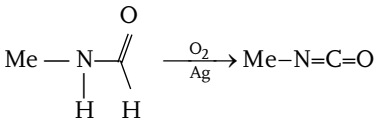
3.3.14.2 **Beneficial Micro Reactor Properties for the Synthesis of Methyl Isocyanate**
The main expectations of industrial researchers focused on improving heat management and increasing safety for hazardous process [71].

Gas-phase reaction 12 [GP 12]: synthesis of methyl isocyanate



Methyl isocyanate is obtained by oxidation of methylformamide over a silver catalyst [71].

3.3.14.3 **Typical Results**
Conversion/selectivity/yield
[GP 12] [R 15] For the synthesis of methyl isocyanate from methylformamide similar conversions as for the conventional synthesis could be determined at low selectivities [71]. One reason for this is seen in the non-ideal temperature profiles within the reaction zone of the microstructured reactor packing.

Since then, numerous industrial laboratory investigations have been carried out [71].

3.4
Hydrogenations

3.4.1
Cyclohexene Hydrogenation and Dehydrogenation

Peer-reviewed journals: [74, 122]; proceedings: [20, 73, 123–126]; sections in reviews: [90, 94, 97].

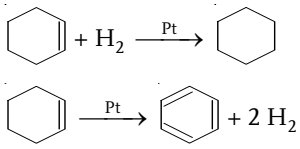
3.4.1.1 **Drivers for Performing the Cyclohexene Hydrogenation and Dehydrogenation**
The reaction of cyclohexene in the presence of hydrogen at a Pt catalyst can lead to cyclohexane via hydrogenation and benzene via dehydrogenation. The hydrogenation and dehydrogenation of cyclohexene over a Pt catalyst are model reactions for important reaction classes in the petroleum industry and thus were studied extensively by many groups (see original citation in [74]). They serve to model hydrotreating, reforming and fuel processing.

3.4.1.2 **Beneficial Micro Reactor Properties for Cyclohexene Hydrogenation and Dehydrogenation**
The present investigations were largely motivated to show the serial-screening capabilities of the reactor concept used. The speed of process-parameter changes, consumption of small volumes only, preciseness of kinetic information, and robustness were major micro reactor properties utilized.

Chemical Micro Process Engineering: Fundamentals, Modelling and Reactions
Volker Hessel, Steffen Hardt, Holger Löwe

ISBN: 3-527-30741-9

Gas-phase section 13 [GP 13]: hydrogenation and dehydrogenation of cyclohexene



3.4.1.3 Typical Results

Conversion/selectivity/yield

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, an initial conversion near 50% is found at room temperature (0.3 sccm hydrogen; 1.0 sccm argon saturated with cyclohexene vapor; 25–200 °C; 1 bar) [74]. An increase in temperature up to 55 °C leads to almost 100% conversion. At 120 °C and higher, conversion declines steeply, independent of temperature and only as a function of time (Figure 3.55). Conversion at 200 °C after several hours of operation was 55%, so nearly matching the initial room-temperature activity.

This room-temperature result followed by the steep increase in conversion up to 55 °C is correctly predicted by a reactor model [74]. The decline in conversion is not anticipated and is not due to equilibrium effects.

Product selectivities for cyclohexane (hydrogenation path) and benzene (dehydrogenation path) were monitored as a function of temperature (0.3 sccm hydrogen; 1.0 sccm argon saturated with cyclohexene vapor; 25–200 °C; 1 bar) [74]. Initial selectivities were about 60% for cyclohexene and 40% for benzene, but displayed transient behavior, i.e. shifted to larger cyclohexane contents with time. At 60 °C, selectivities are stable, as are the conversions. Now, 100% cyclohexane is formed.

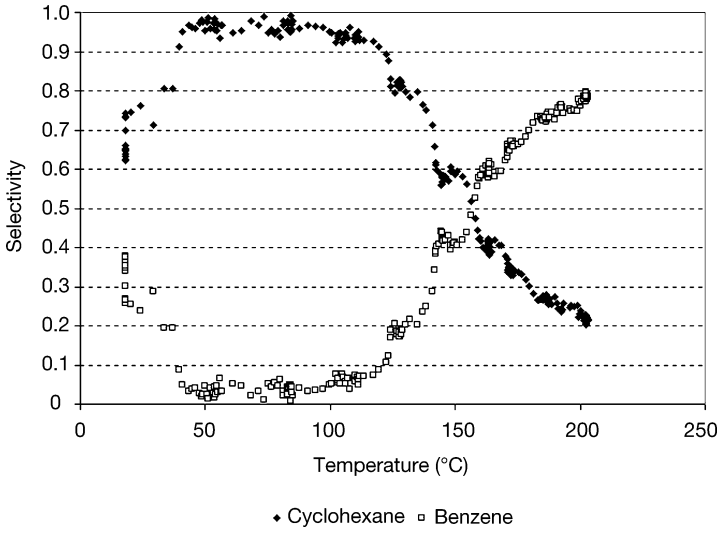


Figure 3.55 Selectivity of cyclohexane and benzene depending on reaction temperature [74].

At temperatures exceeding 120 °C, selectivity shifts to the formation of benzene. This shift starts before the conversion decline, and hence is not related solely to it. At 200 °C, 80% benzene is generated.

Temperature dependence

[GP 13] [R 12] The results determined by increasing temperature via ramps are discussed in the previous section [74].

See also the section Characteristic inner diameter.

Transient catalyst behavior

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, the initial transient shows that the catalyst is readily active for conversion of cyclohexene [74]. This shift is explained by establishing steady-state conditions on the catalyst surface. It needs time until the surface of the catalyst is covered by chemisorption of cyclohexene species. Hence local areas of the surface can promote dehydrogenation for a while until coverage is completed. The decline in catalyst activity is explained by an irreversible change of the catalyst surface. Irreversible species adsorption blocks the active catalyst sites and leads to poisoning.

See also the section Characteristic inner diameter.

Micro-channel dimensions

[GP 13] [R 12] A parametric study on the impact of channel depth (Figure 3.56) and length on conversion, based on a reaction probability model, was investigated for the dehydrogenation of cyclohexane to benzene, using literature-reported reaction probabilities for various Pt-carrier catalysts [10]. As expected, the channel dimensions have a large impact on conversion owing to the role of diffusion.

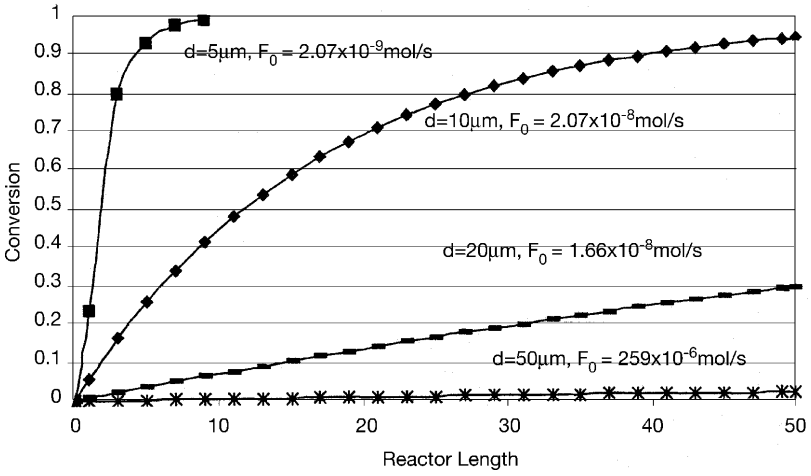


Figure 3.56 Results of a parametric study on the impact of channel depth on benzene conversion. Reaction probability = 10^{-6}; $T = 200$ °C; $p_{in} = 1.1$ atm; $p_{out} = 1$ atm [10].

For certain process parameters, complete conversion is achieved in a 5 μm channel, whereas zero conversion is given for a 50 μm channel. Similarly, the catalyst activity has a strong effect.

Hydrogen/cyclohexene partial pressure

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, the benzene yield is the higher the lower is the ratio of partial pressures of the two reactants $p_{H_2}/p_{C_6H_{10}}$ ($p_{H_2}/p_{C_6H_{10}}$: 0.5–27; 0.3, 0.6, 1.0 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar) [74]. This is in line with the chemical equilibrium favoring dehydrogenation, at low hydrogen contents. In turn, high hydrogen amounts favor hydrogenation. Not evident at first sight, dehydrogenation does not occur unless small initial hydrogen contents are available. This is explained by the need to condition the catalyst surface with hydrogen.

The cyclohexane yield, different from benzene, depends only weakly on the $p_{H_2}/p_{C_6H_{10}}$ ratio [74].

See also the section Characteristic inner diameter.

Residence time

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, the benzene yield is higher with increasing residence time (0.3–0.3 sccm hydrogen; 0.3, 0.6, 1.0 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar; 120–570 ms) [74]. The cyclohexane yield has no strong effect. Hence increasing the reactor length at constant flow will result in more benzene formation (Figure 3.57).

See also the section Characteristic inner diameter.

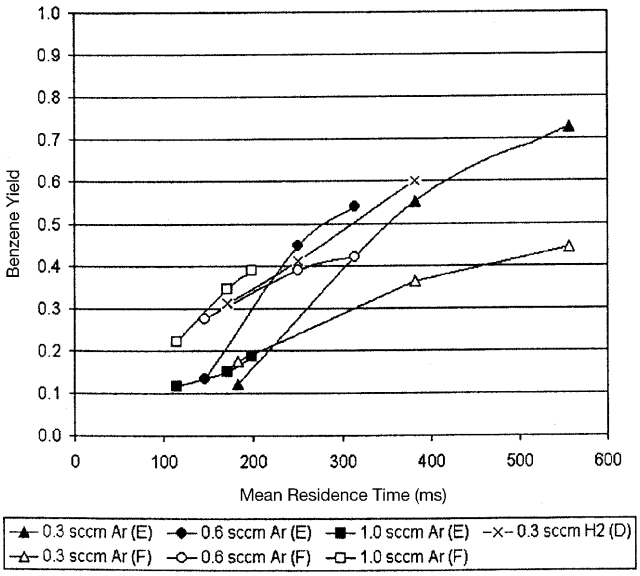


Figure 3.57 Strong effect of residence time on benzene yield [74].

Space–time yield

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, the space–time yield strongly depends on the concentration of both reactants [74]. Increasing the hydrogen partial pressure reduces the benzene yield (p_{H_2}: 50–580 Torr; 0.3, 0.6, 1.0 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar); naturally, increasing the cyclohexene concentration has the opposite effect (0.3 sccm H_2; $p_{H_2}/p_{C_6H_{10}}$: 20–80 Torr; 0.3, 0.6, 1.0 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar). Cyclohexane formation has no distinct dependence on either reactant.

The maximum space–time yield observed at 200 °C is $8.0 \cdot 10^{-4}$ kg $m^{-2}_{(cat)}$ min^{-1} for benzene and $4.3 \cdot 10^{-4}$ kg $m^{-2}_{(cat)}$ min^{-1} for cyclohexane.

See also the section Characteristic inner diameter.

Reactant consumption/environmental

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, only 3.1 g of cyclohexene were consumed in over 140 h of reaction [74]. Such designed silicon micro reactors in principle could be disposable, assuming economic mass fabrication and the installation costs of the fluidic peripherals to be relatively low. Overall, this implies an economical solution for process development and catalyst testing.

Only 32 mg of cyclohexene were needed for conducting an 18 h experiment [73].

Characteristic inner diameter

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, the channel width was varied to study the impact of such enhanced mass transport on the conversion or selectivity as a function of various process parameters [74]. Two different reactor designs were employed, having micro channels of 100 and 5 μm width, respectively. The number of channels was adjusted to the ratio of widths, so that 39 and 780 channels were operated in parallel, respectively.

Concerning the dependence of conversion on mean residence time, the 5 μm channels show only a slight dependence, the 100 μm-channel whereas show a distinct increase in conversion with increasing residence time (0.1-, 0.3-, 1.0 sccm hydrogen; 0.3, 0.6, 1.0 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar; 150–650 ms) [74].

Concerning the dependence of conversion on the partial pressure ratio $p_{H_2}/p_{C_6H_{10}}$, the 5 μm channel show only a slight downwards slope, the 100 μm-channel whereas show a steep upwards slope with increasing ratio (0.1 sccm hydrogen; 0.3, 0.6 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar; $p_{H_2}/p_{C_6H_{10}}$: 1–27)[74]. At low ratios, both reactors have an initial upwards slope. Under the conditions applied, benzene formation dominates.

Concerning the dependence of selectivity towards cyclohexane and benzene on the partial pressure ratio $p_{H_2}/p_{C_6H_{10}}$, the 5 and 100 μm channels show qualitatively similar behavior. However, the 5 μm channels yielded similar contents of cyclohexane and benzene over the range of ratios studied, whereas the 100 μm-chan-

nels give about four times more benzene than cyclohexane (0.3, 1.0 sccm hydrogen; 0.3, 1.0 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar; $p_{H_2}/p_{C_6H_{10}}$: 1–27) [74].

Concerning the dependence of selectivity towards cyclohexane and benzene on temperature, the 5 and 100 μm channels show qualitatively similar behavior (0.3 sccm hydrogen; 1.0 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar; 25–210 °C) [74]. The slopes are shifted to higher temperatures for the 5 μm channels. In the region of constant selectivity (50–100 °C), a slightly higher benzene selectivity and slightly lower cyclohexane selectivity is found for the 5 μm channels.

Concerning the dependence of benzene space–time yield on cyclohexene partial pressure, the 5 μm channels show nearly constant behavior, whereas the 100 μm channels display a strongly increasing space–time yield with partial pressure (0.3, 1.0 sccm hydrogen; 0.3, 0.6, 1.0 sccm argon saturated with cyclohexene vapor; 200 °C; 1 bar; $p_{H_2}/p_{C_6H_{10}}$: 20–80) [74].

Mechanistic analysis

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, there have been mechanistic discussions on intermediate species formation [74]. Also, it is supposed that carbonaceous coverage, which is larger in 5 than in 100 μm channels, reduces benzene selectivity with decreasing channel diameter.

Kinetic parameters

[GP 13] [R 12] For the reaction of cyclohexene and hydrogen using a sputtered Pt catalyst on silicon, the reaction probability ($1 \cdot 10^{-6.2}$) and turnover frequency (1.7 molecules per site pere second) were determined and found to be in good agreement with other hydrogenation reactions (0.1 sccm hydrogen; 0.1 sccm argon saturated with cyclohexene; 91% conversion; 200 °C; 1.01 bar) [73].

Conversion/selectivity/yield

[GP 13] [R 22] Using a sputtered platinum layer, studies on the impact of the flow regime in micro channels on conversion were done (8 ccm h^{-1} of condensed cyclohexane; 200 °C; feed and exit pressures 150 000 Pa and 1 hPa, respectively) [127]. During flow passage, different successive regimes take place: continuum flow, quickly changing to slip flow, followed by Knudsen flow. The extent of conversion depends on the regime due to the number of reactant–catalyst collisions. This was demonstrated by regionally sputtering the catalyst so that reaction is conducted mainly under one specific regime. Channels coated in their front part show no conversion of cyclohexane (slip conditions), whereas channels coated more downstream have 2–3% conversion (Knudsen conditions). This is consistent with the expected number of collisions of the molecules with the catalyst in each regime. Making the same experiment with a fully coated channel consequently results in 2–3% conversion.

3.4.2
Hydrogenation of *c,t,t*-1,5,9-Cyclododecatriene to Cyclododecene

Peer-reviewed journals: [38, 39]; proceedings: [18, 84, 128–130]; PhD thesis: [131]; sections in reviews: [87, 88, 90, 94–97, 100].

3.4.2.1 Drivers for Performing the Hydrogenation of *c,t,t*-1,5,9-Cyclododecatriene to Cyclododecene

Selective gas-phase reactions of unsaturated hydrocarbons such as *c,t,t*-1,5,9-cyclododecatriene, 1,5-cyclooctadiene and benzene are examples of reactions that are highly exothermic, mass-transfer limited and have high reaction rates [18, 130]. For bench-scale experiments, heat transfer problems can usually be neglected as only dilute mixtures with low reactant concentrations are used. Instead, mass transfer can be studied on the laboratory-scale. For example, the hydrogenation of *c,t,t*-1,5,9-cyclododecatriene to the corresponding monoene needs kinetically controlled conditions to diminish the formation of the most stable product cyclododecane [18].

The selective hydrogenation of the three compounds mentioned above to their corresponding cyclic monoalkenes is of industrial interest, as the latter can be selectively reacted to more valuable products. For example, cyclododecene can be finally converted to nylon or polyalkenamers.

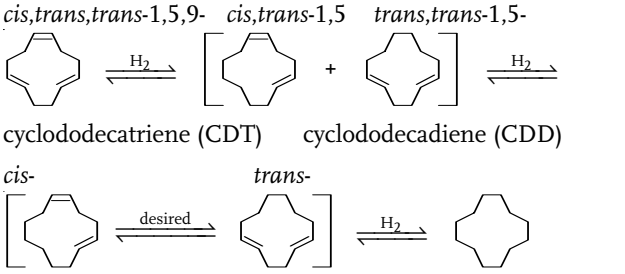
3.4.2.2 Beneficial Micro Reactor Properties for the Hydrogenation of *c,t,t*-1,5,9-Cyclododecatriene to Cyclododecene

Beneficial micro reactor properties mainly refer to exerting process control over residence time as a key for improving a partial reaction in a consecutive sequence. Similar efforts have also been made for oxidations, but focused more on improving heat transfer (see also Section 3.3.1).

In addition, the studies on the hydrogenation of *c,t,t*-1,5,9-cyclododecatriene gave valuable insight into the way of preparing catalysts and in the impact of the catalyst shape and packing. Here, pioneering efforts were made, influencing later studies.

Together with the ammonia oxidation (see Section 3.3.3), this reaction was the first published, giving substantial details on how micro reactor properties affect the performance of gas-phase reactions.

Gas-phase reaction 14 [GP 14]: hydrogenation of *c,t,t*-1,5,9-cyclododecatriene to cyclododecene



Pd/Al_2O_3 catalyst.

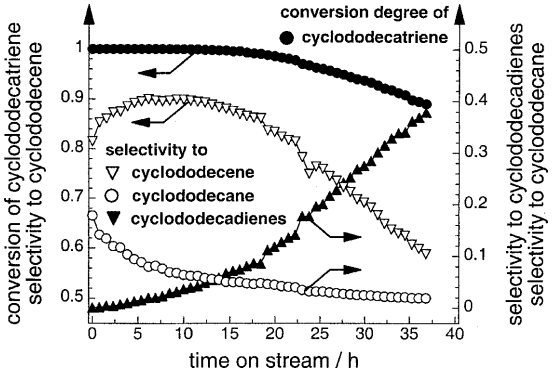


Figure 3.58 Experimental results for partial gas-phase hydrogenation of *c,t,t*-1,5,9-cyclododecatriene in a Pt micro-channel reactor [130].

3.4.2.3 Typical Results

Conversion/selectivity/yield

[GP 14] [R 4] On a Pd catalyst on nanoporous alumina (via anodic oxidation), time-on-stream measurements (40 h) gave a maximum selectivity of cyclododecene of 85–90% (Figure 3.58) (p_{CDT} = 0.11 kPa; p_{H_2} = 0.33 kPa; p = 110 kPa; 150 °C; 87 ms) [130]. The formation of cyclododecadiene increases from 0% initially to 40% after 37 h. In the same period, cyclododecane selectivity decreases from about 40 to 10%.

Time-on-stream

[GP 14] [R 4] On a Pd catalyst on nanoporous alumina (via anodic oxidation), time-on-stream measurements (80 h) showed constant complete *c,t,t*-1,5,9-cyclododecatriene conversion over the whole period (see Table 3.4) [128]. Hydrogen conversion decreased in this period, whereas the selectivity to the cyclic mono-alkene cyclododecene increased. Consequently, the selectivity of the fully hydrogenated product cyclododecane decreased.

Table 3.4 Reaction parameters for the performance of *c,t,t*-1,5,9-cyclododecatriene hydrogenation.

Temperature	393 K	Total pressure[a]	110 kPa
Total flow rate	7–26 l h^{-1}	Partial pressure of CDT	110 Pa
Molar flow rate	0.33–1.2 mmol/h	Partial pressure of H_2	330 Pa

a Equilibrated by nitrogen.

Pore length of anodically oxidized support

[GP 14] [R 4] On a Pd catalyst on nanoporous alumina (via anodic oxidation), the impact of the pore length on selectivity and conversion was determined (see also Figure 3.59) [128]. For this purpose, two pieces of activated aluminum wires which differed in pore length were compared. With increasing overall conversion, the

cyclododecene selectivity increased for both pore lengths. However, at very high concentrations exceeding 90%, a different behavior is found. For the short-pore-length pieces, selectivity becomes constant; for long pores, selectivity decreases.

A too long residence time in the catalyst zone, the nanopore, is said to be responsible for this difference. The species with more double bonds than cyclododecene displace cyclododecene readily from the active sites owing to the stronger interactions of their π-orbitals with the catalyst. This prevents further hydrogenation of cyclododecene to cyclododecane. However, if the concentrations of these species are too low, then total hydrogenation to cyclododecane will occur. This will happen when diffusion in the pores is no longer as fast as the reaction and adsorption/desorption processes, i.e. when the diffusion path is too long as a result of too long pores.

Flow pattern regularity – benchmarking to fixed beds

[GP 14] [R 4] On a Pd catalyst on nanoporous alumina (via anodic oxidation), various catalyst carriers other than microchannel based were tested [128] (see also [18] for a first description). The selection included conventionally coated granules, pieces of activated aluminum wires and fragments of activated aluminum foils (see Table 3.5). The total of four carriers differ in pore system, distribution of the catalytically active component and type of packing. Micro-channel platelets are regular with regard to all these features, whereas granules are irregular. The wire pieces and foil fragments have uniform pores and catalyst distribution, but may suffer from their irregular fixed-bed packing.

For the four catalyst carriers, cyclododecene yield was monitored versus selectivity (see Table 3.4) [128]. The yield when using the conventional granules decreases from 62 to 44% within the range of conversions investigated. For the foil fragments, a nearly constant selectivity of 73% was found, hence regular pores and uniform catalyst distribution have an impact. In addition, foils pack more densely than the granules probably give more uniform flow paths with less dead volume. Wire pieces and the micro-channel reactor both give notably better results than the

Table 3.5 Different types of catalysts used for the hydrogenation of *c,t,t*-1,5,9-cyclooctatriene and classification of these. Concerning the latter, each of the left rows is a "yes" function, the right rows serve as "no" function [128].

Catalyst	Type of the catalyst	Pore system		Cross section of catalyst	Distribution of catal. active component		Fixed bed		Cross section of fixed bed
CAT A	conventionally coated granules		+			+		+	
CAT B1	pieces of activated Al-wires	+			+			+	
CAT B2	pieces of activated Al-foils	+			+			+	
CAT C	stack of activated and microstructured Al-foils	+			+		+		

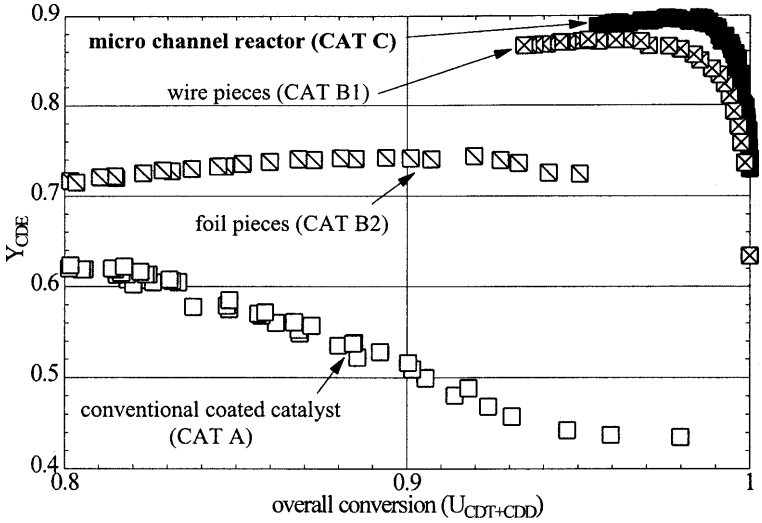


Figure 3.59 Cyclododecene yield vs conversion for different types of catalysts, respectively flow guidances consisting of three fixed beds and one micro-channel passage. Reaction parameters: see Table 3.4. Pore lengths: CAT A, 240 µm; CAT B1, 37 µm; CAT B2, 37 µm; CAT C, 37 µm [128].

foils; the micro-channel reactor is slightly better than the wires. Nearly constant selectivity for a small range is found, decreasing steeply at very high conversions. Wires give still tighter packing than foils which explains their superior performance. Compared with this, the impact of the more uniform flow pattern in the micro channels is relatively small, but exists.

Simulation of concentration profiles in the catalyst carrier's nanopores

[GP 14] [R 4] Using an effective kinetic approach, simulations on the concentration profiles in nanopores, which were models for the alumina support used in the above experiments, were carried out [132]. 'Representative' pores were used for the simulation based on average parameters of the real pores, such as radii and lengths. These virtual pores were grouped in a highly symmetric arrangement. Simulations and experiments matched only for data obtained at the reactor exit.

3.4.3 Hydrogenation of 1,5-Cyclooctadiene to Cyclooctene

Proceedings: [130]; sections in reviews: [90, 95, 97, 100].

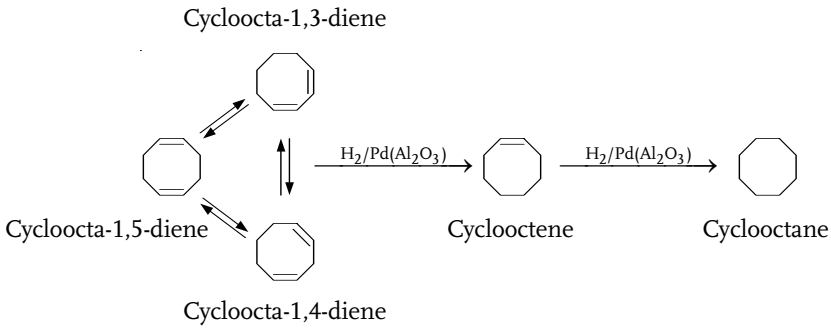
3.4.3.1 Drivers for Performing the Hydrogenation of 1,5-Cyclooctadiene to Cyclooctene

See Section 3.4.2.1.

3.4.3.2 Beneficial Micro Reactor Properties for the Hydrogenation of 1,5-Cyclooctadiene to Cyclooctene

See Section 3.4.2.2.

Gas-phase reaction 15 [GP 15]: hydrogenation of 1,5-cyclooctadiene to cyclooctene



3.4.3.3 Typical Results

Deactivation

[GP 15] [R 4] The selective hydrogenation of 1,5-cyclooctadiene (COD) at a Pd catalyst is more facile than for *c,t,t*-1,5,9-cyclododecatriene, since no deactivation during a catalytic run is found [130].

Hydrogen partial pressure

[GP 15] [R 4] By increasing the partial pressure ratio of hydrogen to COD from 0.75 to 2, cyclooctene selectivity at a Pd catalyst decreases from nearly 100 to 88%, while conversion increases from 80 to nearly 100% (Figure 3.60) (p_{COD} = 220 Pa; p = 110 kPa; 150 °C; 87 ms; 12 l h^{-1}) [130].

Addition of carbon monoxide

[GP 15] [R 4] By increasing the concentration of carbon monoxide from 0 to 400 ppm, the cyclooctene yield at a Pd catalyst increases from 83 to 98% (p_{COD} = 330 Pa; p_{H_2} = 660 Pa; p = 110 kPa; 150 °C; 87 ms; 12 l h^{-1}) [130].

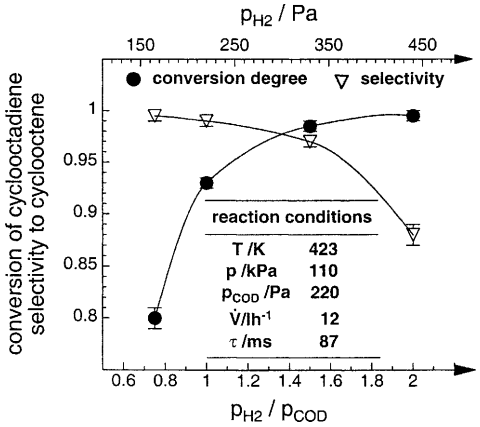


Figure 3.60 Gas-phase hydrogenation of 1,5-cyclooctadiene.
Conversion and selectivity depending on hydrogen partial pressure [130].

Residence time

[GP 15] [R 4] By increasing the residence time from 35 to 115 ppm, the cyclooctene conversion at a Pd catalyst increases from 75 to nearly 100% (Figure 3.61), while selectivity decreases from 99.5 to 98% (p_{COD} = 110 Pa; p_{H_2} = 110 Pa; p = 110 kPa; 150 °C) [130].

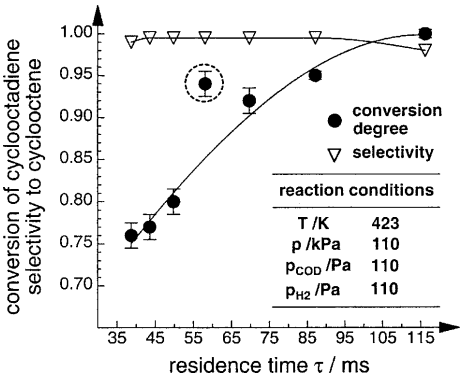


Figure 3.61 Increase of conversion of cyclooctadiene and nearly constant selectivity for cyclooctene with increasing residence time in a Pd micro-channel reactor [130].

Maximization of production

[GP 15] [R 4] By increasing the flux of 1,5-cyclooctadiene from 0.5 to 5.5 mmol h^{-1}, the cyclooctene yield at a Pd catalyst decreases from 98 to 84%, while production increases from 50 to nearly 500 mg h^{-1} (p_{H_2}/p_{COD} = 2; p = 110 kPa; 150 °C; 87 ms; 12 l h^{-1}) [130].

3.4.4 Hydrogenation of Benzene

Proceedings: [84]; sections in reviews: [90, 95, 97, 100].

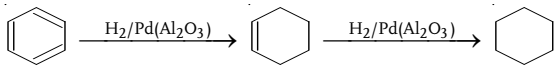
3.4.4.1 Drivers for Performing the Hydrogenation of Benzene

See Section 3.4.2.1.

3.4.4.2 Beneficial Micro Reactor Properties for the the Hydrogenation of Benzene

See Section 3.4.2.2.

Gas-phase reaction 16 [GP 16]: hydrogenation of benzene



3.4.4.3 Typical Results

Catalyst variation

[GP 16] [R 4] An Ru–Zn catalyst was used for benzene hydrogenation, as a Pd-coated micro-channel reactor could not be applied successfully ($p_{benzene}$ = 110 Pa;

$p_{methanol}$ = 330 Pa; p_{H_2} = 44 kPa; p = 110 kPa; 80 °C; 235 ms) [130]. Methanol was added to the reaction mixture to act as diffusion barrier on the catalyst surface to prevent re-adsorption of the intermediate cyclohexene. The time-on-stream behavior over a period of 14 h was observed. The benzene conversion decreased rapidly and fell below steady-state conditions. Selectivity increased initially, until reaching a plateau of 36%.

[GS 16] [R 14] Sputtered and impregnated Pt catalysts were compared (Figure 3.62) regarding their reaction rates (< 1 ml min^{-1}; 100–150 °C; 100–600 ms) [76]. A sol–gel γ-alumina-based catalyst was notably more active than its sputtered counterpart. The temperature dependence of the reaction rate of both types of catalysts was also revealed.

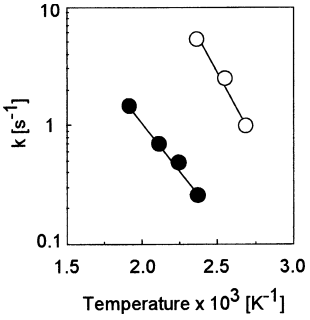


Figure 3.62 Comparison of reaction rates for hydrogenation of benzene in micro reactors: (○) sputtered Pt catalyst; (●) impregnated Pt catalyst [76].

Catalyst deactivation

[GP 16] [R 14] No catalyst deactivation was observed for sputtered and impregnated Pt catalysts in a Si chip reactor in the limits of the reaction conditions applied (< 1 ml min^{-1}; 100–150 °C; 100–600 ms) [76].

Kinetics

[GP 16] [R 14] First-order kinetics of the reaction rates were found for sputtered and impregnated Pt catalysts (< 1 ml min^{-1}; 100–150 °C; 100–600 ms) [76].

3.5 Dehydrogenations

3.5.1 Non-oxidative Dehydrogenation of Propane to Propene

Proceedings: [8]; sections in review: [90, 95, 97, 100, 110].

3.5.1.1 Drivers for Performing the Non-oxidative Dehydrogenation of Propane to Propene

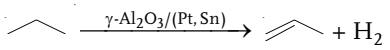
The non-oxidative propane dehydrogenation is highly exothermic (129 kJ mol^{-1} at 550 °C and 0.14 MPa) and limited by the thermodynamic equilibrium (22% con-

version under the same conditions) (see [8] and original citations therein). Coke formation results in rapid catalyst deactivation.

3.5.1.2 Beneficial Micro Reactor Properties for the Non-oxidative Dehydrogenation of Propane to Propene

The non-oxidative propane dehydrogenation served here as model reaction having specific limitations (see Section 3.5.1.1) to validate a completely novel reactor concept. The main benefit stems from combining reaction and separation. Using micro-scale flow serves for ensuring high mass transfer, providing low pressure drop and avoiding coke formation (see Section 3.5.1.3).

Gas-phase reaction 17 [GP 17]: dehydrogenation of propane to propene



3.5.1.3 Typical Results

Hydrodynamics – residence time distribution

[GP 17] [R 21] The exit-age distribution for a filament-bed reactor (i.d.: 7 μm; porosity: 0.8), which was used for propane dehydrogenation, was compared with two random beds (Figure 3.63), differing in shape and size (from 100 μm to 1.5 mm) (response to switch of 30 Nml min^{-1} 10% argon/nitrogen to pure nitrogen; 25 °C; 0.1 MPa; tube-i.d.: 15 mm; tube length: 230 mm) [8]. Under identical conditions, the packed beds have a much broader residence time distribution than the structured filamentous packing, providing relatively well-defined flow conduits.

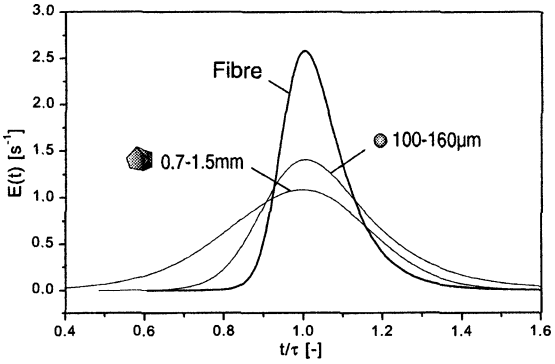


Figure 3.63 Comparison of the residence time distribution for packed-bed and filamentous-bed reactors [8].

Pressure drop

[GP 17] [R 21] The pressure drop in a filamentous-bed reactor (i.d.: 7 μm; porosity: 0.8), which was used for propane dehydrogenation, was compared with a randomly packed powder bed (sphere diameter from 100 to 160 μm) of similar hydraulic dimensions [8]. The filament-bed reactor has a pressure drop about five times lower [120 ml (STP) min^{-1} nitrogen; 25 °C; 1 bar]. The hydraulic diameter of the filament

bed of 70 µm is of the same order as the typical sizes of micro channels of micro reactors.

Benchmark to powder fixed-bed reactor: conversion/selectivity

[GP 17] [R 21] Similar conversions of 24–22% were found in time-on-stream (2 h) measurements for a quartz-tube reactor (i.d.: 6 mm) with powder fixed bed (sphere diameter from 100 to 160 µm) and a filamentous-bed reactor (i.d.: 7 µm; porosity: 0.8; 550 °C; 0.14 MPa; GHSV = 1161 h^{-1}; 3.1 s; m_{cat} = 0.375 g) [8]. The thermodynamic equilibrium (22%) was reached (Figure 3.64). Selectivity was slightly better for the filament-bed reactor. During time-on-stream, selectivity increased slightly to 95%, then being about 7% better than the powder bed. This was explained by a broader residence time distribution in the latter case, favoring cracking reactions of propane. Deactivation due to coke formation is slow for both types of reactors.

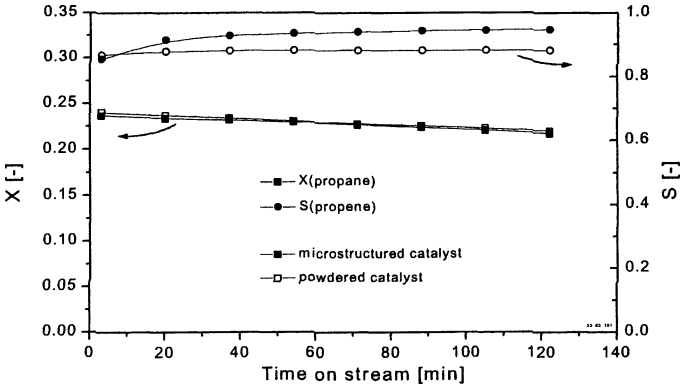


Figure 3.64 Similar conversion for propane was found for the powder fixed-bed and the filamentous-bed reactors, however, selectivity was better for the filamentous-bed reactor [8].

Removal of products by membrane separation

[GP 17] [R 21] If a membrane separation function is added to the filamentous-bed reactor (i.d.: 7 µm; porosity: 0.8), the performance can be further improved [8]. This is achieved by placing the filaments in an outer shell of a tube and separating them from air guidance, through the inner cylindrical conduit formed in that way, by a Pd/Ag membrane, permeable to hydrogen. In this way, hydrogen is removed from the reacting zone and burned to give water.

The measured conversion of 30% exceeds the equilibrium value (22%) for the first 30 min time-on-stream (550 °C; 0.14 MPa; GHSV = 1161 h^{-1}; 3.1 s; m_{cat} = 0.375 g) [8]. Owing to the removal of hydrogen, however, coke removal is more likely so that catalyst deactivation is more pronounced (Figure 3.65). After 140 h, conversion drops to about 12%, now being lower in performance than the powder bed. Propene selectivity is enhanced in the membrane reactor to 97%. Owing to the absence of hydrogen, hydroisomerization and hydrogenolysis reactions are reduced.

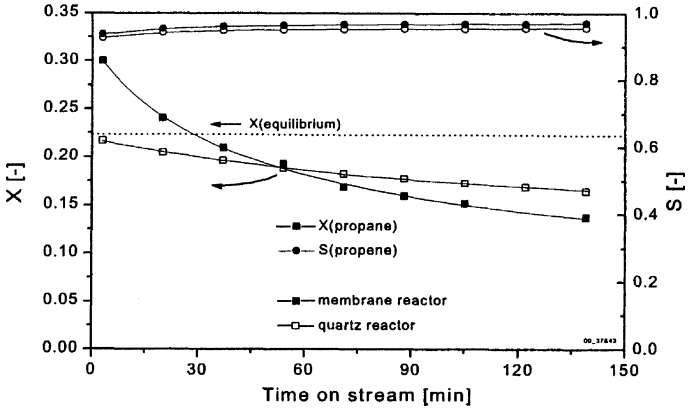


Figure 3.65 Measured enhancement of propane conversion and increased propene selectivity in a membrane reactor equipped with a filamentous catalyst [8].

3.5.2 Oxidative Dehydrogenation of Propane to Propene

Peer-reviewed journals: proceedings: [13]; sections in reviews: [90, 95, 97, 100, 110].

3.5.2.1 Drivers for Performing the Oxidative Dehydrogenation of Propane to Propene

The oxidative propane dehydrogenation is well investigated and also a highly exothermic reaction. In a fixed-bed reactor, steep temperature gradients are observable and the conversion of propane and selectivity of the reaction are strongly determined by temperature and total flow rate [133].

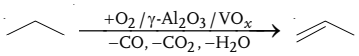
Potential benefits when performing combined oxidative and non-oxidative dehydrogenations by periodic operation have been briefly reviewed [13].

3.5.2.2 Beneficial Micro Reactor Properties for the Oxidative Dehydrogenation of Propane to Propene

The main aspect of the non-periodic investigations was the avoidance of hot-spot formation and the impact of hot spots on the reactor performance. This also allowed a detailed comparison of catalyst performance.

In addition, beneficial properties of micro reactors for periodic processing have been envisaged, details of which are given in [12, 13, 85].

Gas-phase reaction 18 [GP 18]: Oxidative dehydrogenation of propane



3.5.2.3 Typical Results

Conversion/selectivity/yield

[GP 18] [R 6] The selectivity/conversion behavior over a VO_x/Al_2O_3 catalyst was compared for a multi-platelet stack micro-channel reactor and a conventional fixed bed

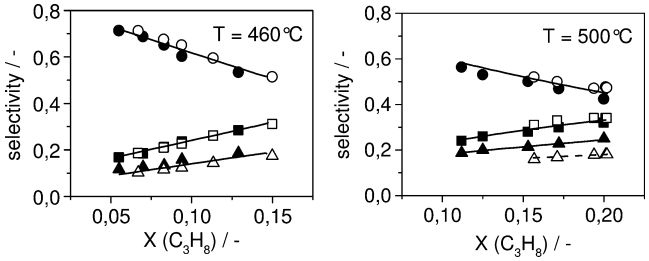


Figure 3.66 Selectivities of propane conversion for a fixed-bed (open symbols) and a micro-channel reactor (closed symbols) for two different inlet temperatures. $C_3H_8/O_2/Ne = 0.3/0.15/0.55$, $F_{tot} = 150$ ml min^{-1}. C_6H_6 (●,○); CO (■,□); CO_2 (▲,△) [133].

at two inlet temperatures (Figure 3.66) [133, 134]. Similar curves resulted, mainly showing that the catalyst was the determining factor for reactor performance. At a 460 °C inlet temperature, selectivity drops from more than 70 to about 50% with increasing conversion (from 5 to 15%). In turn, carbon monoxide and dioxide selectivities increase. To achieve similar conversion, the flow rate has to be varied.

Inlet temperature

[GP 18] [R 6] Experiments at fixed flow rate allowed a comparison of reactor performance over a VO_x/Al_2O_3 catalyst of a multi-platelet-stack micro-channel reactor and a conventional fixed bed as a function of the inlet temperature [133, 134]. The conversions rise steeply with increasing inlet temperature (Figure 3.67).

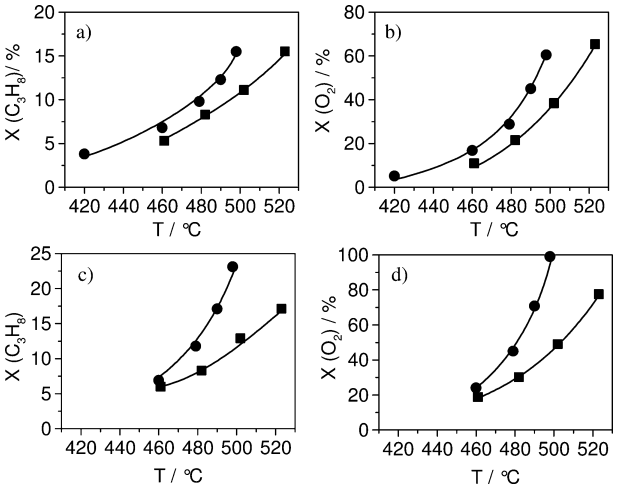


Figure 3.67 Steep increase of propane and oxygen conversions with increasing reactor inlet temperature. (●) Fixed-bed reactor; (■) micro-channel reactor. $C_3H_8/O_2/Ne = 0.3/0.15/0.55$, $F_{tot} = 150$ ml min^{-1} (a,b); $C_3H_8/O_2/Ne = 0.5/0.25/0.25$, $F_{tot} = 120$ ml min^{-1} (c,d) [133].

It turned out that in all cases investigated, higher propene and oxygen conversions result for the fixed-bed reactor. Propene conversions, for instance, differ by as much as about 10%. Measurements of local temperatures confirmed that hot spots are responsible for this difference; hence the real reaction temperatures may differ considerably from the inlet temperature.

Hot spots

[GP 18] [R 6] When using a VO_x/Al_2O_3 catalyst in a fixed bed, remarkable differences between inlet temperature and maximum temperature were found [133, 134]. Depending on the reaction conditions, hot spots ranging from 3 to 100 K were detected (Figure 3.68). Even when using diluted gases, the hot spots are as large as 20 K. Hence no isothermal operation could be established.

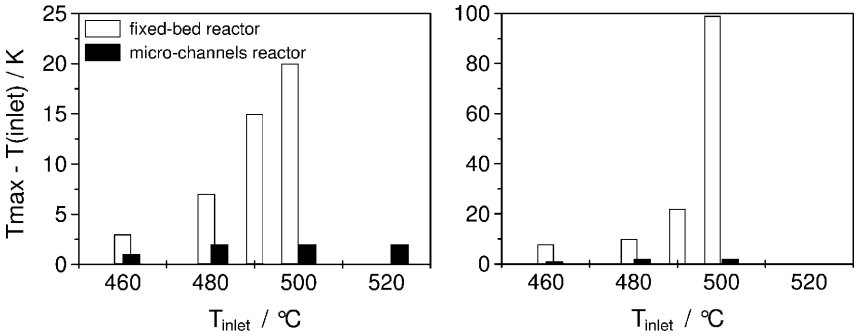


Figure 3.68 Comparison of rise in temperature between inlet and maximum in a micro-channel and fixed-bed reactor.
$C_3H_8/O_2/Ne = 0.3/0.15/0.55$, $F_{tot} = 150$ ml min^{-1} (left);
$C_3H_8/O_2/Ne = 0.5/0.25/0.25$, $F_{tot} = 120$ ml min^{-1} (right).

In turn, using the micro-channel reactor, isothermal processing was achievable for nearly all conditions applied, giving a maximum temperature increase of 2 K [133, 134].

Propene and oxygen partial pressure

[GP 18] [R 6] The influence of the propene and oxygen partial pressure on the space–time yield using a VO_x/Al_2O_3 catalyst was investigated [133, 134]. The fixed bed and the micro reactor give similar performance at an inlet temperature of 460 °C, whereas some differences were observed at higher temperature (fixed bed: 490 °C; micro reactor: 502 °C). At 460 °C, the space–time yield increased linearly (maximum: 0.3 mol kg^{-1} s^{-1}) on increasing the partial pressure of propene from 10 to 50 kPa. For the same temperature, the impact of oxygen partial pressure is less remarkable for both reactors. At higher temperatures (490, 502 °C), more carbon dioxide formation was noted for the micro reactor when increasing the propene partial pressure, which is explained by unspecific total oxidation due to the stainless-steel walls having a large specific area. For increasing oxygen partial pressure at the same temperatures, carbon monoxide formation in the micro reactor is high.

Periodic concentration cycling
[GP 17] [R 6] For a short description of potential process details and catalysts, see [13] (no experimental results are given there).

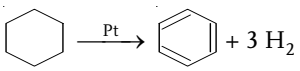
3.5.3
Dehydrogenation of Cyclohexane to Benzol

Proceedings: [127].

3.5.3.1 Drivers for Performing the Dehydrogenation of Cyclohexane
The reaction served as a model reaction for initial experimentation and modeling studies [127].

3.5.3.2 Beneficial Micro Reactor Properties for the Dehydrogenation of Cyclohexane
The studies referred mainly to determining conversion, exhibiting a relationship between pressure drop and internal dimensions, and analyzing collisions functions from kinetic theory under different flow regimes (slip flow; Knudsen) [127].

Gas-phase reaction 19 [GP 19]: Cyclohexane dehydrogenation to benzene



The dehydrogenation of cyclohexane to benzene is an endothermic process (206 kJ mol^{-1}), e.g., performed at 200 °C. The equilibrium conversion amounts to 18.9% [127].

3.5.3.3 Typical Results
Conversion/selectivity/yield
[GP 19] [R 22] Only 2–3% conversion was found at a sputtered catalyst (200 °C; 8 ml h^{-1} condensed liquid; slightly more than 1 s). The fluid enters the micro channel in continuous flow, passes through slip and transitional flow to Knudsen regime. Further details on the activity of the catalyst as a function of the channel length are also provided in [127].

3.6
Substitutions

3.6.1
Chlorination of Alkanes

Proceedings: [29]; sections in review: [95, 97, 100]; trade literature: [30].

3.6.1.1 Drivers for Performing the Chlorination of Alkanes
An industrial investigation studied the radical chlorination of alkanes in micro heat exchangers to analyse thermal effects on radical production [29, 30]. It was known from prior studies in a reactor consisting of two conventional tubes, one for

pre-heating and one for heating, each placed in an oven, that too slow approaching reaction temperature and over-heating are detrimental for reactor performance, i.e. decreasing conversion and space–time yield. Accordingly, a micro reactor with fast thermal ramping and without overshoots for the process fluids is required. In this way, the radicals formed can be most efficiently utilized for reaction, without losses, e.g. by recombination.

3.6.1.2 Beneficial Micro Reactor Properties for the Chlorination of Alkanes

The chlorination reaction benefited from the very efficient heat transfer provided by a micro heat exchanger [29, 30].

In terms of plant construction, the implementation of two such micro devices in a pilot-scale industrial chlorination plant is a good example of multi-scale processing, as only the pre-heating tube was replaced by a micro heat exchanger, while the conventional tube, surrounded by a large oven, was still used for reaction.

Gas-phase reaction 20 [GP 20]: Chlorination of alkanes

$$R_mC_nH_{2n+2-m} \xrightarrow{Cl_2} R_mC_nH_{2n+2-m-o}Cl_o$$

The exact nature of the reactant and the product was not disclosed for confidentiality reasons.

3.6.1.3 Typical Results

Conversion/selectivity/yield

[GP 20] [R 9] With a hybrid plant configuration, using two micro heat transfer modules and a conventional tube reactor attached, a significant increase in conversion by about 25% was achieved (500 °C; 0.3–2.3 s; 500 l (STP) h^{-1}; 0.4 bar) [29, 30].

Selectivity increases with decreasing residence time, both for the conventional two-tube reactor– and the micro module–tube reactor configurations [29, 30]. The equal performance of micro and macro processing is explained by running the process at thermodynamic equilibrium.

Size of equipment

[GP 20] [R 9] Externally heated micro heat transfer modules used for pre-heating in the framework of an alkane chlorination process are several times smaller than the previously used combination of a long tube reactor and a surrounding oven [29, 30].

Fast thermal ramping – thermal overshoots

[GP 20] [R 9] The micro heat transfer modules exhibited a steep increase in temperature of the processing fluid. Ten times faster heating of the reactants is achieved compared with the conventional pre-heating tube used formerly [29, 30].

In this way, the operating temperature is reached without thermal overshoots [29, 30].

Residence time

[GP 20] [R 9] The residence time in the micro heat transfer modules amounts to 10 ms; it is 3 ms when referred to the micro channels only [29, 30]. The residence

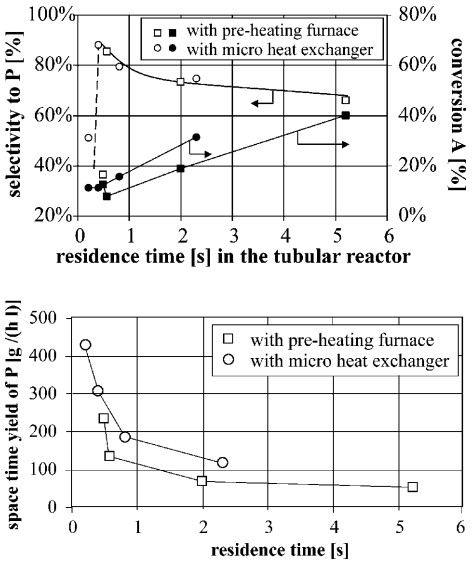


Figure 3.69 Selectivities and space–time yields for the hybrid-plant configuration, using two micro heat transfer modules and a conventional tube reactor attached, and for the conventional tube-reactor plant [29].

time in the conventional tube reactor is 400 ms. When using a conventional pre-heating tube, instead of the micro module, its residence time equals that of the reactor tube, i.e. by micro-flow heating the time could be reduced by a factor of 40.

Space–time yield

[GP 20] [R 9] With a hybrid-plant configuration, using two micro heat transfer modules and a conventional tube reactor attached, a significant increase in space–time yield from about 240 to about 430 g h^{-1} l^{-1} was achieved (Figure 3.69) (500 °C; 0.3–2.3 s; 500 l (STP) h^{-1}; 0.4 bar) [29, 30].

Operational time

[GP 20] [R 9] A hybrid plant configuration, using two micro heat transfer modules and a conventional tube reactor attached, could be run for 24 h without shutdown (500 °C; 0.3–2.3 s; 500 l STP) h^{-1}; 0.4 bar) [29, 30]. Thereafter, incipient corrosion of the micro device was observed. However, this did not lead to immediate shutdown.

3.7 Eliminations

3.7.1 Dehydration of 2-Propanol to Propene

Peer-reviewed journals: [12]; proceedings: [13]; sections in reviews: [90, 95–97, 100, 110].

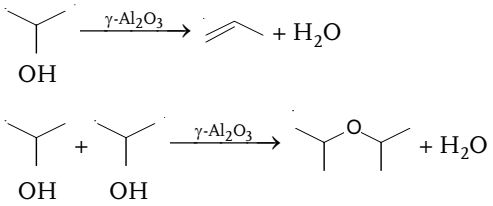
3.7.1.1 Drivers for Performing the Dehydration of 2-Propanol to Propene

Some current micro-reactor investigations on this reaction are concerned with the use of periodic concentration cycling. This is due to the possibility of achieving considerable increases in average reaction rate when switching the concentration from a certain level to zero (see original citations in [12]). This so-called stop-effect can be utilized for the catalytic dehydration of alcohols and deamination of amines on alumina or other amphoteric metal oxides. Different models to describe such periodic processing are available [12]. By this means, reactor performance can exceed the steady-state values. The correctness of such predictions was evidenced by experimental findings, e.g. on the dehydration of ethanol on γ-alumina [12]).

3.7.1.2 Beneficial Micro Reactor Properties for the Dehydration of 2-Propanol to Propene

Advantages of micro-reactor periodic processing have been summarized [12, 13, 85]. In particular, this refers to reducing signal dispersion when guiding the flow through reactors of small internal volumes, i.e. to achieve fast cycling times.

Gas-phase reaction 21 [GP 21]: dehydration of 2-propanol to propene



3.7.1.3 Typical Results

Hydrodynamics – exit-age distributions

[GP 21] [R 6] Exit-age distributions for an experimental set-up for 2-propanol dehydration with and without a multi-platelet-stack micro reactor were calculated, taking into account the measured outlet signal after switching from pure nitrogen to an argon-containing flow [12]. A mass spectrometer was used to determine the dispersion in the set-ups with and without the micro reactor; with the micro reactor attached, dispersion becomes more significant. From the micro-reactor data, dimensionless residence time distributions were derived (see next paragraph).

Hydrodynamics – influence of catalyst coating and type of sealing

[GP 21] [R 6] An analysis of the exit-age distributions for an experimental set-up for 2-propanol dehydration was made using multi-platelet-stack micro reactors, differing in the type of sealing and in the presence or absence of catalyst coatings [12]. The micro reactors were either glued or sealed by graphite sealing, which presumably leads to small variations of the geometry that adversely affects the repartition of flow between different channels. The presence of a coating reduces the cross-sectional area of the channels to an unknown extent.

By these variations, it was found that the micro reactor behaves almost like a plug-flow reactor with a Bodenstein number Bo = 70 for the uncoated and coated

glued reactor and Bo = 33 for the reactor with graphite joints [12]. The catalytic coatings have hardly any influence on the residence-time distribution, whereas the variation in type of sealing has a distinct influence.

Hydrodynamics – calculation method for system response on arbitrary concentration variation

[GP 21] [R 6] By convolution of three functions, inlet function, reactor dispersion model and mass spectrometer response, the response of an experimental set-up with a micro reactor to arbitrary concentration variations at the reactor inlet can be estimated [12]. Measured and predicted curves show nearly perfect agreement.

By this method, the influence of the Bodenstein number and residence time on the response curves was derived [12]. For short mean residence times, the inlet square wave function is only slightly modified; sine functions are formed on applying longer residence times. The larger the dispersion, the more significant is this dependence.

Development of a kinetic model by fixed-bed measurements

[GP 21] [R 6] By making transient experiments (steps 2-PrOH/inert, inert/2-PrOH, and 2-PrOH/H_2O) a kinetic model was elaborated [12]. For this reason, a kinetic model from the literature was modified taking into account experimental findings obtained for 2-propanol dehydration performed in a fixed-bed reactor.

Periodic concentration cycling in the micro reactor

[GP 21] [R 6] Based on the kinetic model developed with the fixed-bed reactor and a reactor model, the dynamic behavior of the multi-platelet-stack micro reactor was simulated [12]. By this means, a quantitative description of experimental dynamic concentration changes was achieved. For this purpose, the concentrations of 2-propanol, propene and ether in a cycle period of 30 s were determined (see also [13]).

Periodic temperature cycling in the micro reactor

[GP 21] [R 6] The thermal behavior of a micro structured multi-channel-platelet reactor was investigated. A theoretical model was developed and compared with the measured transient temperature profiles (switches from 200 to 180 °C) [135]. The thermal response time in the center of the micro channel is of the order of 3 s. Temperature cycling times as short as about 20 s are achievable in the reactor (Figure 3.70).

When carrying out the dehydration of 2-propanol to propene over γ-alumina and imposing a temperature jump (Figure 3.71), the 2-propanol outlet concentration passes a peak as a function of time [135]. This is explained as being due to desorption and reaction phenomena, which gain impact on different time scales [temperature jumps: 190–210, 210–190 °C; 2-propanol: 0.92 mol m^{-3} (STP); 1.5 bar; 0.66 cm^3 s^{-1} (STP)]. The propene concentration adapts more readily to the new stationary value and remains constant after that.

The experimental results obtained at low frequencies can be described by a global kinetic model, whereas at high frequencies a more detailed approach has to be used comprising adsorption, desorption and surface reaction steps [135].

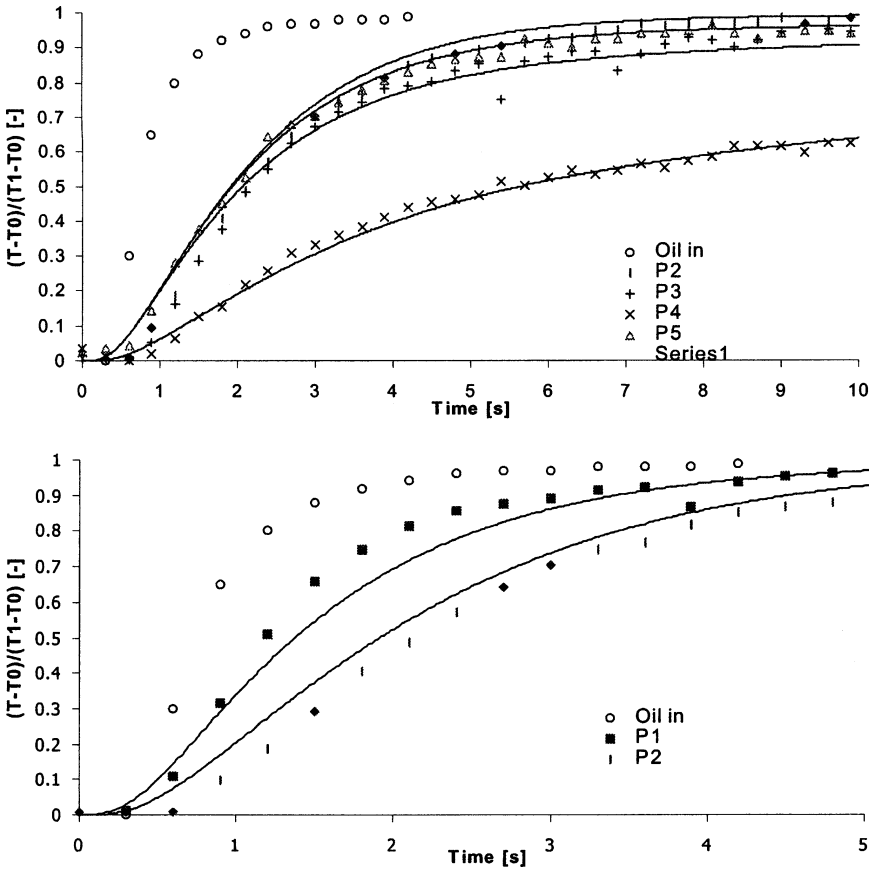


Figure 3.70 Temperature response measured after a heat carrier fluid (oil, velocity 0.35 m s^{-1}) has been switched from 200 to 180 °C at different locations on a micro heat exchanger platelet. Measured values (symbols); model predictions (solid lines) [135].

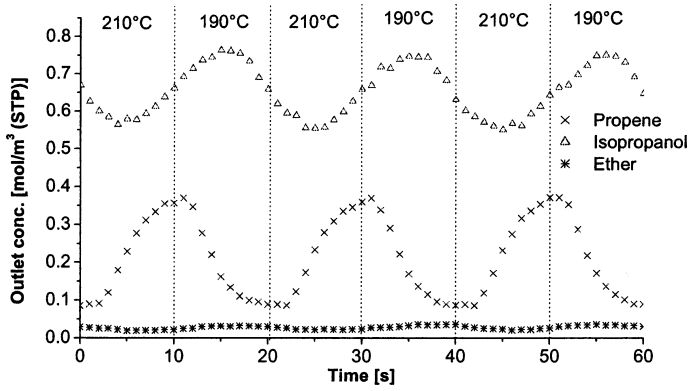


Figure 3.71 Measured product spectra for the dehydration of 2-propanol to propene with periodic temperature variation [135].

3.8
Additions and Coupling Reactions

3.8.1
Phosgene Formation

Peer-reviewed journals: [79]; short mention (no details): [71]; sections in reviews: [87, 88, 92, 114].

3.8.1.1 Drivers for Performing Phosgene Formation

Phosgene is an intermediate utilized in the chemical and pharmaceutical industries for the production of isocyanates for making polyurethane foams and for the synthesis of pharmaceuticals and pesticides (see original citations in [79]). Phosgene is extremely toxic and is an aggressive reactant. The reaction is moderately fast and exothermic (–26 kcal mol^{-1}). Phosgene formation demands specialized cylinder storage, environmental enclosures, and considerable preventive maintenance, just to mention a few differences in technical expenditure compared with other reactions. Hence most phosgene is consumed directly where it is produced.

For these reasons, phosgene formation is one example that potentially does not follow the economics of scale, when considering productivity. Safety and environmental constraints may pose a different view. Serious storage and shipping constraints could demand for production on-site and on-demand.

Micro reactors provide a flexible means to change phosgene productivity, simply by changing volume flow and by numbering-up for even larger flows. Owing to their small hold-up and small productivity per unit, failures may give only small releases. By multi-step processing, the need for transport may be further eliminated. Such an example is described in a patent application [136]. Multi-lamination micro mixers connected to a tube are used for the conversion of phosgene with amines. A flow sheet and an experimental protocol are given for one example, the synthesis of 1-methyl-2,4-diisocyanatocyclohexane from methyl-2,4-diaminocyclohexane by homogeneous gas-phase reaction at 350 °C.

3.8.1.2 Beneficial Micro Reactor Properties for Phosgene Formation

Phosgene formation profits from the small internal volumes of micro reactors due to the hazardous nature of this compound. The light-weight properties of micro reactors and the ability to group them as modules allow one to perform in principle on-site synthesis with flexible output. The latter relates directly to the numbering-up concept of micro reactors.

Gas-phase reaction 22 [GP 22]: phosgene formation

$$Cl_2 + CO \xrightarrow{C} COCl_2 \qquad \Delta H = 26 \text{ kcal mol}^{-1}$$

3.8.1.3 Typical Results

Corrosion

[GP 22] [R 16] Silicon devices are strongly corroded by chlorine etching, as expected (50% chlorine; 50% carbon monoxide; 8 cm^3 (STP) min^{-1}; elevated temperature; 1.35–1.40 atm at inlet) [79]. Protection by thin oxide layers, e.g. 500 nm, made in a wet-oxidation furnace, totally prevents such corrosion (6 h exposure).

Thermal management/heat sink properties

[GP 22] [R 16] When using activated carbon catalysts (1.3 mg; 53–73 μm; surface area 850 m^2 g^{-1}) supported on alumina particles (~3 mg; 53–71 μm) in a wide mini fixed bed, no temperature increase, as monitored by thermocouples, was observed (33.3% chlorine; 66.7% carbon monoxide; 4.5 cm^3 (STP) min^{-1}; elevated temperature; 1.35–1.40 atm at inlet) [79]. This shows the high heat-dissipating capacity of the silicon micro-reactor used, i.e. that it can be used efficiently as a heat sink. In the same way, the heat management is governed by the cartridge heaters, dominating the heat release by reaction.

Conversion/selectivity

[GP 22] [R 16] When using activated carbon catalysts (1.3 mg; 53–73 μm; surface area 850 m^2 g^{-1}) supported on alumina particles (~3 mg; 53–71 μm) in a wide mini fixed bed (Figure 3.72), complete conversion was observed (33.3% chlorine; 66.7% carbon monoxide; 4.5 cm^3 (STP) min^{-1}; temperatures > 200 °C; 1.35–1.40 atm at inlet) [79]. At lower temperatures, a nearly linear increase with temperature was found.

No side products were observed under the above-mentioned conditions, most likely owing to avoidance of hot spots [79].

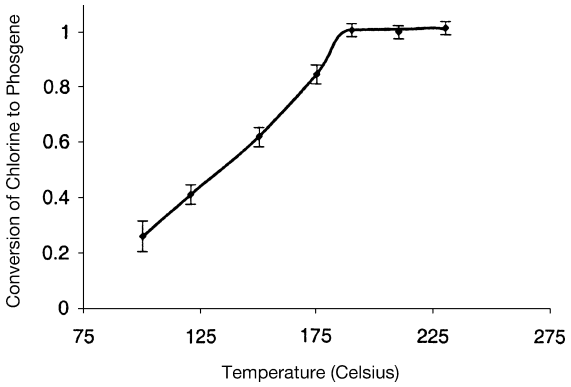


Figure 3.72 Linear increase of chlorine conversion to phosgene with increase in temperature. Experimental results are given for an alumina-supported catalyst in a mini fixed-bed reactor [79].

Catalyst deactivation

[GP 22] [R 16] When using activated carbon catalysts (1.3 mg; 53–73 μm; surface area 850 m^2 g^{-1}) supported on alumina particles (~3 mg; 53–71 μm) in a wide mini

fixed bed, no catalyst deactivation was observed within 6–10 h, possibly owing to the high purity of the gases employed (33.3% chlorine; 66.7% carbon monoxide; 4.5 cm^3 (STP) min^{-1}; 25–200 °C; 1.35–1.40 atm at inlet) [79].

Phosgene productivity

[GP 22] [R 16] When using activated carbon catalysts (1.3 mg; 53–73 μm; surface area 850 m^2 g^{-1}) supported on alumina particles (~3 mg; 53–71 μm) in a wide mini-fixed bed, a phosgene productivity of 3.5 kg a^{-1} (0.40 g h^{-1}) is achieved (33.3% chlorine; 66.7% carbon monoxide; 4.5 cm^3 (STP) min^{-1}; 25–200 °C; 1.35–1.40 atm at inlet) [79]. For a 50% chlorine/50% carbon monoxide mixture at 8.0 cm^3 (STP) min^{-1} flow, a productivity of 9.3 kg a^{-1} (1.1 g h^{-1}) results. Operational limits are not set by the pressure drop or by controlling issues, but rather by the thermal management. Higher flows would induce a thermal runaway of the system.

It is envisaged from prior experience with other reactions that numbering-up can further increase productivity [79]. Indeed, 10-fold units of the wide mini fixed bed exist. By extrapolation it is anticipated that these would probably give 93 kg a^{-1} (11 g h^{-1}), although the exact value certainly has to be validated experimentally.

Intraparticle mass and heat transfer limitations

[GP 22] [R 16] The extent of internal transport limits was analysed for the wide fixed-bed reactor, using experimental data on phosgene formation and matter and process parameter data for the reactants [79]. By applying the Anderson criterion and judging the Weisz modulus, it was found that transfer limitations are negligible.

An order of magnitude analysis was made for the mass transport to the catalyst particle [79]. It was found that concentration gradients are virtually suppressed.

Kinetics: activation energy and rate constants

[GP 22] [R 16] Rate constants for phosgene formation were extracted from wide mini fixed-bed data and were found to match literature data ('micro reactor' activation energy: 7.6 kcal mol^{-1}; literature data: 8.6 kcal mol^{-1}) [79].

3.8.2 Oxidative Coupling of Methane

Proceedings: [55].

3.8.2.1 Drivers for Performing the Oxidative Coupling of Methane

Since methane is available in large amounts, it is desired to convert methane to more valuable C_2 products that are important precursors for many chemicals. Thus, much research is dedicated to enhancing this reaction with acceptable performance. Oxidative methane coupling (OCM), usually performed at temperatures between 750 and 1000 °C, is a very fast reaction and is exothermic. In spite of many attempts to find suitable catalysts over many years, their performance still needs to be improved, e.g. maximum yields reached so far do not exceed 25% (see original citations in [55]).

3.8.2.2 Beneficial Micro Reactor Properties for the Oxidative Coupling of Methane

The oxidative coupling of methane is a reaction of industrial interest, which so far suffers from too low performance (see above). It is the general hope that the well-known beneficial properties of micro reactors as a new process-engineering tool can help to make the next step in the development of the reaction. Demonstration of feasibility is needed here to be able to provide more details on which property is the key to this.

Gas-phase reaction 23 [GP 23]: Oxidative coupling of methane

$$CH_4 + O_2 \xrightarrow{LiAlO_2} H_2, CO, CO_2, H_2O, \text{ethane, ethylene, acetylene, propane}$$

3.8.2.3 Typical Results

Benchmarking to monolith performance

[GP 23] [R 8] In a benchmarking study, the performance of two catalysts in micro-channel systems was compared with that of two catalysts in monoliths [55]. The 'micro-channel catalysts' were two $LiAlO_2$ materials made by a sol–gel method or by *in situ* decomposition of a metallic salt solvent. The 'monolithic' catalysts were of the same material, either a micromachined sintered compact with 17% porosity or as a ceramic slurry coated on a polymer foam with 75% porosity.

Both conversion and selectivity, and hence yield, for the micro-channel catalysts were much lower than for the monolithic (Figure 3.73). A yield of only 1.5% was found for the process parameters which correspond to a maximum monolith performance, 6.1% (total flow: 100 ml min^{-1}; methane/oxygen: 2; 950 °C).

Methane-to-oxygen ratio

[GP 23] [R 8] Using two types of $LiAlO_2$ catalysts coated in micro channels, it was shown that with increasing methane-to-oxygen ratio the conversion of methane rises from about 10 to 20% (total flow: 100 ml min^{-1}; methane/oxygen: 1, 2, 4; 950 °C) [55]. A qualitatively similar behavior was also exhibited by two monoliths having catalysts of the same material, but ranging from about 15 to 50%.

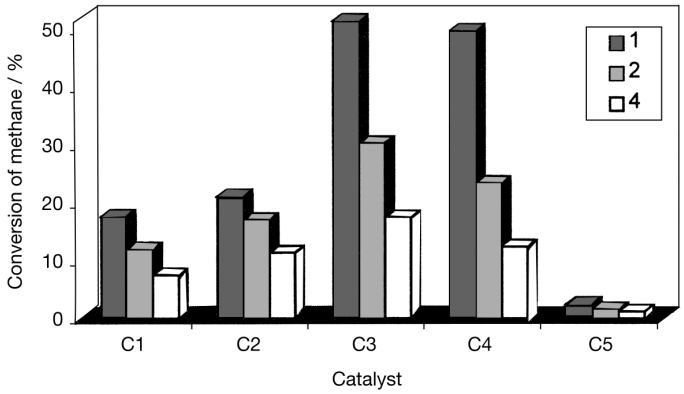


Figure 3.73 Comparison of methane conversion at various methane/oxygen ratios for micro-channel catalyst reactors (C1, C2) and monolithic catalyst reactors (C3, C4); non-coated catalyst (C5) [55].

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