used to compensate the differences in channel length. CFD simulation was used to determine the mixer channel width values and confirmed 99% mixing for all flow rates investigated. Two types of mirror-imaged platelet designs allow the creation of gas multi-lamellae in an alternating stack arrangement. The second recess originally contained a stack of silver reaction platelets made by LIGA and electroforming [4, 26, 40]. In a later version, also chemically etched steel and milled Aluchrom steel platelets were used [4]. Aluchrom is an

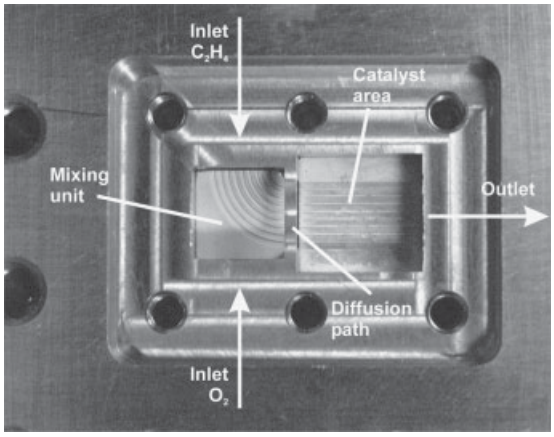

Figure 3.4 Magnified view inside a steel multi-plate-stack reactor.
Mixing unit (left), diffusion zone (middle) and stacked silver catalyst platelets (right).

Reactor type	Multi-plate-stack with mixer-reactor sections	Diffusion zone length	1 mm
Mixer + reaction platelet/housing material	nickel-gold plated + silver/stainless steel	Diffusion zone volume (= explosive volume)	0.042 cm^3
Heating	Forced convection flow	Reaction channel (laser-LIGA) width; depth; length	500 µm; 50 µm; 9.5 mm
Operating temperature	200–350 °C	Reaction channel (etched) width; depth; length	500 µm; 80 µm; 9.5 mm
Operating pressure	1–25 bar	Reaction channel (Aluchrom) width; depth; length	500 µm; 90 µm; 9.5 mm
Mixing channel width; depth	148–469 µm; 200 µm	Reaction plate thickness	300 µm
Mixing plate thickness	300 µm	Total number of reaction plates	14
Total number of mixing plates	14	Total number of reaction channels	126

aluminum containing stainless steel normally used metallic support for automobile exhaust catalysts (Krupp VDM e-20Cr-5Al). Heating the Aluchrom material to 1100 °C with air oxygen creates an α-Al_2O_3 surface.

The surface of the silver reaction channels was enhanced by means of the oxidation and outgassing reduction (OAOR) process, which relies on oxidation at 250 °C using pure oxygen and subsequent reduction. An increase in surface area by a factor of 2–3 was reached as indicated by chemisorption data.

3.2.1.3 **Reactor 3 [R 3]: Modular Multi-plate-stack Reactor**

A modular concept was developed to fit to the typical demands of laboratory reactors, flexibility, ease of handling, and fast change of parameters (Figure 3.5). It is based on five different assembly groups, namely microstructured platelets, a cylindrical inner housing, two diffusers and a cylindrical outer shell with a flange [42, 43]. The microstructured platelets are inserted in a recess of the bottom part of the inner housing, which is a rectangular mill cut (10 × 10 × 50 mm). Cylindrical 1/8 in tube connectors guide the flow from the reactor inlet via the diffuser to the platelet stack in the mill cut. The flange and cylindrical outer housing are held by six 5 mm screws and tightened via insertion of a copper gasket. The platelets are fabricated by means of thin-wire µEDM in the alloy AlMg3. Each platelet has 14 parallel micro channels. The surface of the micro channels was rough.

The micro reactor can be operated at temperatures up to 480 °C [44]. Platelet exchange can be performed in a short time, needing only 15–30 min of cooling from operational to ambient temperature. Heat production rates of about 30 W can be achieved without the need for external cooling [43].

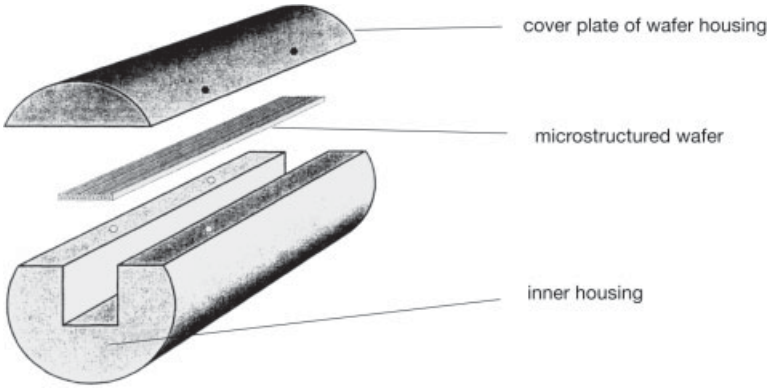

Figure 3.5 Schematic of the modular multi-plate-stack reactor [43].

The micro reactor was made in two versions:

(a)

Reactor type	Multi-plate-stack in cylindrical housing	Reaction channel width; depth; length	700 µm; 300 µm; 50 mm
Platelet material	AlMg3	Sputtered catalyst layer thickness	50–1400 nm
Operating Temperature	480 °C	Sol–gel catalyst layer thickness	1 µm
Operating pressure	3 bar	Total number of micro channels	14
Outer platelet dimensions: width; depth; length	10 mm; 1 mm; 50 mm		

For this micro reactor version, the catalyst was coated on the AlMg3 platelet as a thin silver layer by sputtering [43, 44]. A further set of platelets was covered with an α-alumina layer by sol–gel technique and impregnated by a three-step procedure with silver lactate.

(b)

Reactor type	Multi-plate-stack in cylindrical housing	Outer platelet dimensions (length No. I; No. II; No. III) = reaction channel length	12.5 mm; 37.5 mm; 50 mm
Platelet material	AlMg3	Reaction channel No. 1 width; depth	400 µm; 400 µm
Heating	external	Reaction channel No. 2 width; depth	200 µm; 200 µm
Operating Temperature	400 °C	Reaction channel No. 3 width; depth	80 µm; 80 µm
Operating pressure	0.1 MPa	Total number of micro platelets: No. 1; No. 2; No. 3	4; 8; 8

For this micro reactor version, the microstructured platelets were treated by anodic oxidation to obtain a nano-porous layer and impregnated with precursor solutions in organic solvents to obtain a $V_2O_{5/}P_2O_{5/}TiO_2$ catalyst.

3.2.1.4 **Reactor 4 [R 4]: Multi-plate-stack Micro Reactor with Diffusers**

This reactor is a professional tool made by small-series manufacturing that is nearly ready for commercialization [18, 43, 44]. A cylindrical reactor core is connected to two diffusers at each end that serve for gas-stream equipartition and collection. The reactor core contains a stack of microstructured metallic platelets (Figure 3.6). The platelets are made by mechanical micromachining using micro milling with special cutting tools. A thicker plate with borings for thermocouples can be inserted in the center of the stack so that temperature monitoring can be applied.

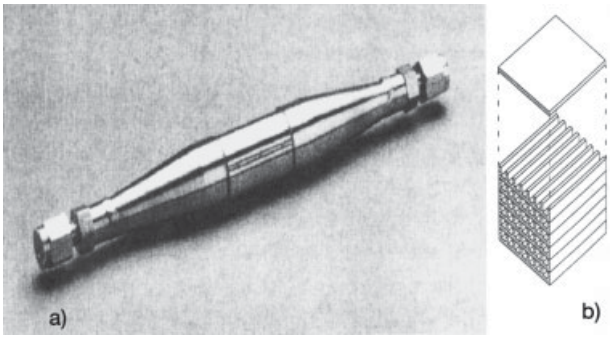

Figure 3.6 Multi-plate-stack reactor with diffusers.
Photograph (left) and schematic of the plate stack (right) [42].

The multi-plate stack micro reactor was made in two versions:

(a)

Reactor type	Multi-plate-stack with two diffusers	Outer platelet dimensions: width; depth; length	10 mm; 0.3 mm; 50 mm
Platelet material	AlMg3	Reaction channel width; depth; length	200 µm; 200 µm; 50 mm
Heating	Electrical	Sputtered catalyst layer thickness	1200 nm
Operating temperature	210 °C	Total number of micro channels	33
Operating pressure	3 bar	Total number of reaction plates	26
Increase in surface-to-volume ratio by anodic oxidation	10^4–10^5	Typical length of reactor (with diffusers)	17 mm

For this version, the micro structured AlMg3 platelets were coated with silver by CVD in [43]. In [44], the platelets were either totally made of silver (as construction material) or of AlMg3 and then coated by PVD with silver. In the latter version, two sub-versions were made with and without anodic oxidation to a generate nano-porous surface structure.

(b)

Reactor type	Multi-plate-stack with two diffusers	Reaction channel No. 1 width; depth; length	400 µm; 400 µm; 50 mm
Platelet material	AlMg3	Reaction channel No. 2 width; depth; length	200 µm; 200 µm; 50 mm
Heating	Electrical	Reaction channel No. 3 width; depth; length	80 µm; 80 µm; 50 mm
Operating temperature	400 °C	Alumina catalyst layer thickness	40 µm
Operating pressure	0.1 MPa	Total number of micro channels: No. 1; No. 2; No. 3	255; 550; 1165
Outer platelet dimensions: width; length	10 mm; 50 mm	Total number of reaction plates	15; 25; 37

For this version, the microstructured platelets were treated by anodic oxidation to obtain a nano-porous layer and impregnated with precursor solutions in organic solvents to obtain a $V_2O_5/P_2O_5/TiO_2$ catalyst.

3.2.1.5 **Reactor 5 [R 5]: Cross-flow Multi-Plate Stack Micro Reactor**

This professional tool, available in small series, is a derivative of a micro heat exchanger [31, 45–47] made by FZK, which was developed earlier. By insertion of catalytically active material, the 'micro heat exchanger' functions as a reactor. Quadratic platelets with straight micro channels are assembled into a stack so that two adjacent platelets have a 90° turn (Figure 3.7 and Figure 3.8). By this means, a cross-flow configuration is created with two separated fluid passages for reacting and heat transferring fluids.

Microfabrication of the parallel channels was performed by mechanical surface cutting of metal tapes [31]. In the case of aluminum alloys, ground-in monocrystalline diamonds were used [45]. In the case of iron alloys, ceramic micro tools have to be used owing to the incompatibility of diamonds with that material. Such a microstructured platelet stack is provided with top and cover plates, diffusion bonded and connected to suitable fittings for the inlet and withdrawal ducts by electron beam welding (Figure 3.9).

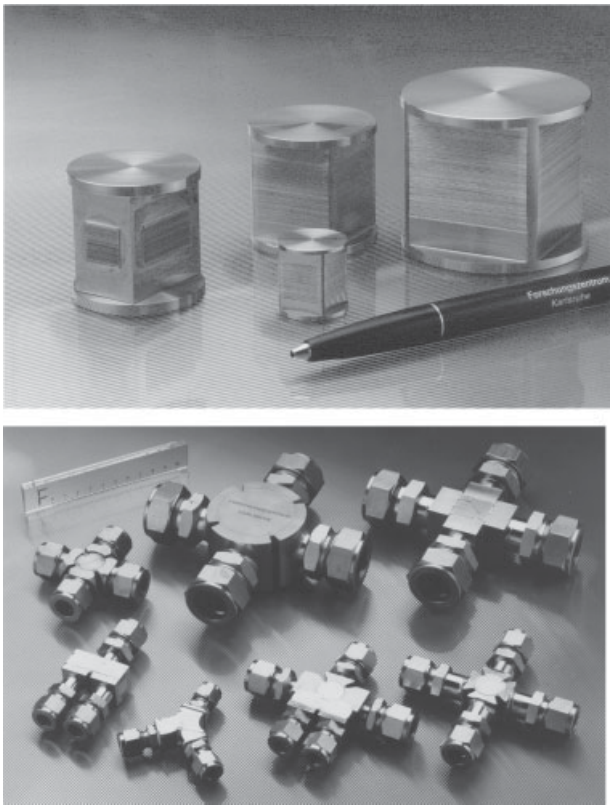

Figure 3.7 Alternated 90° turned adjacent platelets forming a stacked cross-flow configuration. Image of thermally bonded devices (top). Complete mounted multi-plate stack micro reactors (bottom) [45].

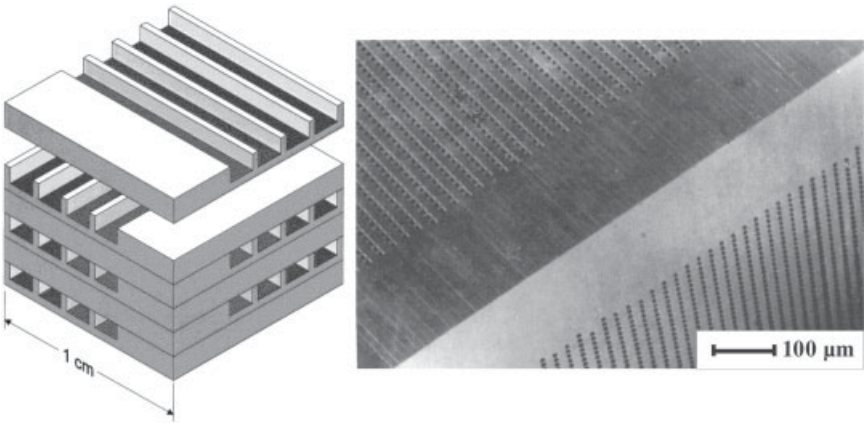

Figure 3.8 Schematic of stacked platelets (right) and a micrograph showing micro channel openings from a corner (left) [115].

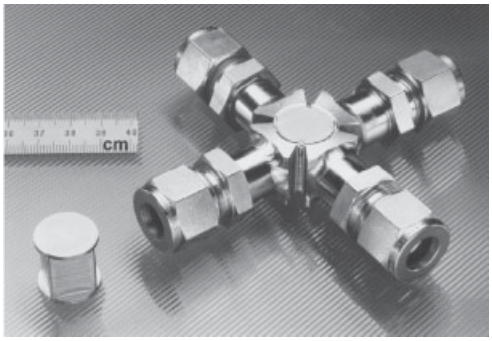

Figure 3.9 Image of a completely mounted cross-flow micro heat exchanger with 1 cm^3 active volume [46].

Optimized microfabrication and advanced assembly led to the use of thin platelets, in an original version 100 µm thick with a 80 µm micro channel depth, so that very thin walls (20 µm in the case sketched) remain for separating the fluids. Therefore, also the total inner reaction volume with respect to the total construction volume or the 'active internal surface area' is very large. The latter surface amounts to 300 cm^2 (for both the heat transfer and reaction sides) at a cubic volume of 1 cm^3. Indeed, the micro heat exchangers exhibited high heat transfer coefficients for gas [46] and liquid (Figure 3.10) [47, 48] flows.

The reactor can be obtained in many materials such as aluminum alloys, copper, silver, titanium and stainless steel. The number of stacked platelets, the dimensions of the micro channels on the platelets and the fluidic connectors were also varied. Pressure tightness up to 25 bar and He tightness were demonstrated, although this is certainly not the upper limit.

More details on the reactor are available [1, 49–51].

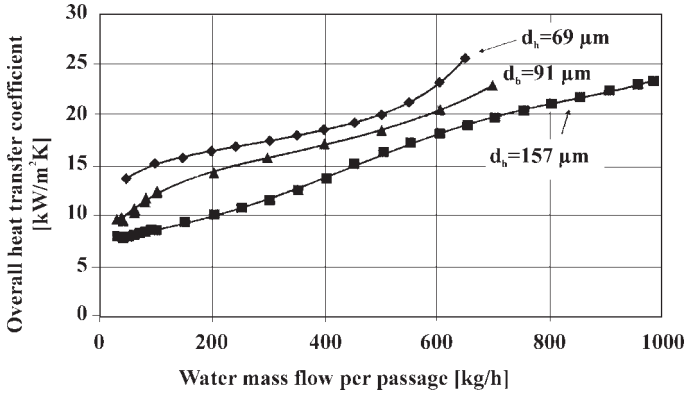

Figure 3.10 Calculated heat transfer coefficient depending on micro-channel dimensions and water flow rate. Experimental data are given in [47].

Reactor type	Multi-plate-stack, cross-flow	Operating pressure	–
Platelet/housing material	Silver/stainless steel	Reactor cube dimensions	10 mm × 10 mm × 10 mm
Heating	Cross-flowing gas	Reaction channel width; depth; length	400 µm; 300 µm; 10 mm
Operating Temperature	390 °C	Total number of channels per passage	200

3.2.1.6 **Reactor 6 [R 6]: Counter-flow Multi-plate Stack Micro Reactor**

This micro reactor consists of a stack of two sets of microstructured platelets which are arranged in such a way that two alternately positioned flow configurations are generated [13, 27]. Thereby, two fluids can be guided in a counter-flow mode, although by using one set of platelets only a parallel transport of one fluid can also be achieved. In the first case, a reactor/heat exchanger configuration is created, whereas only a reactor is set up in the second case (Figure 3.11).

The stack of platelets is encompassed by two end caps bearing the external fluidic connections. If desired, a third housing part can be introduced in between the end caps to shield the stack. As a further design modification, ceramic Macor™ insulating plates can be inserted between the end caps and platelet stack to prevent heat losses from the stack to the housing.

The platelets comprise an array of parallel micro channels with microstructured triangular-shaped headers at both ends. In the headers holes form conducts to the external feed fluid supply. Optimization of the shape of the header with respect to flow equalization was the topic of various simulation studies [52, 53].

The micro channels were made by isotropic wet chemical etching of metal plates. The plates were tightened by various means: they were either glued, stacked to-

gether with graphite sealing or fixed within a closed stainless steel housing (Figure 3.12). The micro reactor can be heated by various means, e.g. electrically with heating cartridges or frames, by setting it in an oven or by using fluid heat exchange in the counter-flow mode.

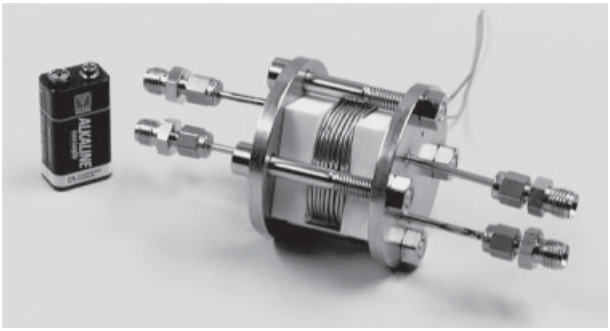

Figure 3.11 Photograph of the multi-plate stack reactor, originally designed as a counter-flow heat exchanger; this type of reactor was also used for periodic operation [13].

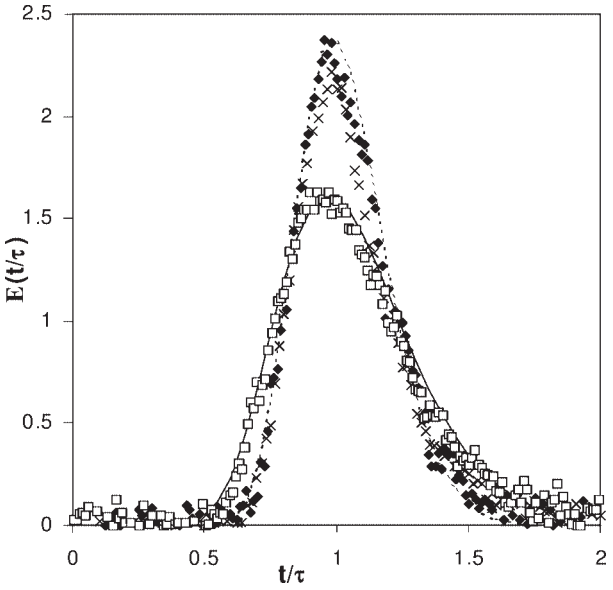

Figure 3.12 Residence time distribution in a micro reactor which is tightened by different means. (♦) Glued reactor without catalyst coating; (X) glued reactor with catalyst coating; (□) reactor with graphite joints. Calculated curves for tubular reactors with the Bodenstein number Bo = 33 (solid line) and Bo = 70 (dashed line).

Reactor type	Multi-plate-stack with counter-flow guidance	Total number of reaction platelets	6; 10
Housing (end cap) material	Stainless steel	Platelet material	Aluminum
Heating	Forced convection flow; oven; electrical heating	Number of reaction channels per platelet	34
Operating temperature	480 °C	Micro channel hydraulic diameter; length	230–280 µm; 20 mm
Operating pressure	1.2 bar	Catalyst material; formation	$V_{30}Ti_{70}O_x$-SiO_2; suspension + impregnation; finally anodic oxidation
Stack dimensions	40 mm × 40 mm × 0.5 mm		

3.2.1.7 **Reactor 7 [R 7]: Multi-Plate Stack Micro Reactor in Heatable Holding Unit**

The central part of this reaction system is an Rh construction material monolith made from a welded stack of platelets carrying parallel micro channels [3]. As initial material for this stack, hard-rolled Rh foils were first thermally treated and then micro structured. Micro milling can be applied for channel widths exceeding 200 µm. To generate smaller internal dimensions, thin-wire µEDM is applicable. Rectangular shapes were achieved by milling, whereas µEDM led to U-shapes. Laser or electron beam welding are the favored interconnection techniques, although diffusion bonding works is also satisfactory (Figure 3.13).

The welded Rh stack was welded to a cover plate and inserted into a ceramic holder, made of a special shrinkage-free material that can be machined as green compact [3]. The ceramic holder prevents heat losses from the metallic stack.

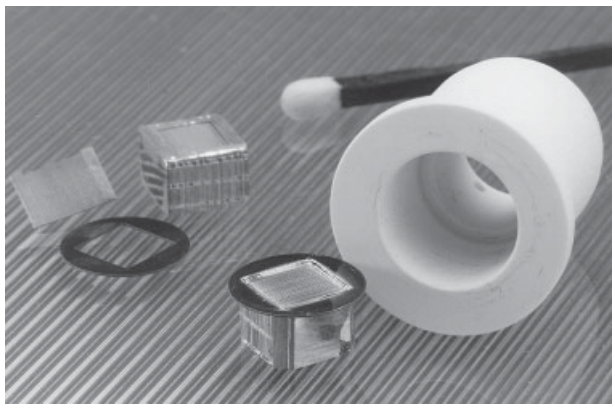

Figure 3.13 Photograph of welded stacks of Rh platelets and supporting parts [3].

The outer wall of this holder is provided with a spiral groove for insertion of a heating wire. The holder is installed into a pressure vessel via a few screw connections, giving a gas-tight system. Quartz glass inspection flanges at both ends of the vessel serve for pyrometric inspection to judge the catalyst temperatures at the stack inlet and outlet.

Compared with laboratory fixed-bed reactors or conventional extruded monoliths, such a microstructured monolith is smaller in characteristic dimensions, lower in pressure loss by optimized fluid guiding and constructed from the catalytic material solely [3]. The latter aspect also leads to enhanced heat distribution within the micro channels, giving more uniform temperature profiles.

The whole set-up for partial oxidation comprises a micro mixer for safe handling of explosive mixtures downstream (flame-arrestor effect), a micro heat exchanger for pre-heating reactant gases, the pressure vessel with the monolith reactor, a double-pipe heat exchanger for product gas cooling and a pneumatic pressure control valve to allow operation at elevated pressure [3].

The micro reactor was made in three versions, termed a–c, differing in internal dimensions [3].

Reactor type	Multi-plate-stack, welded and with external heating	Platelet width; length; thickness	(a) 5.5 mm; 5.0 mm; 200 µm (b) 5.5 mm; 5.0 mm; 200 µm (c) 5.5 mm; 20 mm; 200 µm
Housing	Special ceramic	Reaction channel width; depth; length	(a) 120 µm; 131 µm; 5.5 mm (b) 60 µm; 137 µm; 5.5 mm (c) 120 µm; 108 µm; 20.0 mm
Heating	Electrical heating by heating wire	Hydraulic diameter	(a) 125 µm; (b) 83.5 µm; (c) 114.1 µm
Operating temperature	1090–1190 °C	Total number of channels per stack	(a) 644; (b) 1152; (c) 675
Operating pressure	0.15–12 MPa	Residence time, $1\,l\,h_{STP}^{-1}$	(a) 3.0 ms; (b) 2.8 ms; (c) 10.6 ms
Stack dimensions (W × H × L)	(a) 5.5 × 5.5 × 5.0 mm^3 (b) 5.5 × 5.5 × 5.0 mm^3 (c) 5.5 × 5.5 × 20.0 mm^3	Geometric surface per cm reactor length	(a) 32.4 cm^2; (b) 45.4 cm^2; (c) 30.9 cm^2

3.2.1.8 **Reactor 8 [R 8]: Ceramic Platelet Micro Reactor**

This micro reactor contains an exchangeable platelet with a multi-channel reaction zone (Figure 3.14) [54, 55]. The housing is symmetric, i.e. inlet and outlet diffusers and tube connectors are the same and have mirror-imaged positions. Between the triangular-shaped diffusers a recess is placed where the reaction platelets are inserted. The reaction housing is covered with a top plate. Highly polished ceramic surfaces allow tight sealing. This version of the reactor is referred to as *Model A*.

Model B was especially designed for methane conversion to ethylene [54, 55]. This reaction needs pre-heating to a defined temperature before reaction. This is achieved by ceramic heaters in the housing. In addition, the gases do not enter as a

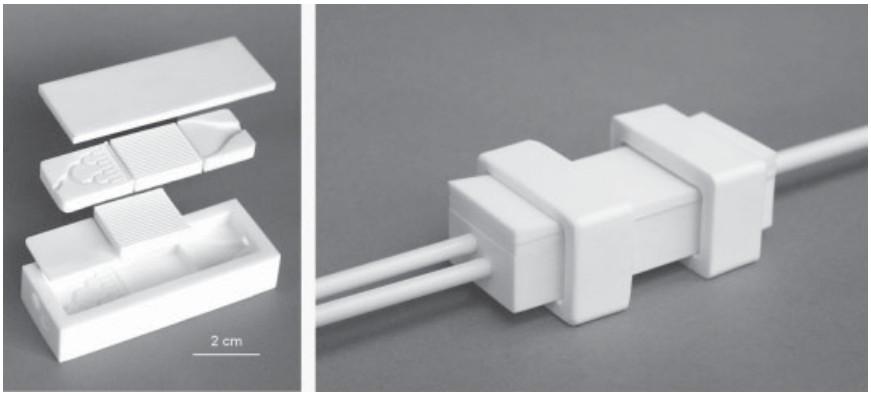

Figure 3.14 Ceramic platelet micro reactor; bottom housing with recess for platelet stack, platelets and top plate [54].

mixture, but are separated and only mixed shortly before reaction. The model has an almost constant cross section over the reactor length to give an even flow. The catalyst-coated platelets are again exchangeable.

Fabrication was done by a combination of stereolithography and low-pressure injection molding [54, 55]. A 3D-CAD model was transferred in silicone polymer molds by stereolithography. These were filled with an alumina feedstock. After demolding, organic residues were removed from the green bodies by slow heating. Thereafter, sintering up to 1700 °C was applied. The tubes for gas feed were joined by a commercial glass–ceramic.

Reactor type	Ceramic platelet reactor	Micro channel width; length (type A + B)	500 μm; 25 mm
Catalyst material	$LiAlO_2$ (sol–gel)	Device inner volume	650 mm^3
Device length	70 mm	Operational temperature	1000 °C
Feed and withdrawal tubes	2 mm	Operational pressure	1.2 bar
Length of diffuser zone	16 mm		

3.2.1.9 **Reactor 9 [R 9]: Micro Heat Transfer Module**

The micro heat transfer module (Figure 3.15) comprises a stack of micro structured platelets which are irreversibely bonded [29, 30]. The module is heated by external sources, e.g. by placing it in an oven or by resistance heating. The single parallel flows are all guided in the same direction on the different levels provided by the platelets. Before and after, distribution and collection zones are found, connected to inlet and outlet connectors.

The micro structured plates are made by wet-chemical etching. The platelet stack is bonded by laser welding. The inlet and outlet connectors are also laser welded.

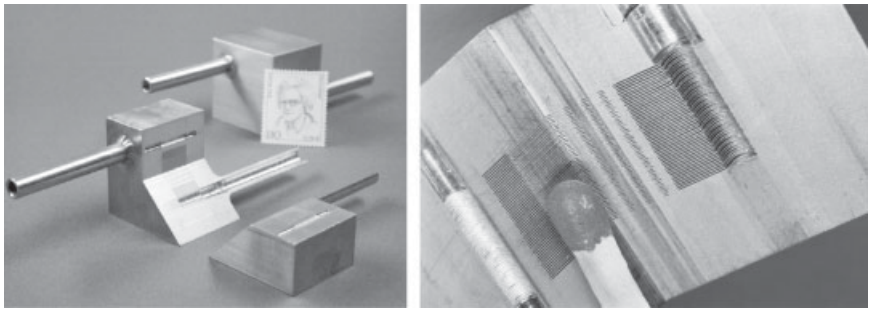

Figure 3.15 Micro heat transfer module [29].

Reactor type	Micro heat transfer module	Device inner volume	$2.6 \cdot 10^{-7}$ m^3
Module material	Stainless steel	Operational temperature	Up to 600 °C
Number of platelets	50	Operational pressure	0.4 bar
Number of channels on one platelet	13	Operational pressure	0.4 bar
Micro channel width; depth; length	500 μm; 100 μm; 8 mm	Outer device dimensions	32 mm × 32 mm × 26 mm
Total micro-channel surface area	$6.24 \cdot 10^{-3}$ m^2	Tube connectors: inner diameter; length	6 mm; 40 mm

3.2.2 Chip Micro Reactors

The design and fabrication of some gas-phase micro reactors are oriented on those developed for chip manufacture in the framework of microelectronics, relying deeply on silicon micromachining. There are obvious arguments in favor: the infrastructure exists at many sites world-wide, the processes are reliable, have excellent standards (e.g. regarding precision) and have proven mass-manufacturing capability. In addition, sensing and control elements as well as the connections for the whole data transfer (e.g. electric buses) can be made in this way.

Accordingly, chip micro reaction systems are frequently described in the literature. Most of them are made of silicon (see, e.g., [19, 56–62]); Glass can be manufactured by similar routes as for silicon and could hence constitute gas-phase micro reactors; however, the glass chip micro reactors described so far were made for liquid-phase applications (see, e.g., [63–70]).

Today's chips are often simple two-wafer bonded microstructured devices. However, exceptions are known. Complex multi-wafer arrangements, having a separte function on each level, have been described already in the pioneering phase of chemical micro processing and investigated by the chemical industry [71]. Another pioneering chip comprised a multitude of heating and sensing functions [19, 56–62].

3.2.2.1 Reactor 10 [R 10]: Catalyst Membrane Si-chip Micro Reactor with Sensing and Heating Functions

An Si-chip micro reactor (Figure 3.16) contains an etched micro channel of T-shape which was covered by a thin membrane [19, 56–62]. The membrane bears on its bottom side, i.e. facing the micro channel, a thin layer of catalyst material and on its top side heating elements and temperature sensors. Besides these carrier functions, the main task of the membrane is to transfer heat from the reaction zone to the outside by means of convective mechanisms. Accordingly, by variation of the material, i.e. change of thermal conductivity, control over heat removal can be exerted and, therefore, over the reaction temperature. For a given reactor configuration with a given membrane, heat generation and reaction temperature are determined by the exothermic release of the reaction and the power input of the heaters.

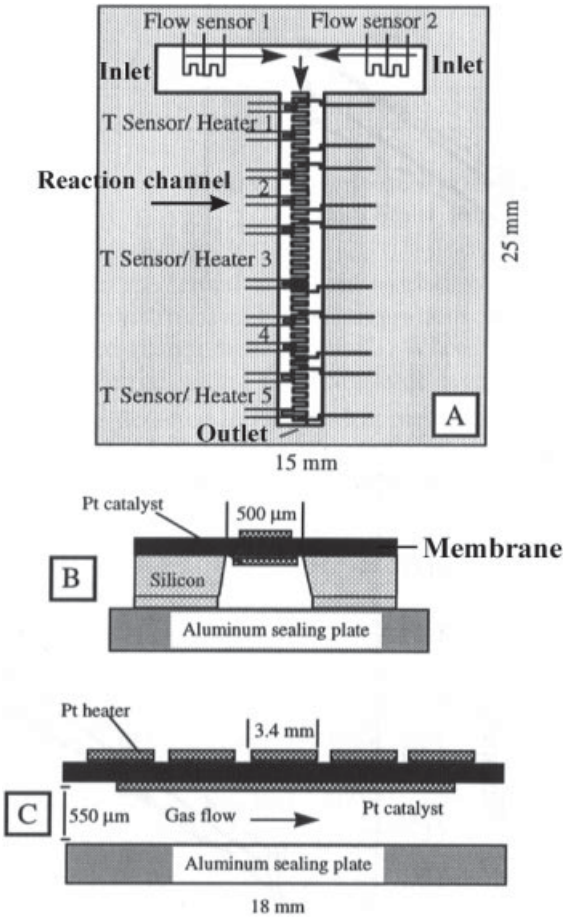

Figure 3.16 Schematic of Si-chip catalyst membrane micro reactor. Top view (A), end-on cross section of reaction channel (B); side-view cross section of reaction channel (C) [60].

An optimized design with an Y-shaped configuration (see also [57]) mainly served for reducing the mechanical stress in the chip device which can lead to rupture, especially under high temperature and pressure operation [19]. By changing the configuration, the large area of the free-standing membrane in the mixing intersection is reduced. The improved design withstands much higher temperatures and pressures (see table below) [19].

The micro reactor was made from a double-side, polished (100 mm diameter) Si wafer coated with 1 µm thick low-stress SiN_x that comprises the membrane [57]. SiN_x/Si reactors were fabricated in an Si-on-insulator (SOI) wafer with a 2.6 µm Si device layer covered by 150 nm of low-stress SiN_x. The SiN_x on the back side of the wafer was patterned by photolithography and plasma etched to expose the underlying silicon. Pt heaters and sensors were defined by patterning lift-off photo resist on the front side of the wafer, followed by e-beam deposition (with Ti as adhesion layer). The gas flow channels were formed from the back side by either etching the exposed Si in KOH solution or using deep reactive ion etching. The latter process allowed more freedom concerning structural design. The wafer was thereafter diced into the individual micro reactors and each die was affixed to the Al-base plate. Inlet and outlet holes matched the fluidic connections of the experimental rig. Electrical connections to bond pads of the heaters and sensors were made using a probe card (Figure 3.17).

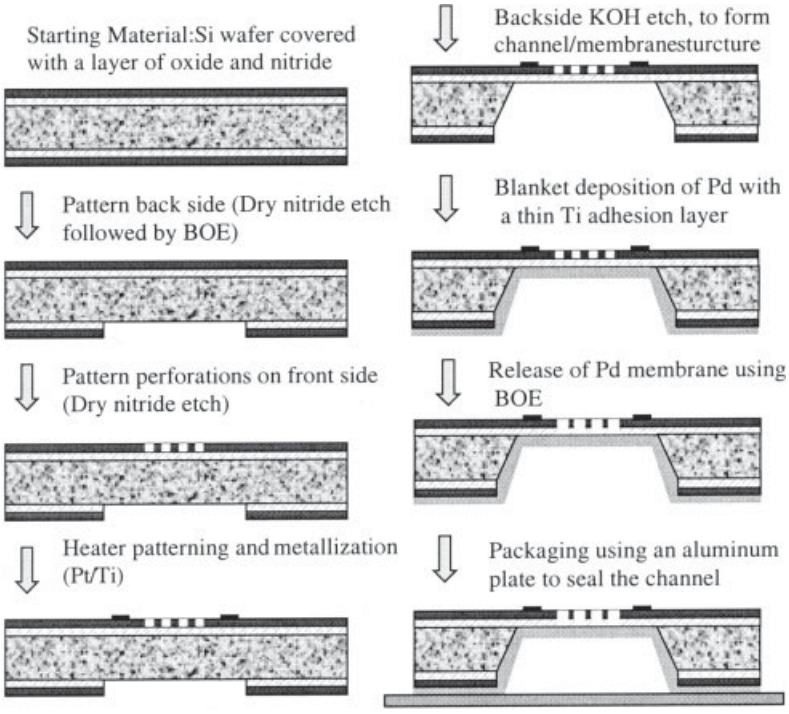

Figure 3.17 Microfabrication sequence for the silicon component of the catalyst membrane micro reactor [57].

Reactor type	Chip reactor with thin-film sensors and membrane	Catalyst material	Pt
Chip material	Silicon, aluminum	Catalyst layer thickness	0.1 µm
Membrane material	SiN_x; Si	Reaction channel width; depth; length	500 µm; 550 µm; 18 mm
Membrane thickness SiN/Si	1; 1.5, 2.6	Overall chip dimensions	15 mm × 25 mm
Maximal temperature	650 °C original design, 800 °C optimized design	Reaction channel (Aluchrom) width; depth; length	500 µm; 90 µm; 9.5 mm
Maximal pressure	0.5 bar original design, 2.7 bar optimized design	Reaction plate thickness	300 µm
Operating temperature	570 °C original design	Total number of reaction plates	14
Operating pressure	–	Total number of reaction channels	126
Chip material	Silicon, aluminum	Catalyst layer thickness	0.1 µm

3.2.2.2 **Reactor 11 [R 11]: Single-channel Chip Reactor**

This reactor comprises a single-channel reaction zone followed by a quenching (cooling) zone [72]. Gases, pre-heated in a separate zone, are contacted in an T-junction and mixed in a short passage thereafter. Such mixed gases enter the above-mentioned reaction zone.

Fabrication was done by photolithography and deep reactive ion etching (DRIE). The catalyst was inserted by sputtering. Such a prepared microstructure was sealed with a Pyrex cover. The bonded micro device was placed on a heating block containing four cartridge heaters. Five thermocouples monitored temperature on the back side. A stainless-steel clamp compressed the device with graphite sheets.

Reactor type	Single-channel reactor	Operating temperature	530 °C
Catalyst material	Sputtered silver	Operating pressure	1 atm
Reaction channel width; depth	600 µm; 130 or 70 µm		

3.2.2.3 **Reactor 12 [R 12]: Multi-channel–One-plate Chip Reactor**

This simple reactor concept is based on a microstructured silicon chip (Figure 3.18) covered by a Pyrex-glass plate by anodic bonding [73, 74]. The silicon microstructure comprises, in addition to inlet and outlet structures, a multi-channel array. Only the Pyrex-glass plate acts as cover and inlet and outlet streams interface the silicon chip from the rear.

Standard silicon micromachining processes were applied. The starting material was a 100 mm silicon (110) orientation wafer covered with thermal oxide. Stand-

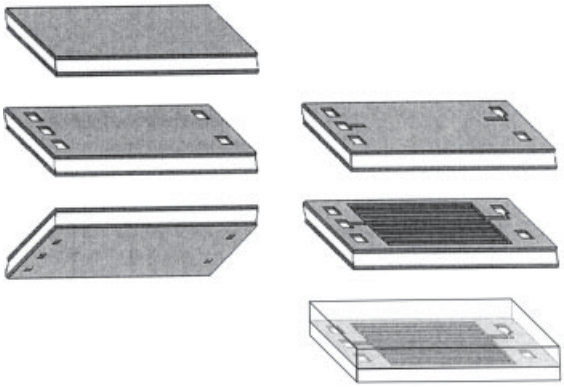

Figure 3.18 Schematic drawing of fabrication steps for Si-based micro reactors. The fabrication is carried out batch-wise on an 100 mm Si-wafer [73].

ard photolithography and KOH etching processes were applied for micro structuring. Separation into individual pieces was done using a diamond wafer saw.

Catalysts can be incorporated by the various known methods. So far, sputtered platinum was used. Such films are dense so that the catalyst surface area equals the channel surface.

Reactor type	Multi-channel chip reactor	Pt film thickness	10–40 nm
Catalyst material	Platinum	Catalyst surface area	2.2×10^{-4} m^2 (100 μm) 2.8×10^{-3} m^2 (5 μm)
Chip materials	Silicon; Pyrex glass	Operating temperature	200 °C
Channel width, depth, length	100 μm; 100 μm; 18/19 mm or 5 μm; 100 μm; 18 mm	Operating pressure	1 bar
Number of channels	39 (100 μm); 780 (5 μm)		

3.2.2.4 **Reactor 13 [R 13]: Micro-strip Electrode Reactor**

A test reactor was made of stainless steel which contains a so-called micro-strip electrode array [75]. This array is composed of thin strips surrounded by larger objects. The anodes are thin gold strips evaporated on glass bulk. The cathodes have a more complex bulky pattern similar to an oval.

Reactor type	Micro-strip electrode reactor	Cathode width	500 μm
Catalyst material	Gold emitting electrodes	Period (from anode to anode)	1000 μm
Anode width	12 μm	Size of electrode array	30 mm × 30 mm

3.2.2.5 **Reactor 14 [R 14]: Self-heating Chip Micro Reactor**

Thermally oxidized silicon wafers were structured by photolithography and wet-chemical etching [76]. In this way, a meandering pre-heating channel structure followed by a meandering reactor channel structure was prepared (Figure 3.19). Next to the channel connecting these two units a thermocouple well was placed. On the back side of the wafer a meandering Pt heating element was patterned. Glass plates covered the double-sided Si structure on both sides via anodic bonding. Holes were drilled for gas inlet and withdrawal and stainless-steel tubes attached.

A Pt catalyst was applied by dry and wet techniques. By means of sputtering using a mask process protecting parts of the microstructure, the micro channel bottom was coated selectively. In addition, an γ-alumina layer was applied by the sol–gel technique. Initially, the whole micro structure was covered by such a layer. Then, photoresist was applied and patterned so that only the channel part remained covered. After removal of the exposed photoresist and unprotected γ-alumina, only the channel bottom was coated with γ-alumina.

Reactor type	Self-heating chip reactor	Pt heating element: diameter; length	100 µm; 200 mm
Catalyst material	Pt (sputtered); Pt/γ-alumina (sol–gel) 2.5 µm	Glass plate thickness	1 mm
Si wafer	10 mm × 40 mm	Steel tube diameter	300 µm
Reactor channel: upper width, lower width; depth; length	600 µm; 515 µm; 60 µm; 78 mm	Thermocouple element wire diameter	100 µm
Reactor channel: width; depth; length	200 µm; 60 µm; 95 mm	Operational temperature	150 °C

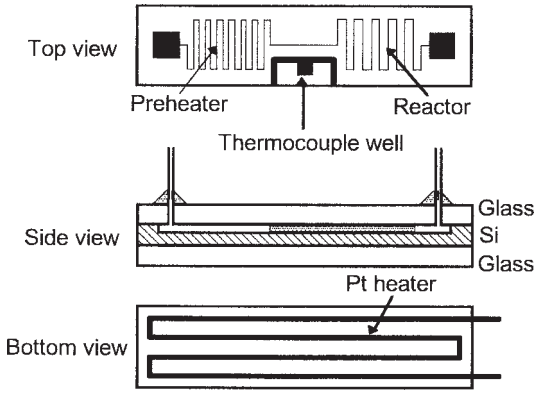

Figure 3.19 Schematic of a self-heating micro reactor [73].

3.2.2.6 **Reactor 15 [R 15]: Modular Multi-functional Chip Reaction System**

This micro-chip reaction system was developed for pioneering industrial investigations at the beginning of micro-reactor developments [71].

It comprises several wafers with different functional elements such as micro heat exchanger, mini fixed-bed catalyst chambers, manifolding structures and other components not disclosed. The flow partitioning was performed in a hierachic manner. A patent gives deeper insight into the generic construction architecture of the micro-reaction system. The wafers were bonded to a stack and equipped with fluid connections [137].

Heat transfer was accomplished by guiding flows throught different wafer levels, some acting as energy source, others as heat sink. For cooling, circulating liquids were applied.

The microstructured plates were made by wet-chemical etching. The platelet stack was bonded by standard welding. The inlet and outlet connectors were also welded.

Reactor type	Modular multi-functional chip reaction system	More details are given in [137]
Module material	Silicon	

3.2.3 **Mini Fixed-bed Micro Reactors**

Fixed-bed technology is a very common approach in conventional gas-phase processing, on a laboratory and industrial scale. The difficulty in transferring this concept to the micro scale stems from the restrictions on the availability of fixed-bed particles much smaller than the internal dimensions of the micro device. If they are available, handling of the particles certainly causes expenditure, as the tiny particles have to be filled into a micro channel, packed properly, should not dislocate on operation, and may have to be removed completely afterwards. In addition, the smaller the size of the bed particles, the more care has to be taken to achieve a proper packing, e.g. avoiding large conduits. For this reason, regular-sized particles were applied recently which result in a tight packing having interstices of the order of the internals of typical micro channels [7, 77–80]. For these beds, first considerations on mass and heat transfer based on the Weisz modulus and the Anderson criterion were made.

The undoubted advantage of mini fixed-bed micro reactors is that they follow a widely accepted processing path and in principle can use all of the commercial catalysts, if they can be crushed to a size much below the micro-channel diameter. Hence catalyst material flexibility is a major driver.

Today's massive efforts in nanotechnology will certainly provide more well-defined, regular-shaped particles in the submicron range, and mini fixed-bed technology will profit from that.

3.2.3.1 Reactor 16 [R 16]: Wide Fixed-bed Reactor with Retainer Structures, Pressure-drop Channels and Bifurcation-cascade Feed/Withdrawal

This concept, also termed cross-flow reactor, integrates multiple, short packed beds to one entity, a continuous, wide packed bed [7, 77, 78]. This is done for reasons of increasing the effective catalyst area and enlarging the throughput. The same residence time as an axial-flow reactor is claimed, but at larger throughput or smaller pressure drop, respectively. Owing to the short contact time, the reactor is amenable to differential operation (low conversions), which is helpful for investigating kinetics.

A bifurcation cascade with micro channels feeds a wide fixed bed (channel void space for particle insertion), followed by a multitude of catalyst retainers, which act like frits, i.e. support the catalyst particles and prevent their loss [7, 77, 78]. Besides supporting the particles, these parts have a size-exclusion function to the lower size limit of about 35–40 μm. The retainers are followed by an array of elongated channels that serve to build up a uniform pressure drop along the wide retainer bed. Finally, the streams are collected in a bifurcation cascade of identical shape as the feeding cascade, but mirror-imaged in position.

The pressure drop in the bifurcation channels is much larger than any other contribution of the whole device, i.e. exceeds the fixed-bed share by far [7, 77, 78]. Hence small deviations therein, e.g. due to different packing or particles of varying size, do not contribute to changing the residence time at one location.

Four side wells for thermocouples are designed to achieve easily thermal equilibrium in the reactor, made of the highly conductive material silicon [7, 77, 78].

One way to fabricate such a reactor is by deep reactive ion etching (DRIE) with a time-multiplexed inductively coupled plasma etcher (most details on fabrication are given in [77]) [7, 77, 78]. Regions of major importance such as the retainers are etched through to avoid differences in structural depth which may cause uneven flow. To generate various channel depths in one design, both front-side and back-

Reactor type	Wide fxed-bed reactor	Pressure-drop channels: number, width, depth	256; 40 μm; 20–25 μm
Catalyst material	Pd/Al_2O_3; Pt/Al_2O_3; Rh/Al_2O_3	Meander net centerline length	~2.2 mm
Catalyst particle diameter	70–100 μm	Silicon wafer: thickness; diameter	500 μm; 100 mm
Feed (bifurcate) channels: width, depth; number	350 μm; 370 μm; 64	Outer device dimensions	15 mm × 40 mm × 1.5 mm
Catalyst bed: width; depth; length; volume	25.55 mm; 500 μm; 400 μm; 5.1 μl	Operating temperature	550 °C (with Pyrex cover); 1000 °C (with Si cover)
Retainer posts: width	50 μm	Operating pressure	0.14 MPa

side etching are performed. Such prepared channels are capped on top and bottom with Pyrex wafers by anodic bonding. Holes are drilled for inlet and outlet flow guiding. A metal cover plate and thin elastomer gaskets are used for housing. Catalyst particles of 50–70 µm diameter are fed through an inlet port using a vacuum applied at the outlet. By applying high pressure, all particles are blown out from the device.

A number of experiments and finite-element simulations were done to confirm even flow distribution, uniform pressure drop and isobaric properties and also to analyse quantitatively mass and thermal transfer for the wide packed-bed reactor [78].

3.2.3.2 **Reactor 17 [R 17]: Mini Packed-bed Reactor**

The central element of this reactor is an elongated channel in which small catalyst particles can be filled to give a mini-packed bed (Figure 3.20) [79, 80]. Gas streams enter this reaction zone as a mixture via an interleaved channel section, which also prevents the small particles penetrating the gas-feed channels. A similar type of microstructured 'frit' is placed at the end of the packed bed for the same function. Next to the inlet channels on the right and the left catalyst-loading channels are placed to insert suspensions with catalyst particles (by applying a vacuum at the exit). Thermocouple wells serve for temperature monitoring.

The structures were etched using a time-multiplexed inductively coupled plasma etch (Figure 3.21). On the back side of such a structured silicon wafer holes were

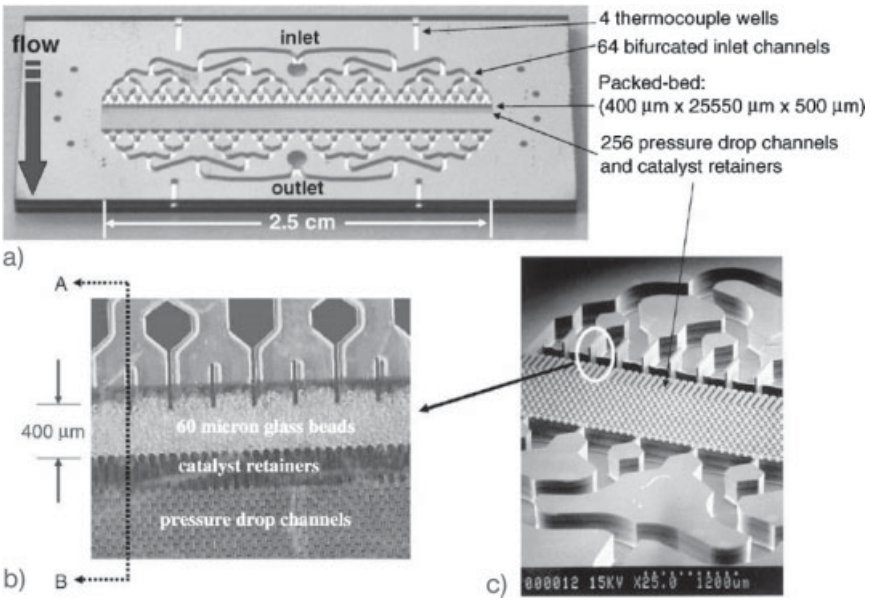

Figure 3.20 Photograph of the mini packed-bed reactor (a); mini packed-bed reactor packed with 50 µm glass beads (b); detailed SEM image (c) [80].

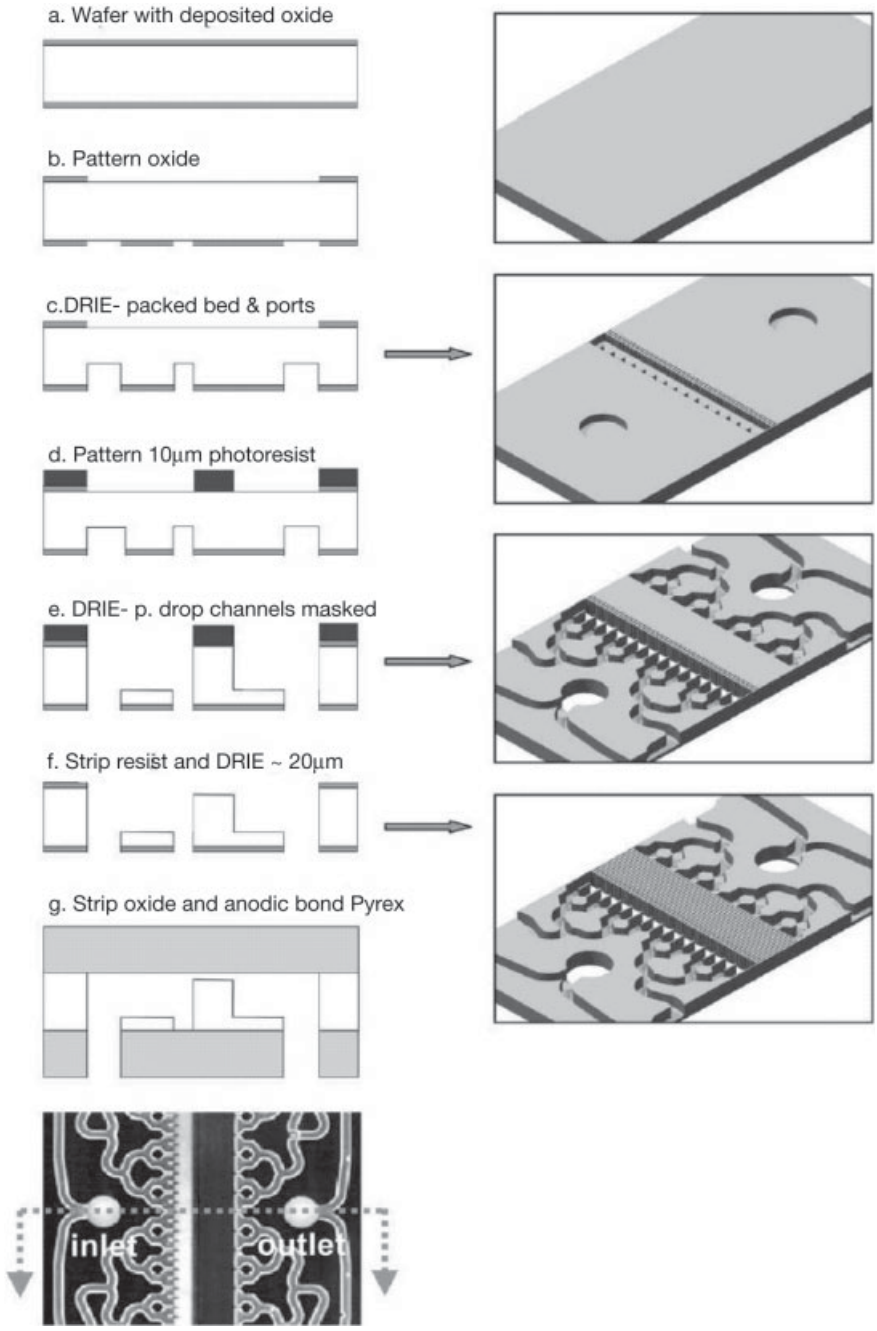

Figure 3.21 Schematic of the fabrication sequence for the mini packed-bed reactor [80].

etched for inlet and outlet flow guiding. A 500 nm silicon dioxide layer, made in a wet-etching furnace, protected the silicon from being etched by chlorine. By anodic bonding, the device was capped with a Pyrex cover. Such bonded wafer stacks were cut with a die saw to obtain individual pieces.

Reactor type	Mini packed bed-reactor	Catalyst-loading channels: width	400 μm
Catalyst material	Activated carbon	Post channels at outlet: width	25 μm
Catalyst particle diameter	53–73 μm	Silicon wafer: thickness, diameter	500 μm; 100 mm
Catalyst surface area	850 $m^2 g^{-1}$	Outer device dimensions	10 mm × 40 mm × 1.0 mm
Reaction channel: width; depth; length; volume	625 μm; 300 μm; 20 mm; 3.75 μl	Operating temperature	25–200 °C
Interleaved channels at inlet: width	25 μm	Operating pressure	1.40 atm

3.2.4 Thin-wire and μGauze Micro Reactors

These micro reactors do not have real micro channels, but rather have holes, in the case of the μgauze, or create microflow conduits, by placing a thin wire in a micro channel. Especially the first concept is derived from laboratory and industrial-scale processing of extremely fast reactions.

3.2.4.1 Reactor 18 [R 18]: Modular Integrated 3D System with Electrically Heated μGauze

This reactor has a rather complex construction (Figure 3.22) concerning the number of microstructured parts, their integration, tight arrangement, the variety of materials and the numerous surfaces that had to be tightened [2, 41, 81]. Since it was built from reversibly sealed parts, the system is modular, e.g. easily allowing the insertion of a different catalyst material or another micro heat exchange unit. The reactor is not a component, but an integrated system as it contains three microstructured components in one assembly, namely a pre-heater with microstructured outlets, a microstructured gauze and a micro heat exchanger.

The pre-heater is a massive stainless-steel block with three bores that guide and heat the gases. This block is heated via three heating cartridges. At the end of the block three outlet bores were made by μEDM drilling. A small chamber serves for mixing the gases and the outlet holes prevent explosions or flames from moving upstream (flame-arrestor effect). Below the mixing chamber, a metallic strip with a micro hole array in the center is positioned. This strip is completely made from the catalytic material via shaping a foil by thin-wire μEDM. The micro holes are drilled

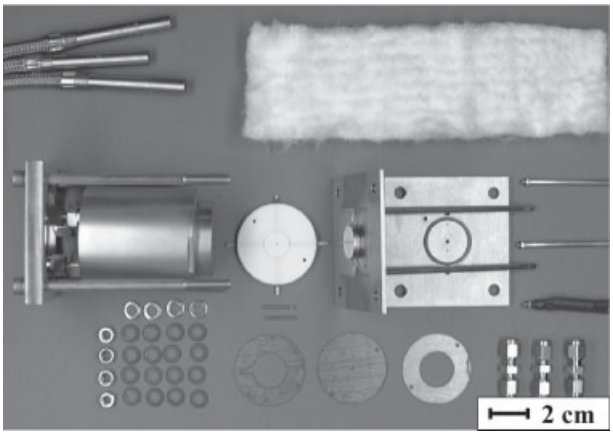

Figure 3.22 Photograph of the dismantled reactor with all parts [2].

by μEDM. The strip has electrical connectors at both ends so that resistance heating can be applied. The center of the strip, i.e. the hole array, has the highest resistance, and hence becomes hottest until glowing is achieved at very high temperatures. At the center of the strip, two smaller lines are attached that serve for temperature monitoring via measuring the thermal change of electrical resistance.

The micro hole array is an arrangement similar to monoliths and particularly to gauzes employed for the same purposes, and hence is termed μgauze in the following. The μgauze strip is inserted in a structured ceramic frame that contains a recess for the strip. Embedded silver and metal solder rods serve for electrical connection via the ceramic material (Figure 3.23).

After leaving the hot catalyst zone, the product gas enters a small chamber made in a plate and is distributed into four micro heat exchange channels of cross-flow type arrangement. Each micro channel is surrounded by two other channels that guide the cooling gas. In addition, the micro heat exchanger plate contains guidance for cooling liquid flow.

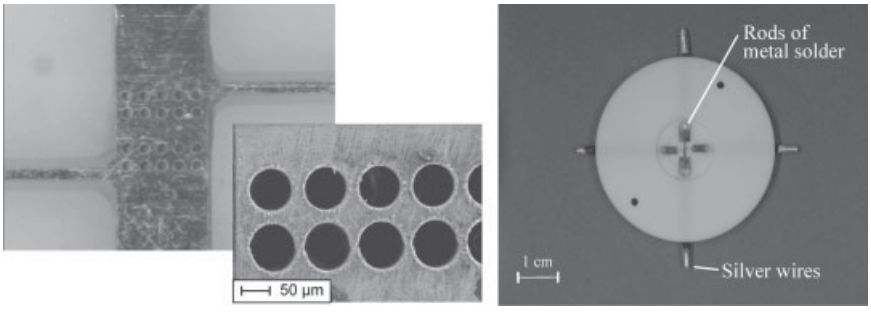

Figure 3.23 Photograph of the catalyst structure inserted in the ceramic support. Close-up of the holes in the platinum catalyst strip [63].

Reactor type	Modular integrated system with µgauze catalyst	Operating temperature	800–970 °C
Pre-heater (with micro mixer) material	Stainless steel	Operating pressure	1 bar
µGauze material; µGauze holder material	Platinum; Macor™ ceramic	Micro hole in mixer: diameter	60 µm
Micro heat exchanger material	Stainless steel	Micro hole in µgauze: diameter; depth	70 µm; 250 µm
Heating	Electrical resistance heating within the µgauze	Product gas channel width; cooling gas channel width	60 µm; 90 µm

3.2.4.2 **Reactor 19 [R 19]: Catalyst-wire-in-channel Micro Reactor**

A simple, but efficient reactor concept was developed based on the insertion of metallic wires that serve as a catalyst into a micro channel. The wire extends over the channel length and can thus be contacted electrically for heating purposes. It is sealed by graphite seals at both reactor ends. In this way, an easy, flexible and cheap concept for catalyst exchange and reactor assembly is provided.

The catalyst wires are inserted either in silicon micro channels, obtained by wet-chemical etching (Figure 3.24) [82], or in commercially available quartz glass tubes with internal dimensions in the sub-millimeter range [9]. The silicon plates are contained in a stainless-steel housing made by µEDM. The quartz glass tubes are mounted in a hollow cylindrical housing made of a machine-workable ceramic. Two separate feed holes at the reactor inlet serve for perpendicular introduction of two gas streams (like a mixing tee) which mix by impinging. An inspection window in the ceramic housing permits optical monitoring, e.g. for documenting glowing of the gas mixture.

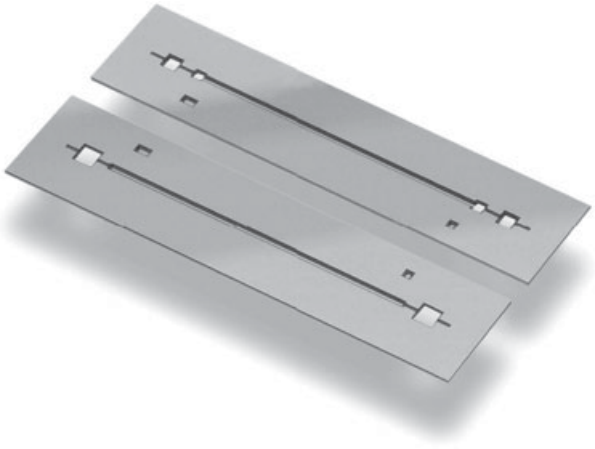

Figure 3.24 Image of the catalyst-wire-in-channel micro reactor [82].

Reactor type	Catalyst-wire-in-channel	Housing a: diameter; thickness	50 mm; 7.5 mm
Catalyst material	Platinum	Housing b: diameter; length	22 mm; 40 mm
Channel carrier a, b	Microstructured silicon platelet; quartz glass tube	Reaction channel a: cross-sectional area; depth; length	0.167 mm^2; 525 µm; 20 mm
Housing material a, b	Stainless-steel plates; ceramic hollow cylinder	Tube b: internal diameter; external diameter; length	600 µm; 6 mm; 20 mm
Operating temperature	1150 °C	Wire diameter	150 µm
Operating pressure	1 bar		

3.2.5 Thin-membrane Micro Reactors

Membrane reactors are known on the macro scale for combining reaction and separation, with additional profits for the whole process as compared with the same separate functions. Microstructured reactors with permeable membranes are used in the same way, e.g. to increase conversion above the equilibrium limit of sole reaction [8, 10, 11, 83]. One way to achieve this is by preparing thin membranes over the pores of a mesh, e.g. by thin-film deposition techniques, separating reactant and product streams [11].

3.2.5.1 Reactor 20 [R 20]: Permeable-separation Membrane Chip Reactor

The membrane in this device serves to control the flux of one gas penetrating another gas [11]. The membrane separates two gas streams while being permeable for one of the gases. By adjusting membrane thickness, gas pressure drop over the membrane and temperature, the gas flow through the membrane can be adjusted. This serves to remove the product from the reaction mixture to enhance the yield, prevents undesired complete mixing of gases, e.g. when operating in the explosive regime, allows the use of gas mixtures when only one component thereof is needed (e.g. as for syngas) or can enhance selectivity.

A special version of the membrane reactor using Pd was made for separating hydrogen and oxygen and their controlled reaction.

The design of the Pd-membrane reactor was based on the chip design of reactor *[R 10]*. The membrane is a composite of three layers, silicon nitride, silicon oxide and palladium. The first two layers are perforated and function as structural support for the latter. They serve also for electrical insulation of the Pd film from the integrated temperature-sensing and heater element. The latter is needed to set the temperature as one parameter that determines the hydrogen flow.

Microfabrication of the silicon part of the device is done by processing a silicon wafer with LPCVD and other thin-film techniques, standard photolithography, dry

and wet etching. Temperature resistors are obtained by e-beam deposition and a standard lift-off process. By special etching, very thin Pd membranes can be made. One channel is made by KOH etching (in the framework of the above-mentioned technology steps), the other by a molding process using an PDMS mold and an epoxy cast.

Reactor type	Membrane chip reactor	Membrane width	700 μm
Catalyst material	Palladium	Operating temperature	500 °C
Chip materials	Silicon; PDMS	Operating pressure	5 bar
Channel length	12 mm	Membrane width	700 μm
Pd film thickness	A few tens of μm		

3.2.6 Micro Reactors without Micro Channel Guidance – Alternative Concepts

Micro-flow processing is not an exclusive domain of micro-channel devices made by microfabrication. This approach can be applied to any packing of regular-shaped objects which results in interstices of the same internal dimensions and the same precision as given for micro channels. Obviously, interstices made from extended, but thin objects resemble best the nature of micro channels. Hence the use of filaments for constituting a micro-flow assembly was recently described [8].

It is to be expected that in the near future more of such concepts will find application, simply for cost reasons. Laboratory-scale investigations with precisely microfabricated reactors in advance of the use of such devices can give valuable information, providing a best-case scenario. From then, one can look for alternative micro-flow solutions of lower cost, higher reliability, higher flexibility and so on.

3.2.6.1 Reactor 21 [R 21]: Filamentous Catalytic-bed Membrane Reactor

This is the first reactor reported where the aim was to form micro-channel-like conduits not by employing microfabrication, but rather using the void space of structured packing from smart, precise-sized conventional materials such as filaments (Figure 3.25). In this way, a structured catalytic packing was made from filaments of 3–10 μm size [8]. The inner diameter of the void space between such filaments lies in the range of typical micro channels, so ensuring laminar flow, a narrow residence time distribution and efficient mass transfer.

In addition, the filament reactor can contain a membrane-separation function by grouping threads of filaments around an inner empty reactor core, that guides the permeate and may also increase permeation by reaction. Thus, the tube reactor constructed in such a way comprises two concentric zones, separated by a permeable Pd/Ag alloy membrane in the form of a tube. The reaction takes place in the filament zone. One product such as hydrogen is removed via the membrane and

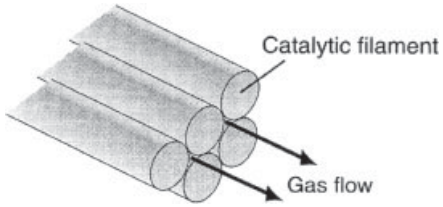

Figure 3.25 Schematic of flow guidance in a packed filament reactor [8].

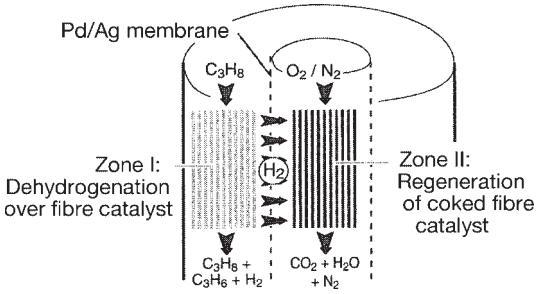

Figure 3.26 Schematic of a membrane reactor packed with filamentous catalyst [8].

reacted in the inner zone. The heat generated in such a way is needed when conducting endothermic processes in the outer zone. Also, a shift from equilibrium can result from this. The coke formed at the catalyst by the reaction can be removed by burning with air.

Reactor type	Filament-bed membrane reactor	Porosity	0.8
Catalyst material	Pt/Sn on alumina/silica filament	Specific surface area	108 $m^2\ m^{-3}$
Filament material	Aluminum borosilicate glass fibers	Membrane material	Pd/Ag (23 wt.-%)
Specific surface area of fibers	2 $m^2\ g^{-1}$ initially; 290 $m^2\ g^{-1}$ after etching	Membrane tube diameter, thickness	6 mm; 70 μm
Thread	100 bundles of 0.5 mm diameter	Quartz tube diameter, length	8.6 mm; 140 mm
Catalyst carrier	γ-alumina (100–230 $m^2\ g^{-1}$)	Operating temperature	550 °C
Catalyst	Pt/Sn	Operating pressure	0.14 MPa

3.2.6.2 **Reactor 22 [R 22]: Various Other Reactor Designs**

All other reactions designs are included in this category. Most of them comprise one multi-channel platelet embedded in a housing.