

3.3 Oxidations

Oxidations and partial oxidations constitute one of the most important classes of gas-phase reactions. For this reason, the drivers for and benefits when undergoing micro-channel investigations of these reactions are discussed here in advance of the class as whole. In addition, the specific drivers and benefits are discussed for the individual oxidation reactions as throughout all chapters of this book with regard to reactions.

3.3.1 Drivers for Performing Oxidations in Micro Reactors

The target or value product of many oxidations is only partially oxidized, whereas complete oxidation leads to the useless carbon dioxide. In terms of elementary reactions, partial and total oxidation can be a series of reactions, rendering the latter a consecutive process. In other cases, total oxidation is a side reaction to the partial oxidation. Cases are even known where total oxidations are both side and consecutive reactions concurrently. As a consequence, controls over residence time and reaction temperature are key points to enhance the selectivity of partial oxidation. Concerning the latter, one has to be aware of the large reaction enthalpies that result from total oxidation. Conventionally, owing to insufficient heat transfer, this can lead to considerable hot spots in the reaction zone, which in turn favor total oxidation as the unselective route. In ethylene oxide synthesis, for example, the reaction enthalpy of the total oxidation to carbon dioxide is more than 10 times larger than that of the partial oxidation which locally induces very hot temperatures (hot spots) with corresponding negative consequences for the reaction course.

Micro heat exchangers and also any kind of micro channel devices, heated or cooled externally, offer considerably improved heat transfer owing to their large internal specific surface areas. Hence they offer unique possibilities to steer oxidations to increased selectivity of the partial-oxidation products.

A further driver for performing oxidations in micro reactors is the hazardous nature of oxidation reactions when using high oxygen contents or even pure oxygen. Flame formation or even explosions may result. As a result, much effort in industry is aimed at the finding of explosive regimes and the installation of security measures to prevent accidents. Usually, this also implies declaring explosive regimes to be 'forbidden zones' for further investigations. This means restricting chemistry to certain process windows and the impossibility of exploiting the full range of process parameters. For some gas-phase processes, such as the oxihydrogen reaction, this basically leads to a more or less total neglect of this process route, at least when facing practical issues concerning throughput, etc.

It has been shown, particularly for the latter reaction and for the ethylene oxide process, that micro reactors allow safe processing of otherwise hazardous oxidations [4, 26, 40, 42, 43, 84]. This is first due to the fact that the inner volume of micro reactors is small so that explosions also 'happen only on a micro scale'. The

associated damage, if can be named such at all, is most often negligible. In a number of cases, it is simply the overcompensation of the large heat release by the good heat transfer properties which make micro reactors safe. Even more referring to an intrinsic 'micro reactor property', the large internal specific surface areas are said to actively change the reaction mechanism in the case of radical-chain-type explosions. Here, chain propagation is 'quenched' by wall collision and oxidations can be performed somehow in a completely new chemical way, with results different from those that were obtained before – with risk to equipment and sometimes even life! Veser [9] refers to this aspect of chemical micro processing as 'intrinsic safety'.

A general further driver for performing oxidations in micro reactors is the possibility of having fast dynamic changes of process parameters such as concentration, temperature, pressure, partial pressure, etc. [12, 13, 27, 85]. Micro reactors are continuously processed tools with an extremely small internal volume that favors fast dynamic changes, at least when dealing with single-channel or single-plate devices, which are perfect measuring tools. Hence the gathering of precise process information in a fast mode is a further benefit of micro-reactor studies. Such detailed investigations have been reported, e.g., for ethylene oxide formation, oxidation with ammonia or syngas generation.

As far as extinction/ignition behavior is concerned, oxidations in micro reactors can exhibit varied temperature profiles [19, 56, 57, 59–61]. As a consequence of their very distinct heat transfer characteristics, micro reactors can allow autothermal operation at a different temperature level compared with processing in conventional reactors. As an example, this may raise the selectivity of value products.

3.3.2

Beneficial Micro Reactor Properties for Oxidations

As indicated above, it has been demonstrated many times that the small reaction volumes in micro reactors and the large specific surface areas created allow one to cope with the release of the large amounts of heat. Knowledge of heat transfer characteristics seems to be a top priority when designing a micro reactor for oxidations.

The precise and, where needed, short setting of the residence time allows one to process oxidations at the kinetic limits. The residence time distributions are identical within various parallel micro channels in an array, at least in an ideal case. A further aspect relates to the flow profile within one micro channel. So far, work has only been aimed at the interplay between axial and radial dispersion and its consequences on the flow profile, i.e. changing from parabolic to more plug type. This effect waits to be further exploited.

Particularly valuable for the viable nature of oxidations is the flame-arrestor effect of micro reactors affecting radical-chain propagation.

3.3.3

Oxidation of Ammonia

Peer-reviewed journals: [28, 61]; proceedings: [19, 56, 57, 59, 60, 98]; sections in reviews: [58, 86–97].

3.3.3.1 Drivers for Performing the Oxidation of Ammonia

The oxidation of ammonia, first of all, is a thoroughly investigated gas-phase process and hence an excellent reference reaction for benchmarking chemical micro processing results [19, 56–62, 75, 86–98]. All the reactions for most conditions are known at atmospheric or low pressure (see original citations in [98]). A detailed mechanism based on a large number of elementary reactions was proposed. For many of these reactions, the rate constants are also known, although for some still large uncertainties exist. After adsorption, ammonia and oxygen form several active adsorbed species on the Pt catalyst surface at different adsorption sites and react via them to give the products.

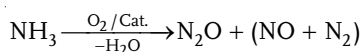
The short contact times required, typically being considerably below, also favor operation in micro channels. Hence high reaction rates and high exothermicity are characteristic of the oxidation of ammonia.

Typical products of the oxidation of ammonia in micro reactors are dinitrogen oxide (N₂O), nitrogen oxide (NO) and nitrogen (N₂), depending on the process conditions. Dinitrogen oxide is a selective oxidizing agent for attractive syntheses e.g. to phenol from benzene via zeolite catalysts [28, 98]. Known conventional syntheses to NO₂, such as the thermal decomposition of ammonium nitrate or by biochemical means via nitrite reduction, are economically not acceptable. Instead, the autothermal oxidation of ammonia at very short contact times and low temperatures, necessitating chemical micro processing, is regarded as a promising alternative [28, 98].

Oxidations of ammonia display ignition/extinction characteristics and autothermal reaction behavior. At low heat supply, only low conversion is observed and temperature remains nearly constant. With increasing heat supply and approaching a certain temperature, the reaction heat generated can no longer be transferred completely totally to the reactor construction material. At this stage, the reaction 'starts up'. Suddenly, the temperature is raised by increased heat production until heat generation and removal are in balance. The reaction can now be carried out without a need for external heat supply, namely in autothermal mode.

3.3.3.2 Beneficial Micro Reactor Properties for the Oxidation of Ammonia

The investigations refer to the general capability of micro reactors to perform short-time processing with highly intensified mass and heat transfer. A special focus of most investigations on the oxidation of ammonia was the heat management. The use of new concepts for heat supply and removal opens the door to operation in new process regimes with very different product spectra.

Gas-phase reaction 1 [GP 1]: Oxidation of ammonia

3.3.3.3 Typical Results

Conversion/selectivity/yield

[GP 1] [R 1] With an optimized diverse micro reactor design (for [R 1]) an N₂O selectivity up to 50% was reached at complete conversion in the temperature range from 300 to 380 °C (0.022–0.543 mg Pt on Al₂O₃; 6 vol.-% NH₃, 88 vol.-% O₂, balance He; 600–4430 cm³ min⁻¹ (STP); 260–380 °C) [98].

Conversion rates

[GP 1] [R 10] Conversion rates over platinum catalyst were determined in a chip-based reactor [56]. In the temperature range from 180 to 310 °C rates from 0 to 0.5 mol m⁻² s⁻¹ were found.

Residence time

[GP 1] [R 1] N₂O selectivity increased with increase in oxygen content, even in the presence of a large oxygen surplus (Pt auf Al₂O₃; 6 vol.-% NH₃, 40 or 88 vol.-% O₂, balance He; 260–380 °C) [98]. Normally, one would have expected a decrease due to follow-up oxidation of N₂O owing to the large excess of oxygen. It is assumed that the special modular design with closely linked furnace and cooler results in efficient cooling. In this way, the residence time at elevated temperature can be reduced to the kinetic needs and especially thermal follow-up reactions can be reduced, as there are no hot parts after the reaction zone any more.

Catalyst thermal behavior/reactor material

[GP 1] [R 1] A change from aluminum to platinum as construction material results in reduced micro-reactor performance concerning oxidation of ammonia, decreasing N₂O selectivity by 20% [28]. This is explained by the lower thermal conductivity of platinum, which causes larger temperature differences (hot spots) within the micro channels, i.e. at the catalyst site, e.g. due to insufficient heat removal from the channels or also by non-uniform temperature spread of the furnace heating.

Pt loading

[GP 1] [R 1] A comparison of four micro reactors (see Table 3.1) with different Pt loadings (Pt impregnated on an anodically oxidized alumina support) confirmed that higher conversions were obtained at higher Pt loadings (6 vol.-% NH₃, 88 vol.-% O₂, balance He; 600–4430 cm³ min⁻¹ (STP); 260–380 °C) [28, 98]. At near complete conversion, 48% N₂O selectivity was found (Figure 3.27).

Table 3.1 Characteristics of platinum catalysts used for experimental investigations [28].

Micro reactor	Pt mass (mg)	Al₂O₃ mass (mg)	Pt loading (wt.-%)	Pt dispersion (%)	Mean Pt cluster size (Å)
A1	0.022	44	0.05	100	< 9
A2	0.086	44	0.2	96	9
A3	0.560	44	1.3	48	19
B	microstructured solid Pt				
C	0.543	16	3.5	40	23

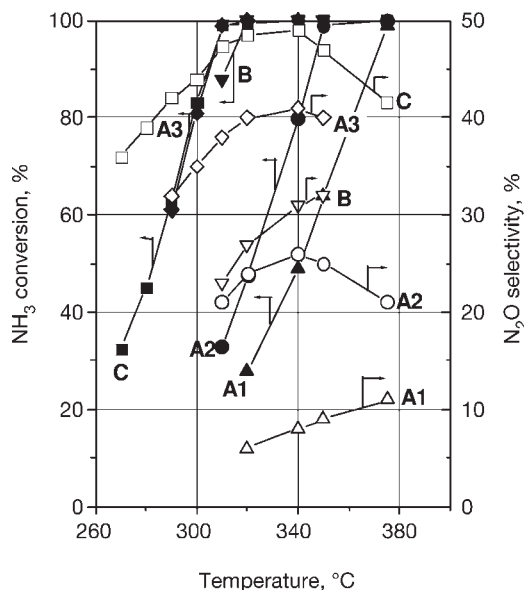


Figure 3.27 Conversion of NH_3 (open symbols) and selectivity to N_2O (closed symbols) for the ammonia oxidation process on Pt catalyst. Micro reactors A1 (\blacktriangle), A2 (\bullet), A3 (\blacklozenge), B (\blacktriangledown) and C (\blacksquare) were used (see Table 3.1) [98].

Pt cluster size

[GP 1] [R 1] A comparison of four micro reactors with different Pt loadings (Pt impregnated on anodically oxidized alumina support) and different Pt structures confirmed that cluster size has an impact on the single Pt-atom activity (6 vol.-% NH_3 , 88 vol.-% O_2 , balance He; 0.51 ms; 260–380 °C) [28, 98]. At low Pt loadings, isolated atoms are formed. Calculated ammonia consumption rates amount to 20 s^{-1} at 300 °C. At high Pt loadings, clusters are formed. Turn over frequencies (TOF) of about 40 s^{-1} are determined.

Steerable catalysis

[GP 1] [R 13] So-called micro-strip electrodes (MSE) can act as electrically steerable catalysts when used to switch on and off the conversion of ammonia at moderate voltages, several hundred volts (6 vol.-% NH_3 , 88 vol.-% O_2 , balance He; 0.51 ms; 260–380 °C) [75]. Thereby, NO formation was observed. By emitting and accelerating electrons in the range of mA cm^{-2} current density from the solid to the gas phase, radicals were formed, typically much more than the number of released electrons, e.g. 10 radicals per electron. This efficient use of energy is referred to as *dynamic catalysis*. The gas phase near the electrodes contains hot and cold radicals, thus providing a two-temperature system.

Time steps of about 60 s between switching on and off were realized. The performance of the MSE structures depends on their geometry, the electric field strength and the gas pressure.

Ignition/extinction behavior

[GP 1] [R 10] The ignition/extinction behavior of the oxidation of ammonia at three different membranes – 1 μm SiN; 1.5 μm Si and 2.6 μm Si – in an Si-chip micro reactor was compared [19]. Whereas the first membrane exhibits ignition already at low power input leading to a temperature rise of up to 570 $^{\circ}\text{C}$ and from there autothermal operation up to 500 $^{\circ}\text{C}$, the latter membrane shows the opposite behavior. For a large power input range of the heating elements only a smooth increase in temperature was observed, followed by only a further small increase by ignition (from ca 270 $^{\circ}\text{C}$ to ca 330 $^{\circ}\text{C}$) [19, 56]. An ignition/extinction hysteresis is hardly developed, which is very different from conventional reactors. The 1.5 μm Si membrane gives intermediate behavior, namely a fast increase up to only ca 520 $^{\circ}\text{C}$, but with pronounced hysteresis formation.

Deformation of SiN membranes during ignition/extinction cycles up to membrane rupture have been reported [57]; images of membrane shapes during the ignition sequence were given. For the SiN membrane, ignition quickly travels upstream and stabilizes at the entrance region of the heater. When the power was decreased, the ignited area was reduced, first downstream.

Process temperature

[GP 1] [R 10] While temperature is more or less fixed in conventional reactors, a set of differently constructed micro reactors now enables temperature to be changed for the ammonia oxidation [19]. As a consequence of this variation of processing temperature by a change of micro-reactor construction, the selectivity of exothermic high-temperature reactions can be changed. For the oxidation of ammonia, the NO/N_2 selectivity was chosen as a sensitive parameter which is increased on raising the reaction temperature. Operation in the chip micro reactor in the range

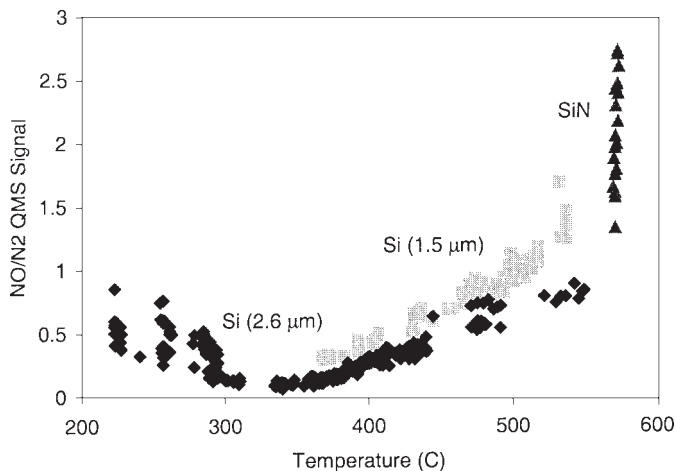


Figure 3.28 Unexpected increase in NO/N_2 selectivity for ammonia oxidation reaction in a micro membrane reactor [19].

from 340 to 570 °C resulted in an increase of the NO/N₂ selectivity from 0.5 to approximately 2.5. Maybe even more remarkable, the micro reactor allowed investigations even below 340 °C, which was not possible so far in conventional reactors. Hence a formerly 'hidden process window' was opened. Indeed, the information gained was surprising. In the low-temperature range an unexpected increase in NO/N₂ selectivity was found (Figure 3.28). This is an indication of a change in reaction mechanism [19].

Temperature distribution in reactor wall

[GP 1] [R 10] By proper heater design, membrane-based reactors with internal heaters allowed one to reach quasi-uniform temperatures at the membrane, which determines the catalyst temperature [19]. This thermal uniformity was checked during reaction, i.e. when large heats were released in the oxidation of ammonia and needed to be transferred out of the reaction zone (Figure 3.29). Thin-film-coated temperature sensors in the center and at the edges of the membrane served to monitor the lateral temperature difference.

When carrying out the reaction at an SiN membrane (1 μm thick) by increasing the power input, the temperature difference follows the ignition/extinction loop, i.e. relatively large temperature differences (maximum 14 K) between the membrane center and edge occur. In the case of the better conducting Si (2.6 μm) membrane, the reaction heat is transferred to the outside more effectively and hence hardly exhibits an ignition/extinction loop; the corresponding maximal temperature difference amounts to 4 K. Uniform catalyst temperatures can thus be achieved even for highly exothermic reactions (Figure 3.30).

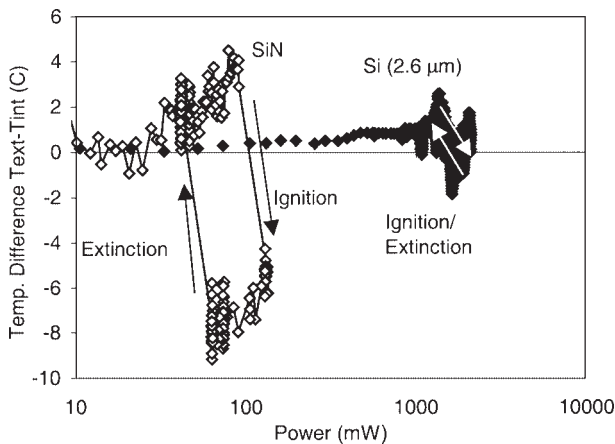


Figure 3.29 Ammonia oxidation over a Pt catalyst in different membrane micro reactors. Experimental results show good temperature uniformity across the catalyst regions [19].

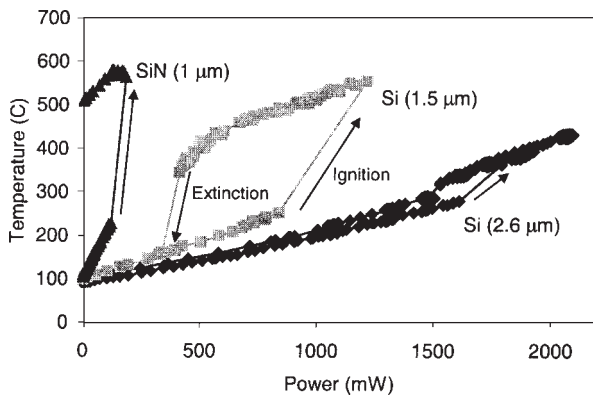


Figure 3.30 Ignition/extinction loops for ammonia oxidation over platinum performed in micro reactors with different membranes [19].

Simulation and modeling

[GP 1] [R 1] A kinetic model for the oxidation of ammonia was coupled to a hydrodynamic description and analysis of heat evolution [98]. Via regression analysis and adjustment to experimental data, reaction parameters were derived which allow a quantitative description of reaction rates and selectivity for all products under equilibrium conditions. The predictions of the model fit experimentally derived data well.

[GP 1] [R 1] Numerical simulations prove that isothermal processing is possible in micro reactors even under severe reaction conditions which correspond to an adiabatic temperature rise up to 1400 °C [98].

Proposals for exploitation of the results on the model reaction

Investigations with the modular multi-channel [28, 98] and silicon chip [19, 56–62] micro reactors demonstrate that by exact temperature control the oxidation of ammonia can be run with increased and deliberately steered selectivity. A major application is provided by carrying out former high-temperature reactions in the low-temperature regime. In the case of ammonia oxidation in the chip micro reactor, the yield of the value product NO was actually lower in that regime. In the case of the multi-plate-stack micro reactor, higher yields of the value product NO₂ were achieved.

However, ammonia oxidation and its products are only seen as models for other high-temperature reactions and substances with potentially more industrial impact when being carried out in a micro reactor. In this context, explicitly mentioned are syntheses of important value products such as anhydrides, ketones or alcohols (see especially [57], but also [19, 56]). Moreover, the work on oxidation of ammonia showed that it is possible to expand the operational regime for laboratory-scale investigations to gather information, e.g., on new product compositions and new process parameters. The feasibility being demonstrated, we are now waiting for more detailed investigations and for transfer to other, hopefully even more important, reactions. In this way, micro reactors may become a widely accepted tool in the field of kinetic analysis of heterogeneous catalysis.

3.3.4

Oxidation of Ethylene – Ethylene Oxide Formation

Peer-reviewed journals: [4, 40]; proceedings: [26, 42, 43, 84]; reactor description: [44, 99]; sections in reviews: [87, 90, 95–97, 100].

3.3.4.1 Drivers for Performing Ethylene Oxide Formation

Heat management is of crucial importance for ethylene oxide synthesis (see original citations in [4]). The reaction enthalpy of the total oxidation to carbon dioxide ($\Delta H = -1327$ kJ/mol) is more than 10 times larger than that of the partial oxidation ($\Delta H = -105$ kJ/mol), which induces locally very hot temperatures (hot spots) with corresponding negative consequences on the reaction course.

Industrial reactors work below or above the explosion regime, hence operation cannot be carried out at any ethylene-to-oxygen ratio (see original citations in [43]). The best industrial processes are based on ethylene and oxygen contents of 20–40 and 8%, respectively, using methane as inert gas. It is known that high oxygen contents improve selectivity.

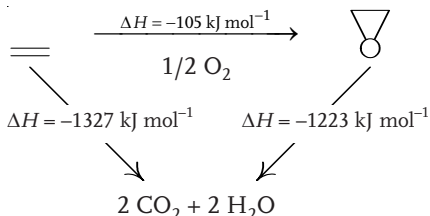
Without promoters, a selectivity of up to about 50–70% is reported (see original citations in [43]); 90% of heat production is due to total oxidation. Advanced industrial reactors have a selectivity of up to 90% and at the lowest a 50% contribution of the total oxidation to the heat generation.

For pure silver catalysts, a selectivity of only 40% was reported (see original citations in [4]).

3.3.4.2 Beneficial Micro Reactor Properties for Ethylene Oxide Formation

Beneficial micro reactor properties mainly refer to improving heat management as a key for obtaining a partial reaction in a consecutive sequence, when large heats are released by reaction steps other than the partial one (see also Section 3.3.1).

Special attention was also paid to the search for operation in the explosive regime as micro reactors are said to have much greater safety here. In this way, improvements in terms of space–time yield were expected.

Gas-phase reaction 2 [GP 2]: Oxidation of ethylene to ethylene oxide

Ethylene oxide synthesis is one of the largest-volume industrial processes with a production rate of some plants of several 100 000 t a⁻¹ (see original citations in [4]). In 1995, the world capacity for ethylene oxide was approximately 11 200 000 t a⁻¹. As industrial catalyst silver on alumina is employed. In addition to large produc-

tion, small-throughput and mobile applications are known. This includes the on-site generation of ethylene oxide for sterilizing purposes, e.g. for cleaning in hospitals. Corresponding small-scale production units are on the market. Ethylene oxide synthesis is, besides its industrial application, a well-studied process. Kinetic data are available in the literature.

3.3.4.3 Typical Results

Start-up behavior

[GP 2] [R 2] New microstructured silver platelets have no initial activity for ethylene oxide formation [26, 40]. After treatment with the OAOR process, a small increase in activity was observed. After 1000 h of operation under oxygen conditions, larger amounts of ethylene oxide were produced.

[GP 2] [R 3a] Initially sputtered silver on aluminum platelets displays high selectivity at low activity. This ratio decreases until a constant performance is reached, typically after 24–48 h (20 vol.-% ethylene, 80 vol.-% oxygen; 3 bar; 0.23–2 s; 250 °C) [43].

[GP 2] [R 3a] Catalysts need to be initially activated on-stream with a mixture of 20% ethylene and 20% oxygen in methane as balance [44]. The temperature was raised until first formation of carbon dioxide became notable. The initial selectivity is close to 70% and after time-in-stream for 1 day at 250 °C decreases to 62% at 1.3% conversion. This loss in selectivity at the expense of conversion is a general phenomenon during all investigations conducted in [44]. Non-promoted catalysts show a certain decrease in selectivity within a few days, particularly at high temperature and conversion.

Conversion/selectivity/yield

[GP 2] [R 2] Initial work with a steel multi-plate-stack micro reactor with microstructured platelets made of polycrystalline silver (OAOR modified) confirmed a selectivity of up to 49% at conversions of about 12% (3 vol.-% ethylene, 50 vol.-% oxygen, balance nitrogen; 5 bar; 4 l h⁻¹; 277 °C) [4, 26, 40].

In a more comprehensive follow-up work, the selectivity on OAOR-modified silver could be raised to 65%, still without the presence of promoters such as 1,2-dichloroethane [4]. This value is by far better than most values known in the literature for the same catalyst. The best value finally obtained was 69% and approaches the 'industrial limit' of 80% that was obtained with promoters and a different, better catalyst, Ag/Al₂O₃. A similar catalyst type (Aluchrom catalyst) was also tested in the micro reactor, but so far yielding lower results, the best selectivity measured being 58%.

Variation of gas composition affects conversion on OAOR-modified silver. At a selectivity of 47%, a conversion exceeding 24% was observed (0.75 vol.-% ethylene, 33 vol.-% oxygen, balance nitrogen; 5 bar; 2 l h⁻¹; 277 °C) [4, 26, 40].

[GP 2] [R 3a] A nearly constant selectivity of up of about 60% at conversions ranging from 20 to 70% was determined for sputtered silver on anodically oxidized (porous) aluminum alloy (AlMg3) with two different ethylene loads (4 or 20 vol.-% ethylene, 80 or 96 vol.-% oxygen; 0.3 MPa; 230 °C) [44]. The highest yield

of 39% was obtained for the same catalyst at 4.5 s residence time (4 vol.-% ethylene, 96 vol.-% oxygen; 0.3 MPa; 230 °C).

[GP 2] [R 3a] The selectivity–conversion behavior was determined for the commercial Shell Series 800 catalyst, in a fixed bed and electrophoretically deposited in micro channels (20 vol.-% ethylene, 80 vol.-% oxygen; 0.3 MPa; 230 °C) [101]; 54% selectivity at 17% conversion was found at the maximum, when processing without promoters.

Temperature and pressure

[GP 2] [R 2] On increasing temperature from 240 to 290 °C, reaction rates on OAOR-modified silver increase from $4.5 \cdot 10^{-5} \text{ mol s}^{-1} \text{ m}^{-2}$ to $1.2 \cdot 10^{-4} \text{ mol s}^{-1} \text{ m}^{-2}$ (3 vol.-% ethylene, 16.5 vol.-% oxygen, balance nitrogen; 5 bar; 0.124 s; 5 l h^{-1}) [4]. The selectivity decreases from 64 to 45%.

An increase from 2 to 5 bar total pressure increases the space–time yield by about 20% (15 vol.-% ethylene, 85 vol.-% oxygen, 2–20 bar; 0.235–3.350 s; 1 l h^{-1}) [4]. At higher pressures, 10 and 20 bar, a decrease activity is observed. Since industrial processes occur at up to 30 bar, at first sight this result is surprising. The decreasing activity with pressure was partially explained by catalyst deactivation, probably as a consequence of the longer residence times applied.

Isothermicity/radial temperature distribution

[GP 2] [R 2] The radial temperature distribution was determined by modeling, using a worst-case scenario (5 Nl h^{-1} ; stoichiometric mixture without inert; 100% conversion; 80% selectivity) [102]. The maximum radial temperature difference amounts to approximately 0.5 K. Thus, isothermal behavior in the radial direction can be diagnosed.

Periodic processing – cycle times and reactor performance

[GP 2] [R 2] A survey on the possibilities of periodic processing regarding to ethylene oxide synthesis is given in [102]. The cycle times of periodic temperature and concentration control differed by 3–4 powers of ten. Cycle times of 0.05 s showed concentration effects, while times longer than 5 s can have temperature effects. The reason for this difference stems from the relatively high thermal inertia of the wall material influencing temperature changes.

The impact of such periodic processing on reactor performance was, however, slightly negative (assuming: 3 mol% ethylene; 20 mol% oxygen; balance nitrogen; 5 Nl h^{-1} ; 10.63% conversion; 59.13% selectivity) [102]. In absolute terms conversion decreased by about 0.2% from 10.63%; hence in relative terms a decrease of 2% is given. Conversion decreased with increasing cycle time to level off at about 0.3 s. A small increase in conversion, but not reaching stationary performance, was observed above 100 s, due to temperature effects. For short cycle times, a small increase in selectivity of about 0.05% was found. For longer cycles, a performance worse than stationary was detected (Figure 3.31).

These mostly negative effects are explained as being due to the mechanistic characteristics of ethylene oxide formation, having a reaction order lower than one [102].

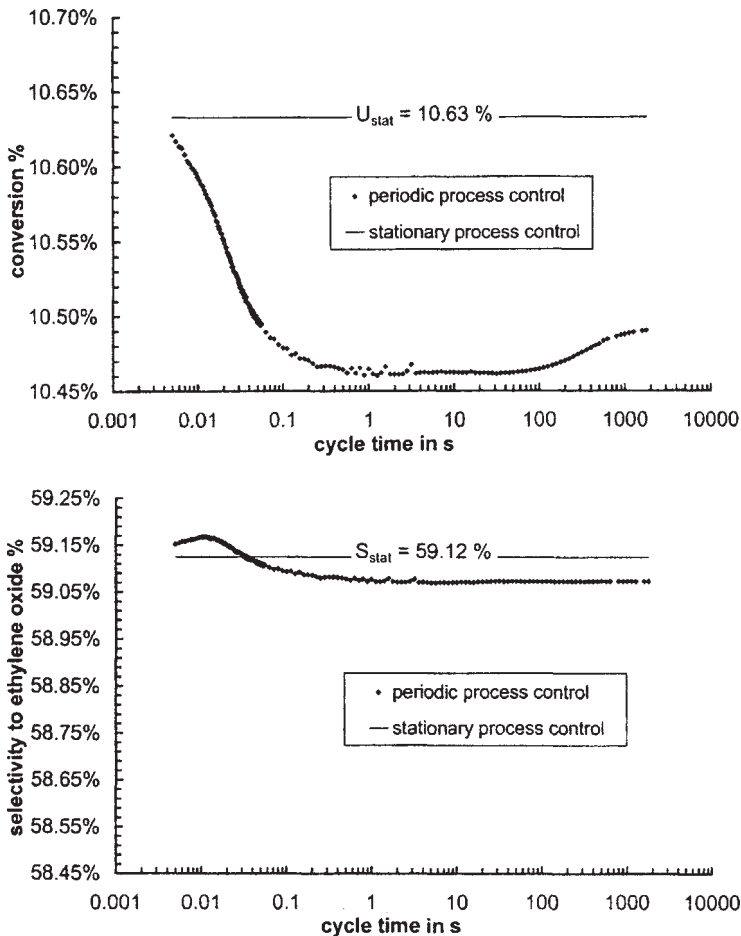


Figure 3.31 Effects of alternating change of the ethylene mole fraction. Conversion (left) and selectivity (right) as a function of cycle time [102].

It could be demonstrated that for any reaction with a reaction order higher than one, positive effects such as a conversion increase can be expected. Also, adaptation of the reactor geometry can improve the positive impact of periodic processing.

Residence time

[GP 2] [R 2] A residence time variation was performed under constant gas composition, temperature and pressure, but with varying flow rate. On increasing the residence time from 0.5 to 8 s, reaction rates on OAOR-modified silver decreased notably from $9.5 \cdot 10^{-5} \text{ mol s}^{-1} \text{ m}^{-2}$ to about $1 \cdot 10^{-4} \text{ mol s}^{-1} \text{ m}^{-2}$ (5 vol.-% ethylene, 50 vol.-% oxygen, balance nitrogen; 20 bar; 0.5–8 s) [4]. The selectivity decreases from 43 to 21%.

[GP 2] [R 3a] [R 4a] An investigation of sputtered silver (dense) on aluminum alloy (AlMg3) platelets and of sol-gel- Al_2O_3 /silver (porous) on aluminum alloy (AlMg3) platelets served to show the impact of residence time [43]. At low conversion, the highest selectivity was found in both cases, which remained constant until 20% conversion. The dense silver had a maximum selectivity of 61%, exceeding the performance of porous sol-gel- Al_2O_3 /silver (51%) (20 vol.-% ethylene, 80 vol.-% oxygen; 3 bar; 230 °C). For conversion exceeding 20%, a steep drop in selectivity was found.

[GP 2] [R 3a] The dependences of conversion, yield and selectivity on residence time were investigated in a comparative study with silver, sputtered silver (dense) on aluminum alloy (AlMg3) and sputtered silver on anodically oxidized (porous) aluminum alloy (AlMg3) as construction materials [44]. The ethylene content was varied, using 4% or 20%. Generally, conversion and yield increased with increasing residence time, whereas selectivity slightly decreased (after a short initial increase) or even remained the same. Proper operation using the construction material silver needed the longest residence times, e.g. up to 14.0 s to achieve 22% at selectivity of 48% (20 vol.-% ethylene, 80 vol.-% oxygen; 0.3 MPa; 250 °C). On lowering the ethylene content to 4%, conversion increases to 27% at a selectivity of 54% and 5 s residence time (4 vol.-% ethylene, 96 vol.-% oxygen; 0.3 MPa; 250 °C). Silver (dense) on aluminum alloy (AlMg3) gives a conversion of 43% at 58% selectivity and 5.5 s residence time (20 vol.-% ethylene, 80 vol.-% oxygen; 0.3 MPa; 250 °C). Sputtered silver on anodically oxidized (porous) aluminum alloy (AlMg3) gives a conversion of 33% at 60% selectivity and 7.0 s residence time (20 vol.-% ethylene, 80 vol.-% oxygen; 0.3 MPa; 230 °C). The performance is similar to that of the dense silver catalyst but at temperatures 20 °C lower. Both sputtered silver catalysts show nearly constant selectivity for the range of conversions investigated. The performance of both sputtered silver catalysts at 4% ethylene follows the trend depicted for the construction material silver. The highest yield of 39% was obtained for the sputtered silver on anodically oxidized (porous) aluminum alloy (AlMg3) at 4.5 s residence time (4 vol.-% ethylene, 96 vol.-% oxygen; 0.3 MPa; 230 °C).

Oxygen partial pressure

[GP 2] [R 2] Studies were performed at constant ethylene content and residence time and with varying ethylene content by exchange versus nitrogen. Selectivity increases from 44.7 to 49.9% at conversions of 10.0 and 11.6%, respectively, on OAOR-modified silver on increasing the oxygen partial pressure by varying the volume content from 10–50% (3 vol.-% ethylene, balance nitrogen; 5 bar; 4 l h⁻¹; 277 °C) [4, 26, 40].

The reaction rate increases with increasing oxygen partial pressure on OAOR-modified silver with an order of 0.78 with respect to oxygen (15 vol.-% ethylene, 0.2–3.5 hPa oxygen partial pressure, balance nitrogen; 4 bar; 0.469 s; 1 l/h; 290 °C) [4]. The selectivity increases from 30 to 37%. The investigations at such high oxygen partial pressures are within the explosion regime.

[GP 2] [R 3a] Studies were performed at constant ethylene content and residence time and by varying the oxygen content by exchange versus methane. An increase

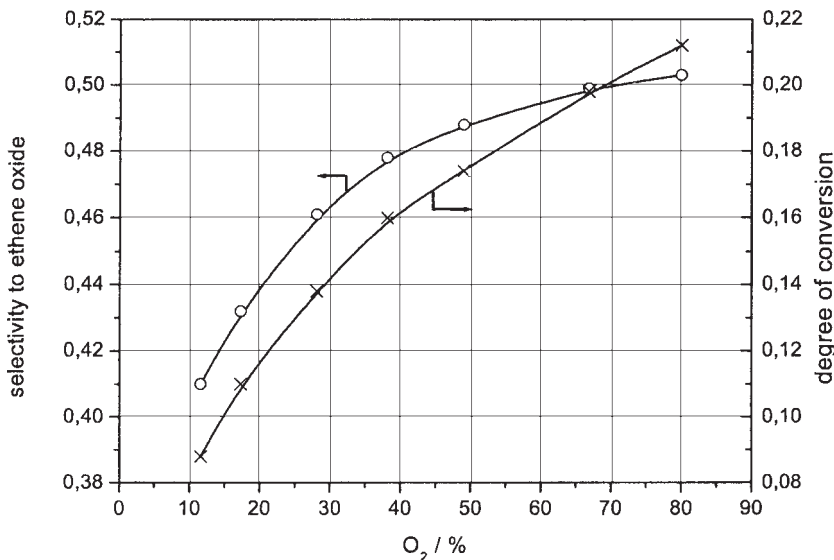


Figure 3.32 Experimental results for the selectivity and the degree of conversion of ethylene as a function of oxygen concentration [43].

in selectivity on sol-gel- Al_2O_3 /silver on aluminum (AlMg3) from 41 to 51% is observed on increasing the oxygen content from 12 to 80% (20 vol.-% ethylene, 12–80 vol.-% oxygen, balance methane; 3 bar; 0.30 s; 210 °C) [43]. Conversion increases slightly from 9 to 21%. Consequently, at 80% oxygen content, the highest yield of about 21% was obtained (Figure 3.32).

Ethylene partial pressure

[GP 2] [R 2] Studies were performed at constant oxygen content and residence time and by varying the ethylene content by exchange versus nitrogen. An increase of the reaction rate on laser-LIGA OAOR silver with ethylene partial pressure at nearly constant selectivity of about 41% is observed, but does not follow first order (1.2–6.5 hPa ethylene partial pressure, 50 vol.-% oxygen, balance nitrogen; 4 bar; 0.235 s; 2 l h⁻¹; 290 °C) [4]. An averaged formal order of 0.53 with respect to ethylene was calculated.

[GP 2] [R 3a] Studies were performed at constant residence time and by varying the ethylene and oxygen content concurrently or individually. An increase of selectivity on sol-gel- Al_2O_3 /silver on aluminum (AlMg3) from 52 to 55% is observed on increasing the ethylene content from 13 to 60% at constant residence time (13–60 vol.-% ethylene, balance oxygen; 3 bar; 0.53 s; 210 °C) [43]. Conversion drops steeply from 21% to 2%. At 30% ethylene content, the highest yield was obtained.

Addition of promotor

[GP 2] [R 2] The addition of the promoter 1,2-dichloroethane improves selectivity from 52 to 69%, but at the expense of reducing the space-time yield from 0.78 to

0.42 t h⁻¹ m⁻³ for laser-LIGA OAOR silver (6 vol.-% ethylene, 30 vol.-% oxygen, balance nitrogen; 5 bar; 0.124 s; 5 l h⁻¹; 290 °C) [4].

Influence of construction material and micro fabrication

[GP 2] [R 2] A comparative study with laser-LIGA OAOR silver, etched OAOR silver and sawn Aluchrom catalyst was reported (Table 3.2) [4]. The selectivity was 44–69% (laser-LIGA OAOR silver), 38–69% (etched OAOR silver) and 42–58% (sawn Aluchrom catalyst); for details of the experimental protocols, see [4]. The conversions were 2–15% (laser-LIGA OAOR silver) 5–20% (etched OAOR silver), and 2–6% (sawn Aluchrom catalyst). The space–time yields were 0.01–0.07 t h⁻¹ m⁻³ (laser-LIGA OAOR silver), 0.03–0.13 t h⁻¹ m⁻³ (etched OAOR silver), and 0.01–0.06 t h⁻¹ m⁻³ (sawn Aluchrom catalyst).

Table 3.2 Process parameters for an industrial process compared with parameters achieved for micro reactors machined by different techniques.

	<i>Oxygen-based industrial process</i>	<i>Micro reactor-based process (laser-LIGA)</i>	<i>Micro reactor-based process (etched)</i>	<i>Micro reactor-based process (Aluchrom)</i>
C ₂ H ₄ (vol.-%)	15–40	1.5–6	3–15	15
O ₂ (vol.-%)	5–9	10–41	5–85	85
CH ₄ (vol.-%)	1–60			
Temperature (°C)	220–275	240–290	240–290	270
Pressure (bar)	10–22	5	2–20	5
Residence time (s)	0.9–1.8	0.1–0.2	0.1–1.5	1.2
C ₂ H ₄ conversion (%)	7–15	2–15	5–20	2–6
Selectivity (%)	80	44–69	38–69	42–58
Space–time yield (t h ⁻¹ m ⁻³)	0.13–0.26 (reactor)	0.01–0.07 (foils) 0.14–0.78 (channels)	0.03–0.13 (foils) 0.18–0.67 (channels)	0.01–0.06 (foils) 0.08–0.36 (channels)

Silver catalyst morphology

[GP 2] [R 2] The smooth surface of the laser-LIGA OAOR silver is roughened and pitted after OAOR treatment and used during more than 1000 h of ethylene oxide synthesis [4]. The etched OAOR silver shows pronounced sintering and agglomeration for the same type of treatment.

[GP 2] [R 3a] The sputtered silver on aluminum alloy (AlMg3) platelets, machined by thin-wire μ EDM, were smooth and dense. On prolonged operation under reaction conditions, small silver particles are generated by surface diffusion so that also the blank aluminum platelet surface is exposed (20 vol.-% ethylene, 80 vol.-% oxygen; 3 bar; 0.23–2 s; 250 °C) [43].

Dense and porous catalysts

[GP 2] [R 3a] [R 4a] Sputtered silver (dense) on aluminum alloy (AlMg3) platelets was compared with sol-gel- Al_2O_3 /silver (porous) on aluminum alloy (AlMg3) platelets [43]. However, investigations were not performed in the same, but rather in two different micro-reaction devices which differ in the specific micro channel surface. The aim was to compensate for the difference in catalyst surface area by varying the micro channel surface area. Hence the intention was not to compare porosity, but catalyst material instead. Investigations were made by varying residence time, thereby affecting conversion. The dense silver had a maximum selectivity of 61%, exceeding the performance of porous sol-gel- Al_2O_3 /silver (51%) (20 vol.-% ethylene, 80 vol.-% oxygen; 3 bar; 230 °C). This performance is constant in both cases up to 20% conversion and then drops steeply.

Silver catalyst particle size

[GP 2] [R 3a] To vary the silver particle size, which is known to have a distinct influence on catalyst activity and selectivity, silver coatings with varying thickness from 50 to 1400 nm were applied on microstructured platelet by multiple-step sputtering (20 vol.-% ethylene, 80 vol.-% oxygen; 3 bar; 0.23–2 s; 250 °C) [43]. For three platelets silver coatings of different thickness, a constant selectivity at a low degree of conversion was found (Figure 3.33). At a certain degree of conversion, the selectivity drops. For the 1400 nm layer this occurs at 30% conversion and for the 400 nm layer at 23%.

Catalysts with very low thicknesses such as 50 nm display a different behavior. A high initial selectivity of 56% at about 2% conversion decreases steeply with a change of conversion to 1%. This is explained, however, as insufficient initial activation of the catalyst (20 vol.-% ethylene, 80 vol.-% oxygen; 3 bar; 0.23–2 s; 250 °C) [43].

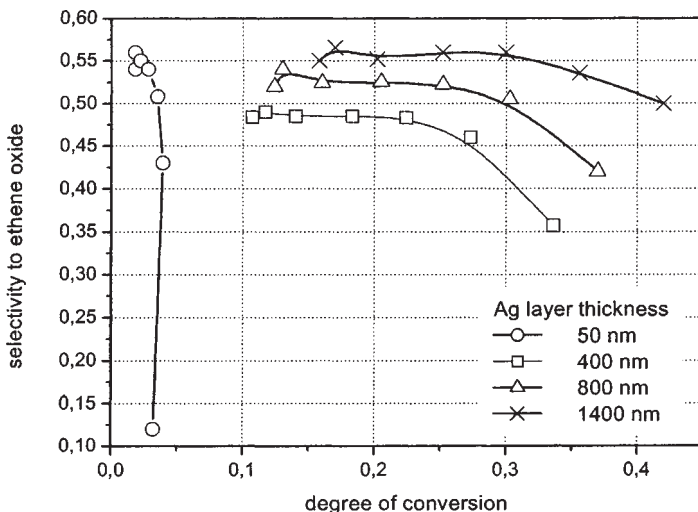


Figure 3.33 Experimental results for degree of selectivity and conversion for ethylene when using micro-channel reactors with different thicknesses of silver coatings [42].

Commercial catalyst as fixed bed and in micro channels

[GP 2] [R 3a] A Shell Series catalyst was measured in a fixed-bed configuration and deposited in micro channels electrophoretically (20 vol.-% ethylene, 80 vol.-% oxygen; 0.3 MPa; 230 °C) [101]. The selectivity was lower in the micro channels (51%) than in the fixed bed (57%) at a conversion of 17%. In a further investigation, a sputtered silver catalyst (cesium promoted) was better than both systems (68%) at higher conversion (25%).

Space–time yield

[GP 2] [R 2] The definition of space–time yield in a micro reactor depends on the definition of the ‘reactor volume’. Owing to the large amount of construction material relative to the reaction channels and the neglect of some reactor parts (‘abstraction to the real reaction zone’), several more or less useful definitions can be made. In the following, two definitions concerning the time yield divided by the ‘pure’ reaction channel volume and the platelet volume were used.

Following the first definition, a space–time yield of $0.78 \text{ t h}^{-1} \text{ m}^{-3}$ using a OAOR-modified silver is obtained, which exceeds the industrial performance considerably ($0.13\text{--}0.26 \text{ t h}^{-1} \text{ m}^{-3}$) [4]. Following the second definition and hence orienting more on outer than on inner dimensions, a space–time yield of $0.13 \text{ t h}^{-1} \text{ m}^{-3}$ is obtained, still within the industrial window.

Benchmarking to industrial reactor performance

[GP 2] [R 2] The selectivity of 49% on OAOR-modified silver (3 vol.-% ethylene, balance nitrogen; 5 bar; 4 l h^{-1} ; 277 °C) is lower than the industrial performance [4, 26, 40]. The latter, however, relies on the presence of chlorine compounds such as 1,2-dichloroethane. At a temperature of 237 °C, a selectivity of 65% is reached, which exceeds values reported for polycrystalline silver catalysts.

For a further comparison of details of the experimental protocols and of conversion, selectivity and space–time yields, see [4].

For a discussion of space–time yields, see the section above.

Benchmarking to fixed-bed reactor performance

[GP 2] [R 3a] The performance of one micro reactor with three kinds of catalyst – construction material silver, sputtered silver (dense) on aluminum alloy (AlMg3), and sputtered silver on anodically oxidized (porous) aluminum alloy (AlMg3) – was compared with three fixed beds with the same catalysts [44]. The fixed beds were built up by hackled silver foils, aluminum wires (silver sputtered) and hackled aluminum foils (anodically oxidized and silver sputtered), all having the same catalytic surface area as the micro channels. Results were compared at the same flow rate per unit surface area.

All three comparisons reveal that the ‘micro reactor catalysts’ have higher conversion and yield, owing to enhanced mass transfer (20 vol.-% ethylene, 80 vol.-% oxygen; 0.3 MPa; 3.17 l h^{-1} ; 230/250 °C) [44]. The selectivity is slightly better in the fixed beds, but, only by about 1–5%. The best fixed-bed and micro reactor selectivity is 65 and 63%, respectively. The best fixed-bed and micro reactor conversion is 37 and 66%, respectively.

A comparison at the same conversion was made for one fixed-bed reactor/micro reactor pair. The micro reactor gave better selectivity at the same conversion, e.g. 66 versus 57% at 62% conversion (4 vol.-% ethylene, 96 vol.-% oxygen; 0.3 MPa; 230 °C).

Activation energy – reaction rate

[GP 2] [R 2] An activation energy of 48 kJ mol^{-1} was observed for ethylene oxide synthesis on OAOR-modified silver [4, 26, 40].

A reaction rate of $4.8 \cdot 10^{-5} \text{ mol s}^{-1} \text{ m}^{-2}$ was observed for OAOR-modified silver (3 vol.-% ethylene, 16.5% vol.-% oxygen; balance nitrogen; 5 bar; 239 °C) [4]. This value is higher than a literature value ($1.7 \cdot 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$ at 2 vol.-% ethylene, 7% vol.-% oxygen; 1 bar; 230 °C). Correcting the micro reactor value for the different experimental conditions, a value of $1.9 \cdot 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$, close to the literature value, was obtained. Doubling the content of reactants leads to an increase in reaction rate by a factor of nearly two for OAOR-modified silver (6 vol.-% ethylene, 33% vol.-% oxygen; balance nitrogen; 5 bar; 4 l h^{-1} ; 267 °C) [4, 26, 40].

An increase in reaction rate with ethylene partial pressure was observed, but does not follow a first-order law. An averaged formal order of 0.53 was calculated [4]. The reaction rate increases with increasing oxygen partial pressure on OAOR-modified silver with an order of 0.78 with respect to oxygen [4].

[GP 2] [R 3a] A reaction rate of $6.0 \cdot 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$ was observed for sputtered silver on aluminum (20 vol.-% ethylene, 20% vol.-% oxygen; balance methane; 3 bar; 250 °C) (see [4, 26, 40] reporting results from [43]).

Operation in explosive regimes

[GP 2] [R 2] Safe operation under explosive conditions using pure oxygen was demonstrated in a steel multi-plate-stack micro reactor (e.g. 3 vol.-% ethylene, 50 vol.-% oxygen, balance nitrogen; 5 bar; 4 l h^{-1} ; 277 °C) [4, 26, 40]. The cross-sections of the various micro channels employed were from $500 \times 50 \text{ }\mu\text{m}^2$ to $500 \times 90 \text{ }\mu\text{m}^2$.

By operating at high oxygen partial pressures on OAOR-modified silver, data on reaction rates could be gathered which previously could be obtained in a similar way only under low-pressure conditions (15 vol.-% ethylene, 0.2–3.5 hPa oxygen partial pressure, balance nitrogen; 4 bar; 290 °C) [4].

[GP 2] [R 3a] [R 4a] No explosion or flame formation was observed when working under 20 vol.-% ethylene, 80 vol.-% oxygen conditions on sputtered silver (dense), on aluminum alloy (AlMg3) platelets and sol-gel- Al_2O_3 /silver (porous) on aluminum alloy (AlMg3) platelets (20 vol.-% ethylene, 80 vol.-% oxygen; 3 bar; 230 °C) [43]. The cross-sections of the micro channels of the two micro reactors employed amounted to $200 \times 200 \text{ }\mu\text{m}^2$ and $700 \times 300 \text{ }\mu\text{m}^2$, respectively.

Exploitation of the results

The very promising results for ethylene oxide synthesis by micro-channel processing given above still await industrial implementation. Selectivity needs to be further improved above 80%, as the costs for ethylene contribute 80% to the overall process costs [4]. In addition to the costs argument, the usual requirements for transfer from laboratory to industrial scale will face the micro reactor: reliability, proper process control and much more.

3.3.5

Oxidation of 1-Butene – Maleic Anhydride Formation

Proceedings: [84, 103]; sections in reviews: [90, 95, 97, 100].

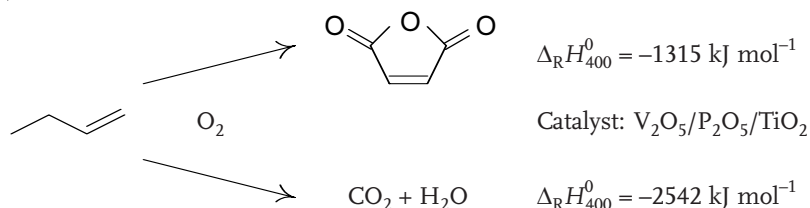
3.3.5.1 Drivers for Performing Maleic Anhydride Formation in Micro Reactors

Maleic anhydride is an important industrial fine chemical (see original citations in [43]). The oxidation of C₄-hydrocarbons in air is a highly exothermic process, therefore carried out at low hydrocarbon concentration (about 1.5%) and high conversion. The selectivity of 1-butene to maleic anhydride so far is low. The reaction is composed of a series of elementary reactions via intermediates such as furan and can proceed to carbon dioxide with even larger heat release. As a consequence, hot spots form in conventional fixed-bed reactors, decrease selectivity and favor other parallel reactions.

3.3.5.2 Beneficial Micro Reactor Properties for Maleic Anhydride Formation

Beneficial micro reactor properties mainly refer to improving heat management as a key for obtaining a partial reaction in a consecutive sequence, when large heats are released by reaction steps other than the partial one (see also Section 3.3.1).

Special attention was also drawn to the search for operation in the explosive regime as micro reactors are said to have much greater safety here. In this way, improvements in terms of space–time yield were expected.

Gas-phase reaction 3 [GP 3]: Oxidation of 1-butene to maleic anhydride**3.3.5.3 Typical Results****Conversion/selectivity/yield**

[GP 3] [R 3b] At conversions from 73 to 85%, selectivity for maleic anhydride of about 33% was achieved with a $\text{V}_2\text{O}_5/\text{P}_2\text{O}_5/\text{TiO}_2$ catalyst (0.4 vol.-% 1-butene in air; 0.1 MPa; 400 °C) [103]. The residence time was varied in these investigations. A 90% conversion in the $80 \times 80 \mu\text{m}^2$ micro channels corresponds to a 25 ms residence time.

Micro-channel diameter

[GP 3] [R 3b] At similar conversion and residence time, smaller micro channels (80 μm) have better selectivity than larger ones (200 μm) with a $\text{V}_2\text{O}_5/\text{P}_2\text{O}_5/\text{TiO}_2$ catalyst (0.4 vol.-% 1-butene in air; 0.1 MPa; 400 °C) [103]. The residence time was varied in these investigations.

The ratio of space–time yields referring to various micro channels equals the ratio of their cross sections.

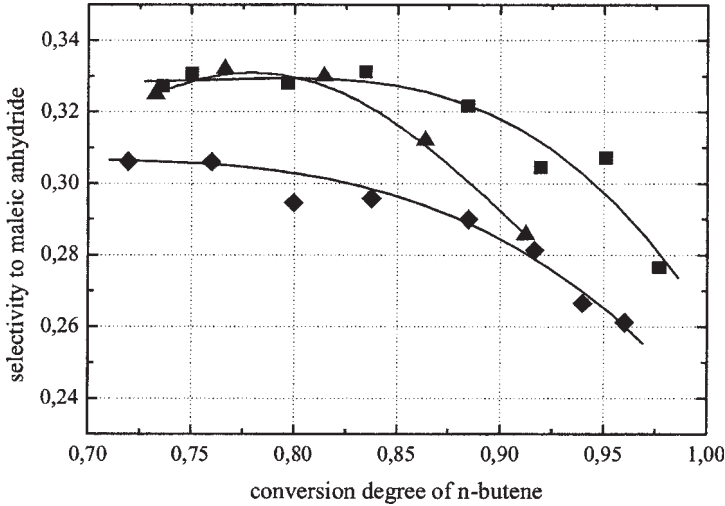


Figure 3.34 Experimental data on selectivity to maleic anhydride vs degree of conversion of 1-butene for different reactor types: (◆) channel width 0.08 mm and (▲) channel width 0.2 mm micro reactor; (■) fixed-bed reactor [103].

Benchmarking to fixed bed

[GP 3] [R 3b] The maximum selectivity of about 33% was the same for the best micro reactor and the fixed bed (Figure 3.34) at the same conversions from 73 to 85% with a $V_2O_5/P_2O_5/TiO_2$ catalyst [103]. At still higher conversion, the fixed bed has a better performance. However, the residence times needed for comparable conversion are one order of magnitude shorter than in the fixed-bed reactor.

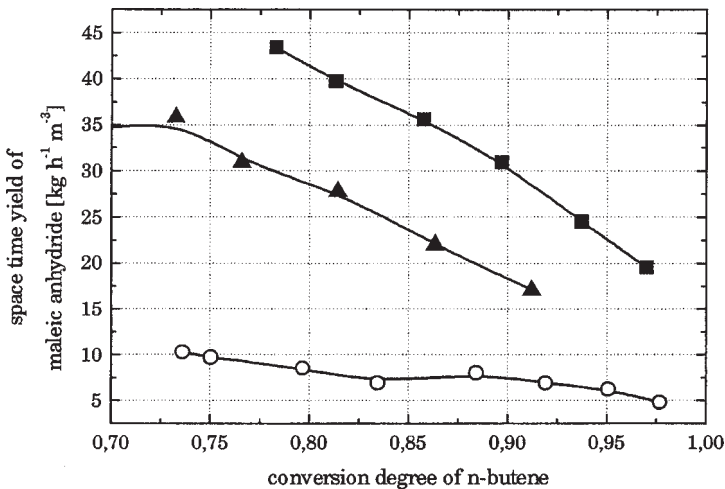


Figure 3.35 Space-time yield of maleic anhydride vs degree of conversion for 1-butene when using different reactor types: (■) channel width 0.4 mm and (▲) channel width 0.08 mm micro reactor; (○) fixed-bed reactor [103].

Space–time yield

[GP 3] [R 3b] The space–time yield of chemical micro processing was a factor of five larger than that of a conventional fixed-bed reactor (Figure 3.35) (0.4% 1-butene in air; 0.1 MPa; 400 °C) [103]. This is due to the shorter residence time needed in the micro reactors for the same conversion as in the fixed bed. Differences from the fixed bed become smaller when operating at very high conversion, up to 95%. The space–time yield of the 400 μm \times 400 μm micro channels exceed that of the 80 μm \times 80 μm micro channels.

The ratio of space–time yields referring to various micro channels equals the ratio of cross sections [103].

Post-catalytic effects

[GP 3] [R 3b] [R 4a] The presence of a metallic diffuser can contribute significantly and in a negative manner to the reaction, e.g. at long residence times by decomposing 21% of the product formed [103]. An exchange against a glass diffuser can notably reduce the product degradation.

Safe operation

[GP 3] [R 3b] [R 4a] Safe operation in the explosive regime was demonstrated [103]. Catalytic runs with 1-butene concentrations up to 10 times higher than the explosion limit were performed (5–15% 1-butene in air; 0.1 MPa; 400 °C). A slight catalyst deactivation, possibly due to catalyst active center blockage by adsorption, was observed under these conditions and not found for lower 1-butene concentrations. Regeneration of the catalyst is possible by oxidation.

An ignition experiment at 1-butene concentrations as high as 5% was performed to test instability in reaction behavior as an indication of unsafe operation (5% 1-butene in air; 0.1 MPa; 400 °C) [103]. The degree of conversion increased linearly and converged without any sign of instability. The power input corresponded to 6.5 W with an adiabatic temperature rise of more than 2000 °C. Plugging, however, was the major concern under these severe conditions.

Additionally, potential strong thermal changes in the micro reactors could be deliberately induced by strong changes in conversion (5% 1-butene in air; 0.1 MPa; 400 °C) [103]. For this reason, pulses of high 1-butene concentration were inserted in the micro reactor. Remarkably low axial temperature gradients within the explosion regime at high thermal power were found. The zone of the highest reaction rate shifts with respect to the micro channel length.

3.3.6

Oxidation of Methanol – Formaldehyde Formation

Proceedings: [72]; sections in reviews: [95, 97, 100].

3.3.6.1 Drivers for Performing Formaldehyde Synthesis in Micro Reactors

The oxidative dehydrogenation of methanol to formaldehyde is a model reaction for performance evaluation of micro reactors (see description in [72]). In the corresponding industrial process, a methanol–air mixture of equimolecular ratio of methanol

and oxygen is guided through a shallow catalyst bed of silver at 150 °C feed temperature, 600–650 °C exit temperature, atmospheric pressure and a contact time of 10 ms or less. Conversion amounts to 60–70% at a selectivity of about 90%.

Both oxidative and non-oxidative routes with similar share are followed, yielding hydrogen or water as additional products. As by-products, carbon dioxide and carbon monoxide, methyl formate and formic acid are generated. It is advised to quench the exit stream as formaldehyde decomposition can occur.

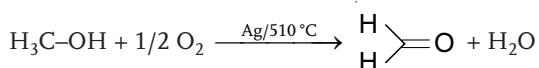
3.3.6.2 Beneficial Micro Reactor Properties for Formaldehyde Synthesis

The reaction is a model reaction, hence the respective investigations evaluate micro reactor properties in a more general way.

Beneficial micro reactor properties mainly refer to improving heat management as a key for obtaining a partial reaction in a consecutive sequence, when large heats are released by reaction steps other than the partial one (see also Section 3.3.1).

Special attention has to be drawn to having good mass transfer at millisecond contact times.

Gas-phase reaction 4 [GP 4]: Oxidation of methanol to formaldehyde



3.3.6.3 Typical Results

Conversion/selectivity/yield

[GP 4] [R 11] For methanol conversion over sputtered silver catalyst, conversions up to 75% at selectivities of about 90% were found (8.5 vol.-% methanol; 10–90% oxygen; balance helium; 510 °C; 10 ms; slightly > 1 atm) [72].

Oxygen content

[GP 4] [R 11] For methanol conversion over sputtered silver catalyst, variation in oxygen content from 10% to more than 90% of the gas mixture results in a slight decrease of conversion from 75 to 70% and of selectivity from 91 to 89% (8.5 vol.-% methanol; balance helium; 510 °C; 10 ms; slightly > 1 atm) [72].

Oxygen reaction order

[GP 4] [R 11] For methanol conversion over sputtered silver catalyst, selectivity is hardly affected by changing the oxygen concentration (8.5 vol.-% methanol; 10–90% oxygen; balance helium; 510 °C; 10 ms; slightly > 1 atm) [72]. This is in line with assuming a zero-order dependence on oxygen concentration and agrees with literature findings.

Catalyst deactivation

[GP 4] [R 11] For methanol conversion over sputtered silver catalyst, no catalyst deactivation at high oxygen : methanol ratios (e.g. over 0.2 : 1) was observed, different from findings in the literature with conventional catalysts and reactors (8.5 vol.-% methanol; 10–90% oxygen; balance helium; 510 °C; 10 ms; slightly > 1 atm) [72].

Since in the literature such deactivation was attributed to a sudden temperature rise and decline under the same process conditions, it was assumed that the improved thermal control of micro channels is responsible for the higher stability.

Temperature

[GP 4] [R 11] For methanol conversion over sputtered silver catalyst, conversion increases almost linearly from 430 to 530 °C (8.6 vol.-% methanol; balance oxygen; 10 ms; slightly > 1 atm) [72]. A slight increase in selectivity towards carbon dioxide at the expense of formaldehyde was observed. At 530 °C, about 75% conversion at 90% formaldehyde selectivity was achieved.

Residence time

[GP 4] [R 11] For methanol conversion over sputtered silver catalyst, conversion increases from 57 to 73% on applying six times longer residence times (8.5 vol.-% methanol; balance oxygen; 510 °C; 4–27 ms; slightly > 1 atm) [72]. Selectivity decreases slightly from more than 90% initially.

Micro-channel diameter

[GP 4] [R 11] For methanol oxidation over sputtered silver catalyst, conversion is higher when using micro channels of smaller diameter (8.5 vol.-% methanol; balance oxygen; 510 °C; 4–27 ms; slightly > 1 atm) [72]. For two channels of the same width, but different depths (70 μm , 130 μm), concentration differences of nearly 10% at the same residence time were detected, all other parameters being equal. The increase in conversion in the 70 μm channel was partly at the expense of selectivity (3–6% in the range investigated).

Kinetics: reaction rate and activation energy

[GP 4] [R 11] For methanol conversion over sputtered silver catalyst, reaction rates and an activation energy (Figure 3.36) of 14.3 kcal mol⁻¹ were reported (8.5 vol.-% methanol; balance oxygen; 10 ms; slightly > 1 atm) [72]. Since the latter is much lower than literature values (about 22.5–27 kcal mol⁻¹), different kinetics may occur or limitations of the reactor model may become evident.

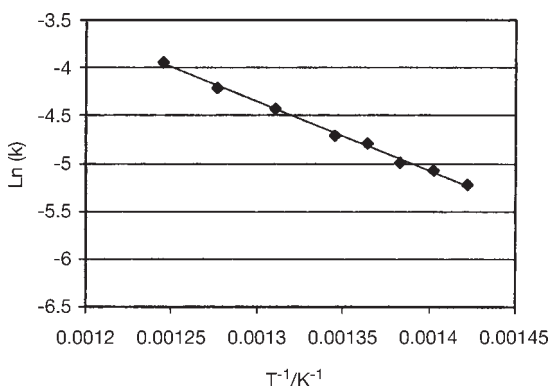


Figure 3.36 Arrhenius plot for the oxidative dehydrogenation of methanol to formaldehyde performed in a micro reactor [72].

A comparison of experimental findings and theoretical predictions is given in [72]. Although qualitatively consistent, experiments confirm a weaker dependence on parameters such as residence time and micro-channel diameter.

3.3.7

Oxidation of Derivatized Alcohols – Derivatized Aldehyde Formation

Peer-reviewed journals: [1, 49]; journals: [50]; proceedings: [51, 72, 104, 105]; reactor description: [31, 32, 46, 47, 106]; sections in reviews: [87, 90, 95–97, 100, 107].

3.3.7.1 Drivers for Performing Derivatized Aldehyde Synthesis in Micro Reactors

The oxidative dehydrogenation of methanol to formaldehyde was chosen as model reaction by BASF for performance evaluation of micro reactors [1, 49–51, 108]. In the industrial process a methanol–air mixture of equimolecular ratio of methanol and oxygen is guided through a shallow catalyst bed of silver at 150 °C feed temperature, 600–650 °C exit temperature, atmospheric pressure and a contact time of 10 ms or less. Conversion amounts to 60–70% at a selectivity of about 90%.

Both oxidative and non-oxidative routes with similar shares are followed, yielding hydrogen or water as additional products. As by-products, carbon dioxide and carbon monoxide, methyl formate and formic acid are generated. It is advised to quench the exit stream as formaldehyde decomposition can happen.

The oxidation of an undisclosed methanol derivative to the corresponding formaldehyde compound is a large-scale BASF process which was established in recent years, whereas the similar methanol-to-formaldehyde process, performed on a much larger scale, has been practised at BASF for more than 100 years [1, 49–51, 108]. The exact nature of the substituent(s) was not disclosed by BASF for reasons of confidentiality, although many publications on that topic appeared. The nature of the substituent makes the derivative, as the results of the investigations show, more labile to temperature.

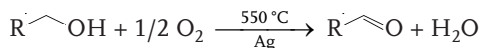
Both processes – referring to the non-substituted and substituted methanol reactant – utilize elemental silver catalyst by means of oxidative dehydrogenation. Production is carried out in a pan-like reactor with a 2 cm thick catalyst layer placed on a gas-permeable plate. A selectivity of 95% is obtained at nearly complete conversion. This performance is achieved independent of the size of the reactor, so both at laboratory and production scale, with diameters of 5 cm and 7 m respectively.

3.3.7.2 Beneficial Micro Reactor Properties for Derivatized Aldehyde Synthesis

The reaction is an industrial process; the micro reactor was taken as a precise instrument giving analytical information which was transferred to the large-scale process in a non-disclosed way.

Beneficial micro reactor properties mainly refer to improving heat management as a key for obtaining a partial reaction which is part of a consecutive sequence, when large heats are released by reaction steps other than the partial one (see also Sectoin 3.3.1). An even more import selectivity issue refers to the suppression of side reactions, which relate to the other functionality present in the reactant. This, again, profits from improved heat transfer.

Gas-phase reaction 5 [GP 5]: oxidation of derivatized methanol to derivatized formaldehyde



3.3.7.3 Typical Results

Conversion/selectivity/yield

[GP 4] [R 5] For an undisclosed methanol derivative, a selectivity of 96% at 55% conversion was found for the micro reactor with silver as construction material (390 °C), which exceeds the performance of laboratory pan-like (40%; 50%; 550 °C) and short shell-and-tube (85%; 50%; 450 °C) reactors (Figure 3.37) using elemental silver [1, 49–51, 108]. At slightly higher conversion, selectivity of the chemical micro processing decreases, and 89% selectivity at 59% conversion is found.

Hot spots

[GP 4] [R 5] For an undisclosed methanol derivative, no hot spot (close to 0 K rise) was found for the construction-material silver micro reactor (operational temperature: 390 °C); hot spots of 160 and 60 K were found for laboratory pan-like (40%; 50%; 550 °C) and short shell-and-tube reactors, respectively, using elemental silver [1, 49–51, 108].

Relevance for industrial process development

[GP 4] [R 5] Formaldehyde synthesis has been known at BASF for more than 100 years [1, 49–51, 108]. Hence it was expected to be able to handle the synthesis of substituted analogue, an undisclosed methanol derivative, with the same processing concepts, major problems not being anticipated. This expectation was still supported by first attempts with the tried and tested pan-like reactor concept (5 cm diameter), which were promising. At 50% conversion, a selectivity of 90% was achieved. However, transfer to production scale using a 3 m production reac-

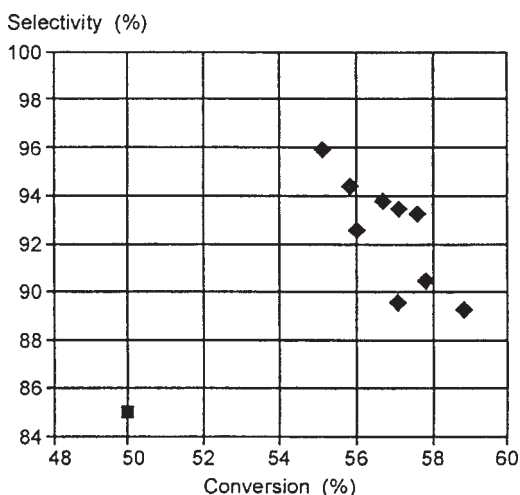


Figure 3.37 Selectivity-conversion diagram of the oxidative dehydrogenation reaction [1].

tor was difficult. At 50% conversion, the selectivity was only 40%. Considering the process again, the solution to prevent this large drop in selectivity became apparent. Hot spot formation due to the large heat release led to an increase in temperature in the reaction zone up to 160 °C. The reactant and product were judged to be more labile than methanol and formaldehyde. Consequently, thermally induced side reactions reduced the selectivity.

Based on this assumption, the needed measures were evident: to reduce the hot spots and, possibly concurrently, the operating temperature and, at best, to reduce the residence time substantially. An ideal combination of all these parameters is provided by operation in the micro reactor. As a result, a much better performance of the micro reactor than the conventional laboratory reactors was found (see the previous section for more details); no hot spot was found.

All conventional reactors, tested before using the micro reactor (simply since micro reactors were hardly available at that time), only fulfilled the demands of one measure, at the expense of the other measures. For instance, a single-tube reactor can be operated nearly isothermally, but the performance of the oxidative dehydrogenation suffers from a too long residence time. A short shell-and-tube reactor provides much shorter residence times at improved heat transfer, which however is still not as good as in the micro reactor.

3.3.8

Oxidation of Propene to Acrolein

Proceedings: [37]; master thesis: [109]; sections in reviews: [90].

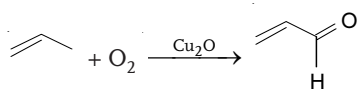
3.3.8.1 Drivers for Performing the Oxidation of Propene to Acrolein

Propene is an intermediate utilized in the chemical and pharmaceutical industries. The partial oxidation of propene on cuprous oxide (Cu_2O) yields acrolein as a thermodynamically unstable intermediate, and hence has to be performed under kinetically controlled conditions [37]. Thus in principle it is a good test reaction for micro reactors. The aim is to maximize acrolein selectivity while reducing the other by-products CO , CO_2 and H_2O . Propene may also react directly to give these products. The key to promoting the partial oxidation at the expense of the total oxidation is to use the Cu_2O phase and avoid having the CuO phase.

3.3.8.2 Beneficial Micro Reactor Properties for the Oxidation of Propene to Acrolein

The reaction was of a scouting nature, actually one of the most common investigations done concerning gas-phase reactions in micro reactors. Hence it addresses in a general way the investigation of general micro reactor properties such as mass and heat transport and residence time.

Of particular concern was the finding of a suitable catalyst. Owing to the scouting nature, virtually no know-how base was available that time. The investigation gave highly valuable hints for later catalyst development. Actually, they motivated a search for catalysts of higher porosity and better defined composition. As a result, anodically oxidized alumina supports for catalysts were developed (see Sections 3.1 and 3.4.2).

Gas-phase reaction 6 [GP 6]: oxidation of propene to acrolein

propene

acrolein

3.3.8.3 Typical Results**Conversion/selectivity/yield**

[GP 6] [R 5] With a stabilized Cu_2O catalyst layer, by addition of bromomethane (ppm level), 20% selectivity at 5% conversion was found (0.5 vol.-% propene; 0.1 vol.-% oxygen; 2.25 ppm promoter; 350 °C) [37]. This is far better than with non-conditioned copper oxide catalysts which contain CuO besides Cu_2O . It is expected that the first species promotes more total oxidation, whereas the latter steers partial oxidation. In the above experiment, selectivity rises from 7 to 30% at slightly reduced conversion after 3 h of promoter conditioning.

Catalyst conditioning

[GP 6] [R 5] For Cu_2O catalyst layers, a non-uniform temperature dependence of the selectivity–conversion behavior was found (0.1 vol.-% propene; 0.02 vol.-% oxygen; 350, 363, 375 °C) [37]. A drop in selectivity with the first temperature variation was followed by a rise. This was attributed to oxidation of the initial Cu_2O catalyst layer during the course of the reaction (see the previous section) so that non-optimized and non-stationary catalyst compositions occur during and between the experiments. This was further evidenced by pre-conditioning of the copper oxide layer by reduction with either CO or propene/nitrogen, giving either Cu_2O - or CuO -rich layers. After 40 h time-on-stream, nearly the same selectivity was achieved in both cases (Figure 3.38).

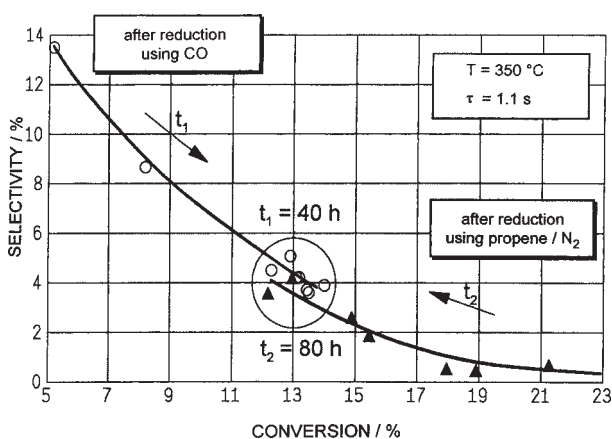


Figure 3.38 Comparison of selectivity to acrolein vs conversion of propene depending on time on-stream. Pre-treated in CO (t_1); pre-treated in propene/nitrogen (t_2) [37].

3.3.9

Oxidation of Isoprene – Citraconic Anhydride Formation

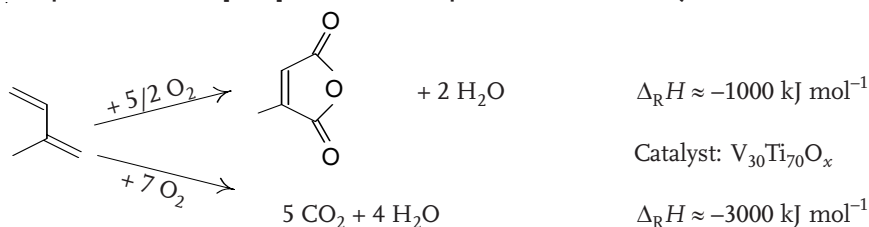
Proceedings: [13, 27, 85]; sections in review: [90, 95, 97, 100, 110].

3.3.9.1 **Drivers for Performing Citraconic Anhydride Formation**

Citraconic anhydride is, among other applications, a starting material in the synthesis of pharmaceuticals (see original citation in [13, 27]). The currently applied synthesis from itaconic acid is complex and hence there is a quest for alternatives. One of these is the partial oxidation of isoprene in the gas phase. Owing to the high reaction enthalpy of 1000 kJ mol^{-1} , generation of large heats at high conversion is possible. In that case, local overheating (hot spots) can promote the total oxidation to carbon dioxide and water.

3.3.9.2 **Beneficial Micro Reactor Properties for Citraconic Anhydride Formation**

Beneficial micro reactor properties mainly refer to improving heat management as a key for obtaining a partial reaction which is part of a consecutive and parallel sequence, when large heats are released by reaction steps other than the partial one (see also Section 3.3.1).

Gas-phase reaction 7 [GP 7]: oxidation of isoprene to citraconic anhydride3.3.9.3 **Typical Results****Conversion/selectivity/yield**

[GP 7] [R 6] The selectivity (up to 28%) for micro-reactor processing using a $\text{V}_{30}\text{Ti}_{70}\text{O}_x\text{-SiO}_2$ catalyst at nearly complete conversion is similar to the performance of a fixed-bed reactor with a $\text{V}_{30}\text{Ti}_{70}\text{O}_x$ catalyst (0.6 vol.-% isoprene, 20 vol.-% oxygen; $p = 1.2 \text{ bar}$) [27]; however, for the same performance, the processing in the micro reactor needs to be done at temperatures exceeding fixed-bed operation by 40 K. The micro reactor is operated at $400 \text{ }^\circ\text{C}$ whereas the fixed bed is processed at $360 \text{ }^\circ\text{C}$. This difference is attributed to using a similar, but not identical, catalyst formulation; the 'micro reactor catalyst' $\text{V}_{30}\text{Ti}_{70}\text{O}_x\text{-SiO}_2$ is regarded as being less active (Figure 3.39). Furthermore, total oxidation of the citraconic acid product may occur in the hot outlet section of the micro reactor. For this reason, an optimized design with a cooler directly behind the reaction zone could be advantageous.

A maximum yield of 23% is found in the micro reactor [27].

[GP 7] [R 8] In a later study, a yield of about 40% is found for the same steel reactor [55]. For a ceramic reactor, an even higher yield of 45% is reported. This is explained by a reduction in blank activity (Figure 3.40) (see the sections Activity of

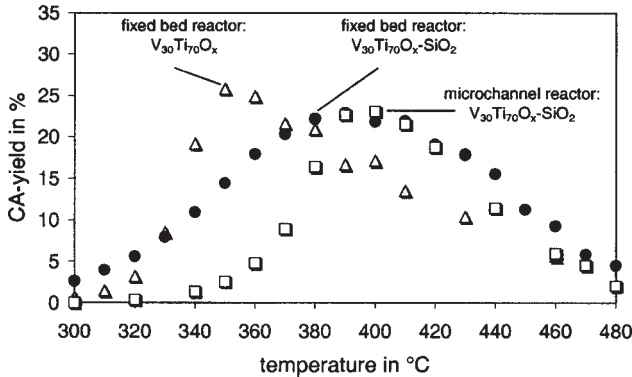


Figure 3.39 Partial oxidation of isoprene in a fixed-bed reactor and a micro reactor. The yield of citraconic anhydride is plotted as a function of reaction temperature and catalyst composition [27].

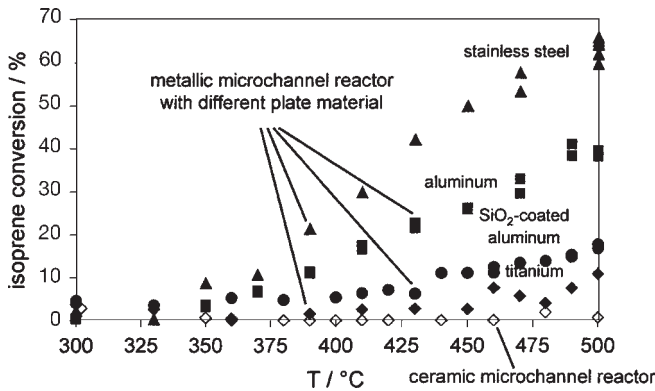


Figure 3.40 Experimental results for isoprene conversion in metallic and ceramic micro reactors. The metallic micro reactors were operated without catalyst to determine blank activity of the various construction materials. In addition, conversion data were calculated. (\diamond) Calculated values for micro-channel reactor model; (full symbols) experimental values for different reactor materials [27].

the same catalyst coating on different microstructured materials and Blank activity of microstructured material below).

Process temperature

[GP 7] [R 6] For a $V_{30}Ti_{70}O_x-SiO_2$ catalyst, conversion increases with temperature until complete conversion is reached at 390–420 °C depending on the volume flow (0.6 vol.-% isoprene, 20 vol.-% oxygen; $p = 1.2$ bar) [27]; the selectivity passes a maximum at 390–420 °C depending on the volume flow. The yield correspondingly exhibits maxima with optimal performance at 390–420 °C.

Blank activity of microstructured material

[GP 7] [R 8] In absence of a catalyst, blank activities were determined for both metallic and ceramic micro-channel reactors [55]. The following sequence of materials with regard to undesired blank activity was determined: steel > aluminum >

titanium. Coating of aluminum with inert layers such as silica can also reduce blank activity. However, the best option is to use ceramic materials. Whereas ceramics have not more than 1–2% isoprene conversion at the maximum temperature investigated of 500 °C, steel has about 60% conversion, leading to total oxidation (0.5 vol.-% isoprene in air; 50 Nml min⁻¹ and 200 Nml min⁻¹).

Similar findings were made by BASF in studies investigating an undisclosed gas-phase reaction in capillaries made of quartz, catalyst material and reactor-wall material [105]. The dimensions were chosen in such a way that they match the of surface-to-volume ratio of a fixed-bed reactor used previously for the same reaction. A quartz capillary shows no conversion, whereas reactor-wall material actually has a greater activity than the catalyst itself. Hence BASF came to the, at first sight, surprising conclusion that in their production process it was the reactor wall, and not the catalyst, which catalyzes the reaction. The reactor wall was 70 times more active than the catalyst; it needs a temperature increase of about 100 °C to have both at equal conversion.

Activity of the same catalyst coating on different microstructured materials

[GP 7] [R 8] For a suspended V₇₅Ti₂₅O_x-SiO₂ catalyst, conversion in a steel reactor is lower than when employing a ceramic reactor at a given temperature [55]. This was explained by more efficient heat removal of the steel construction material. This good isothermicity should in turn promote selectivity; however, this is outperformed by the higher blank activity. At 400 °C, complete conversion is given for the ceramic-supported catalyst, whereas about 40% is found for the steel-supported catalyst (0.6 vol.-% isoprene in air; 6 g_{cat} min mol_{tot}⁻¹). The corresponding yields are about 40 and 10%, respectively.

Catalyst formulation

[GP 7] [R 6] The performances of three different catalysts at constant flow per micro channel were compared (Figure 3.41): V₃₀Ti₇₀O_x-Al₂O₃ (by anodic oxidation and impregnation), V₃₀Ti₇₀O_x-SiO₂ (by a suspension method similar to washcoat treatment) and VO_x-SiO₂ (by a suspension method) [27]. The results for the suspension catalysts were superior. The maximum citraconic anhydride selectivity for the two suspension catalysts was 25 and 22%, whereas the selectivity of the anodic oxidation-impregnated catalyst was only 12% (0.6 vol.-% isoprene, 20 vol.-% oxygen; *p* = 1.2 bar). For the latter, conversion and selectivity curves are also shifted to higher temperatures.

Accordingly, the suspension catalysts were chosen for all subsequent investigations. However, the results were slightly worse compared with the V₃₀Ti₇₀O_x catalyst in fixed bed (see Conversion/selectivity/yield section). The conventional formulation of the catalyst had to be slightly modified (from V₃₀Ti₇₀O_x to V₃₀Ti₇₀O_x-SiO₂) for micro-reactor application to allow insertion in the micro channels via suspension [27]. Investigation of the new V₃₀Ti₇₀O_x-SiO₂ system, in both fixed-bed and micro reactors, shows the same activity, lower than V₃₀Ti₇₀O_x. This is an indication that the higher temperatures needed for comparable micro-reactor operation are due to lower catalyst activity and are not inherent to the chemical micro processing itself.

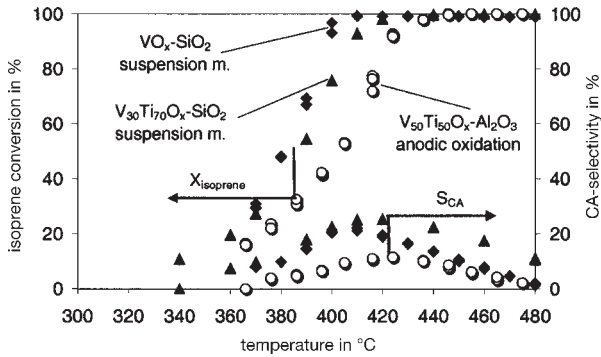


Figure 3.41 Conversion of isoprene and selectivity for citraconic anhydride as a function of temperature and catalyst used [27].

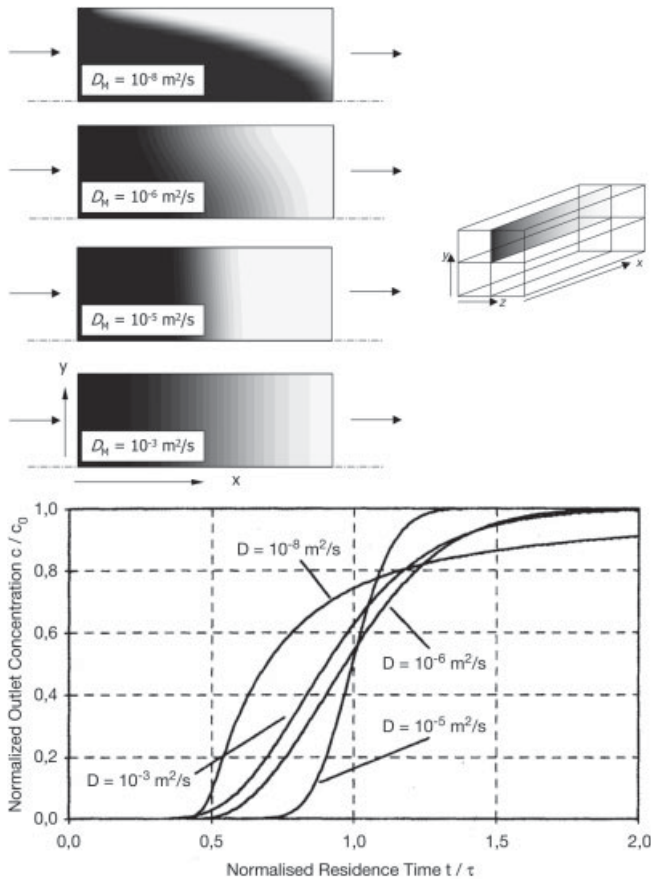


Figure 3.42 Evolution of a pulse at the entrance of a micro channel for different diffusion coefficients. Calculated concentration profile (left) and cumulative residence time distribution curve (channel: $300\ \mu\text{m} \times 300\ \mu\text{m} \times 20\ \text{mm}$; flow velocity: $1\ \text{m s}^{-1}$; $t = 10\ \text{s}$) [27].

Simulations in periodic concentration processing

[GP 7] [R 6] The influence of the channel diameter on the cumulative residence time distribution (RTD) was simulated (Figure 3.42) [85] ($D = 3 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$; channel length: 20 mm; channel diameter: 1200–75 μm ; 1 m s^{-1}). The width of the RTD decreases initially, but remains finite for small diameters such as 75 μm .

The impact of the diffusion coefficient was also analysed; here values of isoprene and oxygen were taken [85]. It was found that the RTD of one component in a cycling experiment may be narrow, while the other component is not at optimum. By changing the channel diameter, such a sequence may even be reversed. It is advised [85] to operate in the diffusion-dominated branch rather than in the convection-dominated branch.

For a short description of the aims of experimental concentration cycling with respect to citraconic acid formation, see [13]. It is also demonstrated there that the response to rectangular concentration pulses for a given reactor configuration of a multi-channel-stack micro reactor can be improved by increasing the number of platelets and channels (while reducing their diameter). Such behavior was shown for an incompressible fluid, i.e. is not solely related to the above-mentioned reaction.

3.3.10

Partial Oxidation of Methane – Syngas Generation

Peer-reviewed journals: [3]; proceedings: [111, 112]; sections in reviews: [86, 87, 90, 96, 97, 113].

3.3.10.1 **Drivers for Performing Syngas Generation**

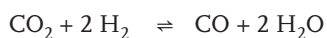
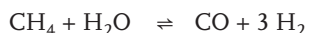
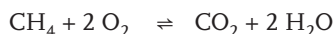
Syngas is a mixture of carbon monoxide and hydrogen made from oxidation of methane. The generation of syngas plays a role in some ideas on future exploitation of natural gas deposits (see original citations in [3]). At remote sites, many small- and medium-volume deposits containing natural gas or mixtures thereof with petroleum exist. Owing to the limited deposit volumes and the difficulty of installing transportation facilities in remote areas, it is usually not economical to exploit such resources. One solution to this problem could be to liquefy the gaseous products, in particular the most prominent species methane, so allowing more facile transportation. The transformation of methane into hydrogen-rich gases is part of this gas-liquefaction strategy, finally yielding liquid products such as methanol or liquid hydrocarbons. For this purpose, mobile, small-scale, efficient and flexible production systems are required. It is generally believed that micro reactors with their flexible numbering-up concept could provide a technical platform that may in future allow economical gas liquefaction at the remote deposit sites.

Partial methane oxidation comprises very high rates so that high space–time yields can be achieved (see original citations in [3]). Residence times are in the range of a few milliseconds. Based on this and other information, it is believed that syngas facilities can be far smaller and less costly in investment than reforming plants. Industrial partial oxidation plants are on the market, as e.g. provided by the Syntroleum Corporation (Tulsa, OK, USA). Requirements for such processes are operation at elevated pressure, to meet the downstream process requirements, and autothermal operation.

3.3.10.2 Beneficial Micro Reactor Properties for Syngas Formation

The efficient mass and heat transfer in general render micro reactors interesting for this very fast reaction. Given such performance, high throughputs or space-time yields are in principle achievable; therefore, the use for real production, of whatever capacity, is not out of discussion. Favorably, this will be applied for small, compact and light-weight systems for energy generation where the syngas formation is one step.

Gas-phase reaction 8 [GP 8]: Syngas generation by partial oxidation of methane



3.3.10.3 Typical Results

Start-up behavior

[GP 8] [R 7] Ignition occurs at a rhodium catalyst at catalyst temperatures between 550 and 700 °C, depending on the process parameters [3]. Total oxidation to water and carbon dioxide is favored at low conversion (< 10%) prior to ignition. Once ignited, the methane conversion increases and hence the catalyst temperature increases abruptly.

Catalyst formation

[GP 8] [R 7] Rhodium catalysts generally show no pronounced activation phase as given for other catalysts in other reactions [3]. In the first 4 h of operation, methane conversion and hydrogen selectivity increases by only a few percent. After this short and non-pronounced formation phase, no significant changes in activity were determined in the experimental runs for more than 200 h.

Operational changes of the catalyst

[GP 8] [R 7] The structure of the rhodium catalyst changed during operation. Owing to the microfabrication process (thin-wire μ EDM), the surface of the micro channels was rough before catalytic use [3]. After extended operational use, small crystallites are formed, especially in oxygen-rich zones such as the micro channels' inlet. Thereby, the surface area is enlarged by a factor of 1–1.5.

Noble metal loss of about 0.1 wt.-% of the honeycomb rhodium catalyst was observed during 200 h of operation; similar effects are also known in commercial ammonia combustion processes [3]. This did not lead to a decrease in catalyst activity as rhodium was the only construction material.

By inspection windows and use of a pyrometer, visual inspection of the catalyst and temperature monitoring on-site in a contactless manner were performed. It turned out that a glowing, homogeneous texture occurs at catalyst temperatures between 900 and 1200 °C, GHSV values up to 10^6 h^{-1} and pressures less than 1 MPa [3]. This is an indication of the absence of soot deposits. At lower temperatures or

higher pressures, separate soot nests were detected and can be completely removed by oxidation.

In-Site temperature monitoring

[GP 8] [R 7] By pyrometric analysis, local temperatures at the rhodium catalyst surface were determined, although the accuracy is limited [3]. In this way, temperatures at the inlet were found to be 50–120 K higher than at the outlet for the operational range investigated. Conditions favoring conversion such as a pressure increase lead to even steeper temperature profiles. This is consistent with predictions that the entire oxygen amount is spent at the inlet region and that endothermic reforming reactions, reducing temperature, should dominate thereafter.

Conversion/selectivity/yield

[GP 8] [R 7] In the temperature range between 1090 °C and 1190 °C, complete oxygen conversion was achieved at a rhodium catalyst [CH_4/O_2 : 2.0; 0.12 MPa; $7.8 \cdot 10^5 \text{ h}^{-1}$ (STP)] [3, 112]. At 1190 °C, CO and H_2 selectivities of about 92 and about 78%, respectively, are found at about 63% methane conversion (Figure 3.43).

At a different methane/oxygen ratio (Figure 3.44), the methane conversion increases to 96%, giving CO and H_2 yields of 85 and 80%, respectively [CH_4/O_2 : 1.5; 0.15 MPa; $7.8 \cdot 10^5 \text{ h}^{-1}$ (STP)] [3].

The equilibrium values are not reached at a rhodium catalyst on a microstructured reactor within the limits of the experimental conditions and the constructional constraints [3]. As possible explanations post-catalytic reactions at lower temperatures or, more likely, insufficient catalyst activity concerning the short residence times are seen.

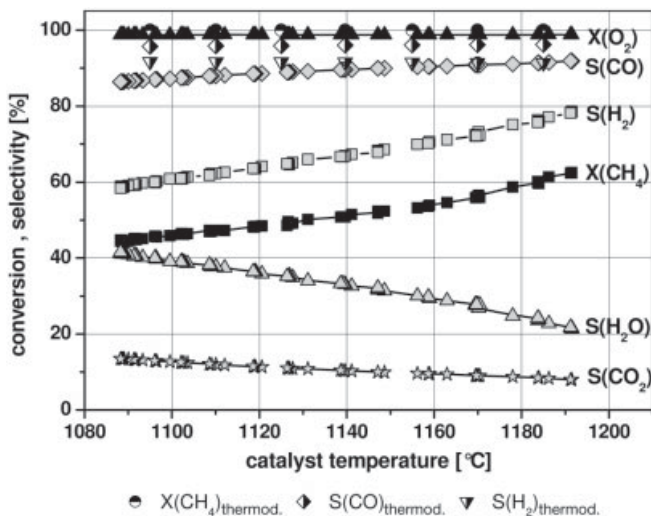


Figure 3.43 Conversion rates and product selectivity of partial methane oxidation as a function of the catalyst temperature. Experimental data (points) and calculated thermodynamic values (lines) [112].

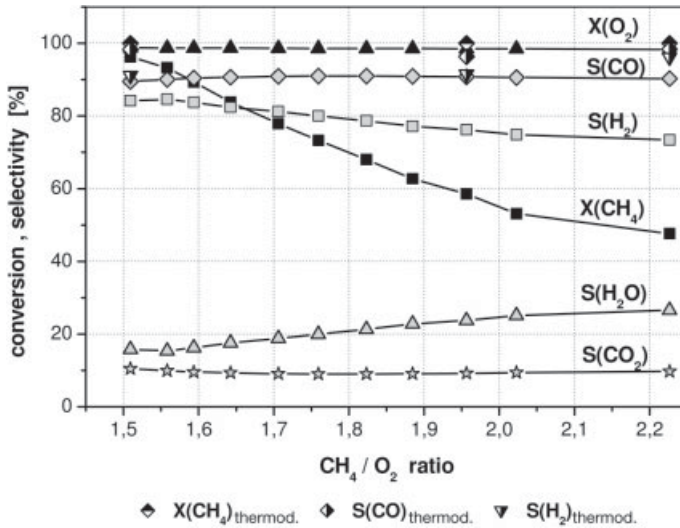


Figure 3.44 Conversion rates and product selectivity of partial methane oxidation performed under constant heating power as a function of the methane/oxygen ratio [112].

Process temperature

[GP 8] [R 7] Oxygen conversion at rhodium catalyst is complete within the temperature range 1090–1190 °C [CH₄/O₂: 2.0; 0.12 MPa; 7.8 · 10⁵ h⁻¹ (STP)] [3]. This shows that all oxygen is consumed by total oxidation of methane. With increasing temperature, CO and H₂ selectivities increase at increasing methane conversion owing to the increasing contribution of reforming reactions.

Process pressure

[GP 8] [R 7] Given constant catalyst temperature and GHSV, methane conversion and CO and H₂ selectivity decrease with increasing pressure at total oxygen consumption for a rhodium catalyst [CH₄/O₂: 2.0; 1–12 MPa; 1.17 · 10⁶ h⁻¹ (STP); 1200 °C] [3]. The decrease is larger than thermodynamically expected.

Methane/oxygen ratio

[GP 8] [R 7] Given process pressure, heating power and GHSV, the syngas yield decreases with increasing methane/oxygen ratio at a rhodium catalyst, as well as with the CO and H₂ selectivities, and particularly strong with the methane conversion [CH₄/O₂: 1.5–2.23; 0.15 MPa; 95 W; 7.8 · 10⁵ h⁻¹ (STP)] [3].

Residence time by changing flow velocity

[GP 8] [R 7] Residence times were varied at a rhodium catalyst by changing the flow velocity (GHSV). Methane conversion and CO and H₂ selectivity decreased by about 10% decreasing the flow velocity in the range investigated [CH₄/O₂: 1.66; 0.15 MPa; 2.0 · 10⁵ – 1.2 · 10⁶ h⁻¹ (STP); 1090 °C] [3]. The decline was attributed to

reaction kinetics, since it could be ruled out that mass transfer limitations exist for the operational conditions and the micro channel geometry investigated.

Residence time by changing micro channel length

[GP 8] [R 7] Residence times were varied at a rhodium catalyst by changing the micro channel length from 5 to 20 mm. Concerning different ways of comparison – in the autothermal state, for the same heating power and for the same GHSV – higher methane conversion and H₂ selectivity were observed for the longer micro channel (20 mm) reactor, whereas CO selectivity was slightly lower [CH₄/O₂: 2.0; 0.30 MPa; 2.9 · 10⁵ – 1.16 · 10⁶ h⁻¹ (STP); autothermal or 130 W] [3]. The better performance, however, is at the expense of an increased pressure drop and four times more construction material. Lower temperatures at the micro channels' outlet were found for the 20 mm reactor compared with the 5 mm reactor owing to an increased contribution of reforming reactions and more heat losses due to the reactor volume increase.

Dilution of inert gas

[GP 8] [R 7] Dilution with the inert gas argon served to simulate the oxidation behavior when using air. Methane conversion and H₂ and CO selectivity remain constant for a long range of dilution until they finally drop at inert gas contents above 50% [CH₄/O₂: 2.0; 10 – 57 vol.-% Ar; 0.15 MPa; 7.8 · 10⁵ h⁻¹ (STP); 105 W] [3]. Oxygen conversion is near-complete for all experiments. The micro channels' outlet temperatures drops on increasing the amount of inert gas.

Using air and a 20 mm long micro-channel reactor with rhodium catalyst results in high rates of syngas formation (CH₄/O₂: 1.75; oxygen at air level, balance nitrogen; 0.15–2 MPa; 1.95 · 10⁵ h⁻¹ (STP); 1100 °C) [3]. However, to obtain high H₂ and CO selectivities, additional heating is required. Oxygen conversion was near complete for all experiments.

Benchmarking to laboratory scale reactor performance

[GP 8] [R 7] Syngas generation with commercial Pt–Rh gauzes, metal-coated foam monoliths and extruded monoliths has been reported. For similar process pressure, process temperature, and reaction mixture composition, methane conversions are considerably lower in the conventional reactors (CH₄/O₂: 2.0; 22 vol.-% methane, 11 vol.-% oxygen, 66 vol.-% inert species; 0.14–0.155 MPa; 1100 °C) [3]. They amount to about 60%, whereas 90% was reached with the rhodium micro reactor. A much higher H₂ selectivity is reached in the micro reactor; the CO selectivity was comparable. The micro channels' outlet temperatures dropped on increasing the amount of inert gas.

This is explained by a possible higher activity of pure rhodium than supported metal catalysts. However, two other reasons are also taken into account to explain the superior performance of the micro reactor: boundary-layer mass transfer limitations, which exist for the laboratory-scale monoliths with larger internal dimensions, are less significant for the micro reactor with order-of-magnitude smaller dimensions, and the use of the thermally highly conductive rhodium as construction material facilitates heat transfer from the oxidation to the reforming zone.

3.3.11

Oxidation of Carbon Monoxide to Carbon Dioxide

Peer-reviewed journals: [78]; proceedings: [7].

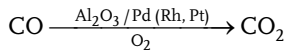
3.3.11.1 Drivers for Performing the Oxidation of Carbon Monoxide to Carbon Dioxide

This reaction serves for removal of carbon monoxide from gas mixtures and is usually carried out over supported metal catalysts. In reforming techniques, carbon monoxide, poisonous for the catalyst in fuel cells, is removed in such a way. It is also applied in automobiles for reducing the exhaust gas carbon monoxide to an environmentally acceptable level.

The carbon monoxide reaction is well studied and the observed kinetics are well understood. Of particular interest is the so-called 'CO-inhibiting regime', characterized by carbon dioxide covering and blocking the surface, so that the reaction rate is governed by CO desorption rate (see original citations in [78]).

3.3.11.2 Beneficial Micro Reactor Properties for the Oxidation of Carbon Monoxide to Carbon Dioxide

Owing to its nature as a test reaction, rather the reactor and its operational modes were tested, mainly to determine mass transfer limits (see Section 3.3.11.3). It was also used for kinetic studies on the performance of various catalysts.

Gas-phase reaction 9 [GP 9]: Oxidation of carbon monoxide to carbon dioxide**3.3.11.3 Typical Results****Kinetic data: turn-over frequency (TOF) and activation energies**

[GP 9] [R 16] The reaction rate and activation energy of metal catalysts (Rh, Pt or Pd) supported on alumina particles (~3 mg; 53–71 μm) were determined for conversions of 10% or less at steady state (1% carbon monoxide; 1% oxygen, balance helium; 20–60 sccm; up to 260 °C) [7, 78]. The catalyst particles were inserted into a meso-channel as a mini fixed bed, fed by a bifurcation cascade of micro-channels. For 0.3% Pd/Al₂O₃ (35% dispersion), TOF (about 0.5–5 molecules per site

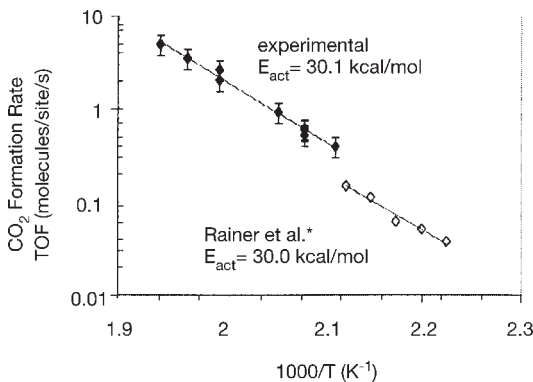


Figure 3.45 Experimental TOF for CO oxidation. Data given in [78].

and second) and apparent activation energy ($30.1 \text{ kcal mol}^{-1}$) values compare well with literature values (Figure 3.45). The same was found for Pt/Al₂O₃ and Rh/Al₂O₃ catalysts.

Kinetic data: reaction orders

[GP 9] [R 16] When using metal catalysts (Rh, Pt or Pd) supported on alumina particles (~3 mg; 53–71 μm) in a wide mini fixed bed, experimental reaction orders of 0.79 for CO and +1.0 to +1.5 for O₂ were found (Figure 3.46) and compare to literature data [78].

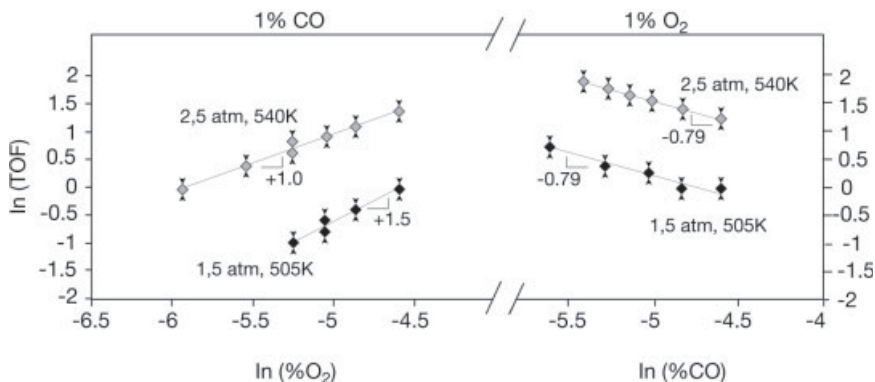


Figure 3.46 Determination of reaction orders for CO and O₂ for CO oxidation at different temperatures [78].

Thermal management/heat-sink properties

[GP 9] [R 16] When using metal catalysts (Rh, Pt, or Pd) supported on alumina particles (~3 mg; 53–71 μm) in a wide mini fixed bed, no temperature increase, as monitored by thermocouples, was observed [78]. 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.

Internal transport limits

[GP 9] [R 16] The extent of internal transport limits was analysed for the wide fixed-bed reactor, using experimental data on carbon monoxide conversion and matter and process parameter data for the reactants [78]. The analysis was based on the Weisz modulus and the Anderson criterion for judging possible differences between observed and actual reaction rates. As a result, it was found that the small particles eliminate internal transport limitations.

External transport limits

[GP 9] [R 16] The extent of external transport limits was made in an approximate manner as for the internal transport limits (see above), as literature data on heat and mass transfer coefficients at low Peclet numbers are lacking [78]. Using a Fick's law analysis, negligible concentration differences from the bulk to the catalyst sur-

face were found. Thus, mass transfer to the catalyst is not limiting. In an analogous manner, it was found that only a negligible temperature difference, such as 0.01 K, from the fluid bulk to the catalyst surface exists.

Diffusional mixing/differential behavior

[GP 9] [R 16] By finite-element reactor modeling, it was shown that for conversions as large as 34%, concentration differences within the mini wide fixed-bed reactor of only less than 10% are found [78]. Thus, the reactor approximates a continuous-stirred tank reactor (CSTR). This means that the mini wide fixed-bed reactor yields differential kinetics even at large conversions, larger than for reactors used so far (< 10% conversion).

Residence time

[GP 9] [R 16] When using metal catalysts (Rh, Pt or Pd) supported on alumina particles (~3 mg; 53–71 μm) in a wide mini fixed bed, residence times in the range 0.6–8.0 ms were applied (1% carbon monoxide, 1% oxygen, balance helium; 20–60 sccm; up to 260 °C) [78].

3.3.12

Andrussov Process

Proceedings: [2]; short mention on the Degussa variant for hydrogen-cyanide synthesis (no details): [71]; sections in reviews: [87, 88, 90, 96, 97, 114]; trade press: [81].

3.3.12.1 Drivers for Performing the Andrussov Process

The Andrussov process is, in addition to the Degussa and BASF processes, the major way to generate hydrogen cyanide which is an important chemical product used for many syntheses such as poly(methyl methacrylate) production. The conventional Andrussov process is performed using several layered nets of platinum as catalyst material, so-called gauzes [2, 81]. Gauzes of various mesh numbers and wire diameters are assembled as a stack to adjust flexibly the overall fluid passage length and porosity. The reactant gases are pre-heated to about 600 °C, pass the gauze catalyst and enter a heat exchanger. Typical process parameters rely on temperatures of about 1050 °C and residence times of 0.1 ms. Methane is also converted completely with a selectivity of about 60%. The ammonia selectivity is still higher, of the order of 60–70%, but conversion is not complete and considerable amounts of ammonia remain unreacted.

3.3.12.2 Beneficial Micro Reactor Properties for the Andrussov Process

The investigations were done in the framework of contract research for six industrial companies. Since it was done in a very early stage of development, it can be considered as a pioneering effort. The motivation was industrially driven, however, in a more generic way, aimed at showing general advantages of micro reactors for commercial use. Not only was performance enhancement envisaged, but also it was intended to demonstrate the robustness and capability of the microfabrication techniques at that time. In this context, one selection criterion for the Andrussov process, besides its prominent nature as an industrial process for hydrogen cy-

nide, was the high temperature requirements ($> 1000\text{ }^{\circ}\text{C}$) for performing this reaction. This posed considerable constraints on material choice and assembly. Furthermore, since hydrogen cyanide is very poisonous, the safe handling of small volumes of hazardous compounds was seen as a beneficial property. Although the investigations were only aimed at proving feasibility, on-site production in flexible quantities was a long-term goal behind such industrial investigations.

Gas-phase reaction 10 [GP 10]: Andrussov Process



3.3.12.3 Typical Results

Conversion/selectivity/yield

[GP 10] [R 18] Ammonia selectivity at a μ -gauze platinum catalyst is 62%, the methane selectivity amounts to 30% (70 ml h⁻¹ methane; 70 ml h⁻¹ ammonia; 500 ml h⁻¹ air; 1 bar; 977 $^{\circ}\text{C}$) [2, 81]. Ammonia and methane conversions are 45 and 98%, respectively. Significant amounts of carbon monoxide and dioxide are formed as total oxidation products. The best HCN yield determined is 31% (70 ml h⁻¹ methane; 70 ml h⁻¹ ammonia; 500 ml h⁻¹ air; 1 bar; 963 $^{\circ}\text{C}$).

Catalyst temperature

[GP 10] [R 18] Below 900 $^{\circ}\text{C}$, no HCN formation at a μ -gauze platinum catalyst was observed, but a significant amount of total oxidation (70 ml h⁻¹ methane; 70 ml h⁻¹ ammonia; 500 ml h⁻¹ air; 1 bar) [2]. At 900 $^{\circ}\text{C}$, about 70% methane conversion is determined, giving about equal amounts of carbon dioxide and carbon monoxide. In the range 900–980 $^{\circ}\text{C}$, an increasing amount of HCN is formed reaching finally a yield of about 31%. At this point, near complete methane conversion is achieved (Figure 3.47).

From 860 to 980 $^{\circ}\text{C}$, the carbon monoxide yield increases from near zero to about 50%, while the carbon dioxide yield decreases from about 30 to 15% [2]. This shift is according to the Boudouard equilibrium.

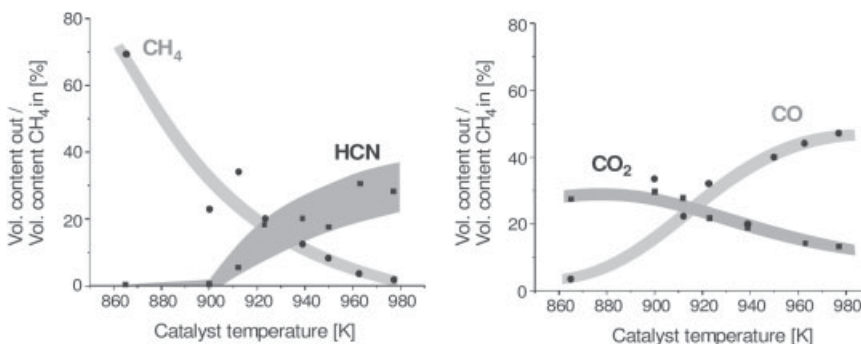


Figure 3.47 Dependence of the volume contents of methane, hydrogen cyanide, carbon monoxide and carbon dioxide, normalized to the methane content, on the reaction temperature (measurements made by BASF) [2].

Reactor cold spots/water condensation

[GP 10] [R 18] Cold spots in the reactor lead to water condensation [2]. This results in dissolution of water-soluble gases such as ammonia and hydrogen cyanide. As a consequence, the measurements of the gas levels of these compounds may differ considerably from the real values. After dissolution they are much too low; after re-evaporation of the aqueous solutions, unrealistically high values appear.

Benchmarking to industrial process

[GP 10] [R 18] The ammonia selectivity of 62% at a μ -gauze platinum catalyst is in the range of the technical process (Figure 3.48); the methane selectivity of 30% is only half the industrial performance (70 ml h⁻¹ methane; 70 ml h⁻¹ ammonia; 500 ml h⁻¹ air; 1 bar; 977 °C) [2, 81]. The reason for this difference is due to much more total oxidation reactions in the micro reactor. The methane conversion of 98% is similar to the industrial performance (but at the expense of selectivity, as mentioned above). The HCN yield of 31% (70 ml h⁻¹ methane; 70 ml h⁻¹ ammonia; 500 ml h⁻¹ air; 1 bar; 963 °C) is about half the value for the industrial process.

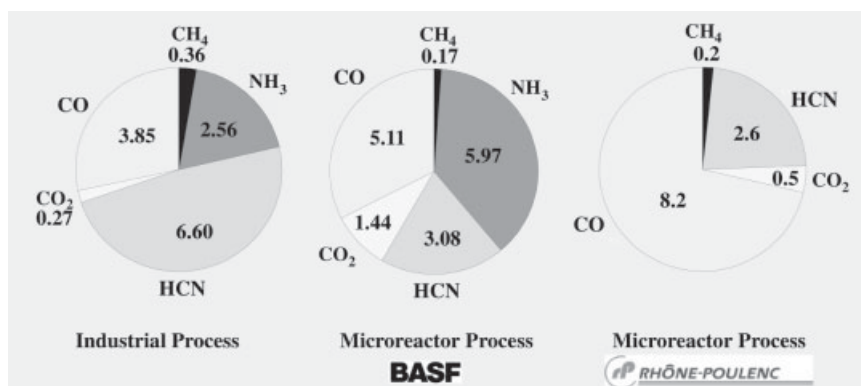


Figure 3.48 Product spectra obtained by measurements of BASF and Rhône-Poulenc compared with results of an industrial process. The data given are vol.-% of the product mixture [2].

Benchmarking to laboratory-scale monolith reactors

[GP 10] [R 18] The best HCN yield of 31% at a μ -gauze platinum catalyst (70 ml h⁻¹ methane; 70 ml h⁻¹ ammonia; 500 ml h⁻¹ air; 1 bar; 963 °C) is much better than the performance of monoliths (Figure 3.49) having similar laminar flow conditions [2]. A coiled strip and a straight-channel monolith have yields of 4 and 16%, respectively. The micro-reactor performance is not much below the best yield gained in a monolith operated under turbulent-flow conditions (38%).

The difference in reactor performance is due to the difference in hydraulic diameters of the reaction channels, i.e. related to varying mass-transfer limitations. The micro channels of the μ -gauze platinum catalyst amount to 70 μ m, whereas the monoliths have channel/pore diameters of 500–1200 μ m.

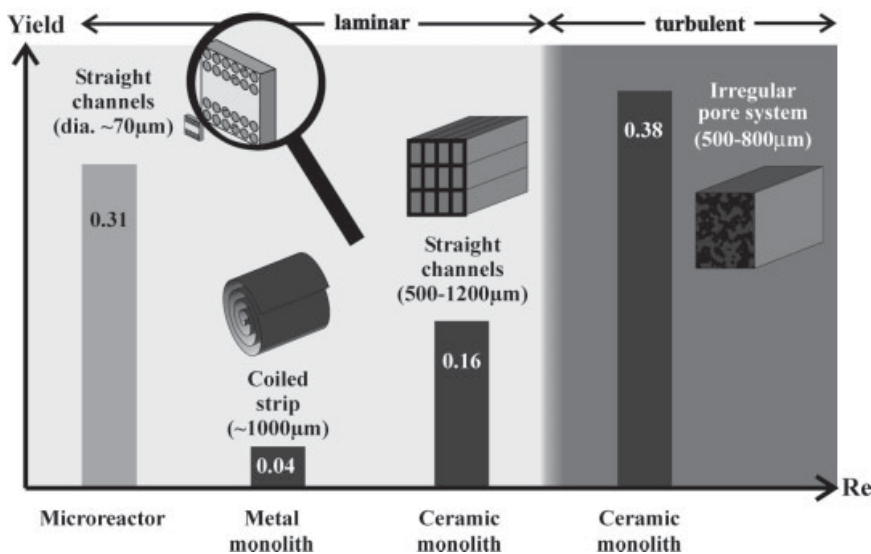


Figure 3.49 Comparison of yields of a micro reactor and monolithic reactors, both operating in the same flow regime [2].

3.3.13

Hydrogen/Oxygen Reaction

Peer-reviewed journals: [9]; proceedings: [82, 115–118]; sections in trade press: [92, 119]; sections in reviews: [90, 95–97, 100].

3.3.13.1 Drivers for Performing the Hydrogen/Oxygen Reaction

The reaction between hydrogen and oxygen leads to the formation of water. This reaction has extended explosive regimes with respect to the p, T, c -parameters. A mechanistic analysis of the elementary reactions is available and the explosion mechanisms are understood in detail. Accordingly, this reaction serves well as a model for other dangerous processes in the explosive regime such as many oxidations with pure oxygen.

Besides forming water as product, hydrogen peroxide can be generated by the oxidation of hydrogen by using special catalysts. Most of these processes involve the presence of a liquid phase in addition to the gas phase, e.g. relying on trickle-bed reactor design. The direct synthesis of hydrogen peroxide is attractive since it is believed to be a more economical and less waste-producing process than the established anthraquinone route. Industrial exploitation so far was hindered by the high safety risk of such processes. Indeed, for the handling of oxygen and hydrogen, a series of explosions, many even with lethal accidents, have been reported in the past.

3.3.13.2 Beneficial Micro Reactor Properties for the Hydrogen/Oxygen Reaction

Already the early pioneering reviews in the field have mentioned safe operation in micro reactors even in the explosive regime as one of the most relevant drivers [71,

120]. Later, much more detailed predictions of safe operation in micro reactors in the explosive regime with the example of the hydrogen/oxygen reaction could be given [9, 82, 117, 118]. It was predicted that micro-channel processing under given conditions can be considered as intrinsically safe.

Safe processing was found experimentally in parallel with this theoretical fundament [115, 116], both leading to further experimentation [9, 82, 117, 118]. Although the hydrogen/reaction is not of direct use itself, it stands as a prominent model reaction for other more valuable processes (see, e.g., [GP 2] and [GP 3]), for which benefits due to safe processing in novel explosive regimes are expected.

Gas-phase reaction 11 [GP 11]: hydrogen oxidation



3.3.13.3 Typical Results

Conversion/selectivity/yield

[GP 11] [R 5] Complete conversion is achievable, provided that proper process conditions are applied [115].

Process temperatures

[GP 11] [R 19] Temperatures close to 1200 °C, near the mechanical limit of the ceramic reactor material, have been achieved [9, 115]. With improved sealing and better material, processing could lead to 1300 °C [9].

Process safety

[GP 11] [R 19] Based on an analysis of the thermal and kinetic explosion limits, inherent safety is ascribed to hydrogen/oxygen mixtures in the explosive regime when guided through channels of sub-millimeter dimensions under ambient-pressure conditions [9]. This was confirmed by experiments in a quartz micro reactor [9].

[GP 11] [R 19] Three kinetic explosion limits for a stoichiometric H_2/O_2 mixture and three different reactor diameters, $d = 1$ splm, 1 mm and 100 μm , are given in [9] (200–1450 °C; $10\text{--}10^8$ Pa).

[GP 11] [R 19] The third explosion limit is discussed in detail in [9] as it is important from both practical and mechanistic viewpoints (230–950 °C; $10\text{--}10^9$ Pa). This limit is normally responsible for the occurrence of explosions under ambient pressure conditions. In addition, these explosions are known to be kinetically induced by radical formation. The formation of these species is sensitive to size reduction of the processing volume owing to the impact of the wall specific surface area on radical chain termination. It turns out that the wall temperature has a noticeable, but not decisive influence on the position of the third limit.

The thermal explosion limit lies below the kinetic limit for all conditions specified above (Figure 3.50) [9].

[GP 11] [R 19] The suppression of explosive homogeneous gas-phase reactions is not due simply to thermal quenching as a result of the heat losses from a micro reactor, but rather to radical quenching [9]. The micro reactor will therefore be safe even when heat losses from the reaction micro channel are reduced by design modifications.

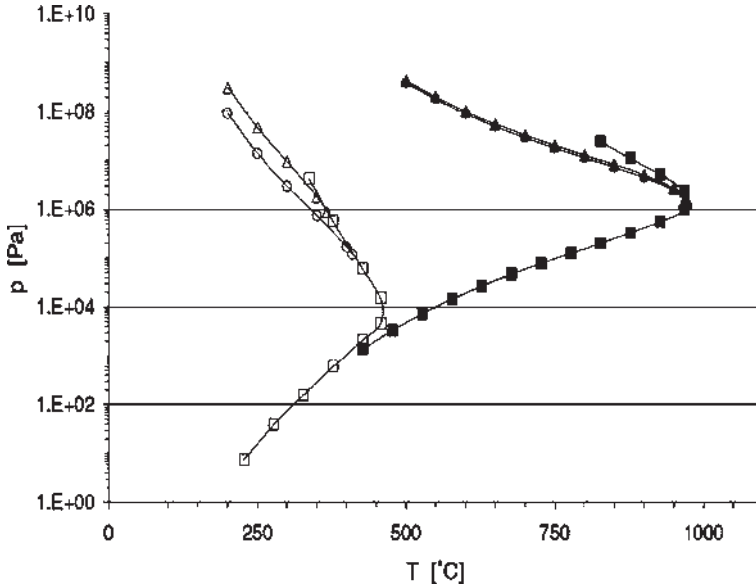


Figure 3.50 Extending kinetic explosion (squares) and thermal explosion limits by using a micro reactor with 300 μm channel diameter (filled symbols). Calculated values for $T_{\text{wall}} = T_{\text{room}}$ (circles) and $T_{\text{wall}} = T_{\text{reaction}}$ (triangles). Comparison with 1 m diameter (open symbols) [9].

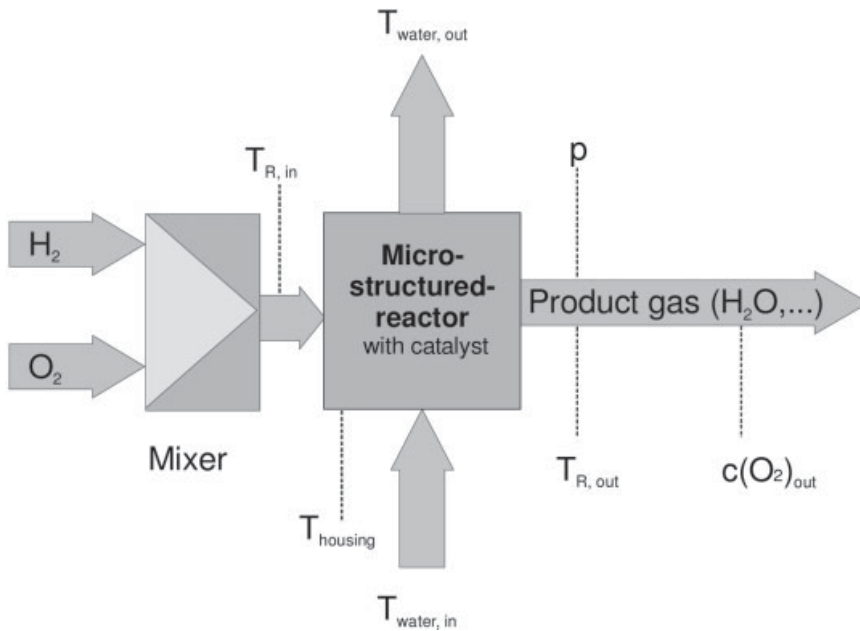


Figure 3.51 Schematic flow scheme of a micro-reactor system used for burning hydrogen and oxygen at large throughputs. A mixer is applied for reducing the volume of the explosive hydrogen/oxygen mixture in advance to the reaction [115].

[GP 11] [R 19] An impressive example of the impact of miniaturization on the explosion limit is given in [9]. For a conventional reactor of 1 m diameter, explosive behavior sets in at 420 °C at ambient pressure (10^5 Pa). In turn, an explosion occurs at about 750 °C when the reactor diameter is decreased to about 1 mm. A further reduction to 100 μm shifts the explosive regime further to higher pressures and temperatures. Even the first explosion limit is above ambient pressure. Now, explosive behavior can be excluded and so the reaction becomes inherently safe.

[GP 11] [R 5] Owing to the possibility of achieving complete conversion, process conditions can be found to yield off-gas, leaving the micro reactor, which is no longer in the explosion envelope [115].

Addition of water/kinetics

[GP 11] [R 5] The addition of up to 7 vol.-% of water has no detectable impact on the oxygen reaction rate [121]. This is a hint that desorption of water generated is not the rate-determining step (Figure 3.51).

Variation of oxygen concentration

[GP 11] [R 5] An increase in oxygen concentration at constant hydrogen concentration did not lead to a maximum of the oxygen reaction rate [121].

Variation of hydrogen concentration

[GP 11] [R 5] An increase in hydrogen concentration at constant oxygen concentration led to a maximum of the oxygen reaction rate (2.0–7.0 mmol l^{-1} hydrogen; 3.6 mmol l^{-1} oxygen; 48–70 °C) [121]. The maximum is found at a hydrogen/oxygen ratio of 1. This behavior could be described by Langmuir–Hinshelwood kinetics.

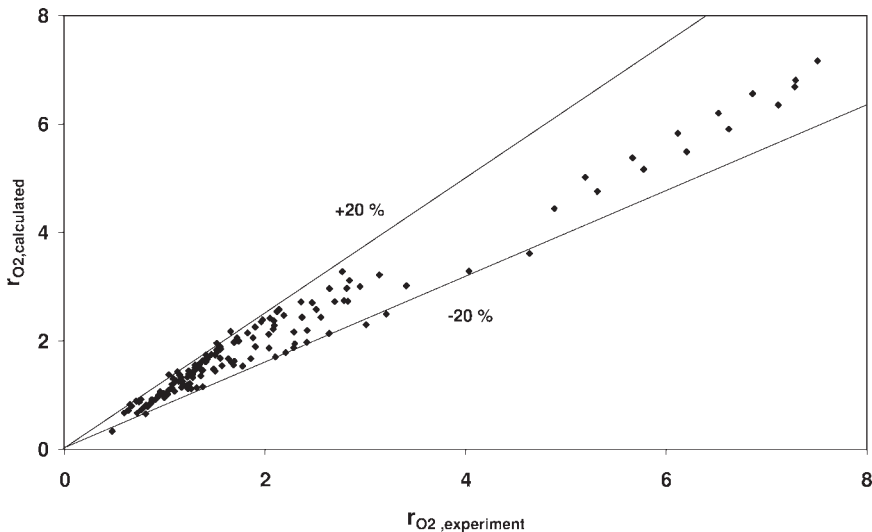


Figure 3.52 Parity diagram based on Langmuir–Hinshelwood kinetics of the oxygen reaction rate [121].

Applicability of Langmuir–Hinshelwood kinetics

[GP 11] [R 5] Langmuir–Hinshelwood kinetics adequately describe the observed results as a parity diagram (Figure 3.52), comparing experimental with theoretical values (2.0–7.0 mmol l⁻¹ hydrogen; 3.6 mmol l⁻¹ oxygen; 48–70 °C) [121].

Kinetic data

[GP 11] [R 5] Numerically iterated parameter values for the Langmuir–Hinshelwood kinetics were listed, including activation energy, oxygen reaction rate, and enthalpy (2.0–7.0 mmol l⁻¹ hydrogen; 3.6 mmol l⁻¹ oxygen; 48–70 °C) [121].

Mass-Transfer limitation/Mears criterion

[GP 11] [R 5] A judgement on mass-transfer limitations on the reaction rate according to the Mears criterion was made [121]. This inequality predicts no such limitations in the boundary layer when the Mears criterion is smaller than 0.15. Using process parameter data applied in a number of experiments, the highest value found is $6 \cdot 10^{-2}$ so that no mass-transfer limitations have to be assumed.

Heat-transfer limitation/Anderson criterion

[GP 11] [R 5] A judgement on heat-transfer limitations on the reaction rate according to the Anderson criterion was made [121]. This inequality predicts no such limitations in the boundary layer when the Anderson criterion is smaller than 1. Using process parameter data applied in a number of experiments, the highest value found was $2.2 \cdot 10^{-6}$ so that no heat-transfer limitations have to be assumed.

Temperature rise

[GP 11] [R 5] No temperature increase of the gas flow in micro channels was observed experimentally, being cooled by a guiding water mass flow of 4 g s⁻¹ through perpendicularly arranged micro channels [121]. Referring to these experimental conditions, a maximum reaction power of 35 W was calculated for a maximum gas flow of 7.5 Nl min⁻¹.

Theoretical benchmarking to other reactor concepts

[GP 11] [R 5] Calculated heat-transfer coefficients, heat-exchange areas and estimated temperature gradients between the inner reactor zone and the outer wall were given, taking into account a reaction with 30 W heat generation [121]. In addition to considering a cross-flow micro reactor, the performances of a fixed-bed reactor and ceramic and metal honeycomb reactors were calculated (Table 3.3). The result was that the micro reactor gives the smallest estimated temperature increase (1.4 K) due to the largest heat exchange area and largest heat transfer coefficient.

Temperature distribution

[GP 11] [R 19] For an autothermal reactor, i.e. a device with neither internal nor external heat transfer, steep temperature profiles along the flow axis were found [9]. Via an inspection window, glowing of the front zone of the wire reactor was observed, indicating complete conversion within a few mm reaction passages. The

Table 3.3 Comparison of the calculated heat-transfer coefficients, heat-exchange areas and the estimated temperature gradients between the central reactor area and the outer wall of the reactor.

	k ($W m^2 K^{-1}$)	A (m^2)	ΔT (K)
Fixed-bed reactor (length 5 mm)	$\sim 7 \cdot 10^3$	$1.5 \cdot 10^{-4}$	27
Ceramic honeycomb reactor (number of honeycombs 32; diameter 0.63 mm; length 14 mm)	$\sim 2 \cdot 10^3$	$2.5 \cdot 10^{-4}$	58
Metal honeycomb reactor (number of honeycombs 17; diameter 1.17 mm; length 14 mm)	$\sim 1.1 \cdot 10^4$	$3.6 \cdot 10^{-4}$	8
Micro reactor (length 14 mm)	$1.539 \cdot 10^4$	$1.1 \cdot 10^{-3}$	1.4

rest of the reactor remained dark, which is explained by massive heat losses, since no special measures for insulation were taken.

[GP 11] [R 19] By increasing the flow rate, the above-mentioned hot spot can be moved downstream in the flow direction, as is evident from the moving zone of glow [9].

Residence time

[GP 11] [R 19] Using the above visual inspection technique, the minimum residence time can be estimated. Flow was increased and so the residence time decreased, until the whole reactor was glowing. This corresponds to a residence time as low as approximately 50 μs (0.1 slpm hydrogen, 0.14 slpm oxygen, 0.45 slpm nitrogen) [9].

Thermal management

[GS 11] [R 5] At high mass flows and with a large heat release, an undesired, substantial temperature increase even for highly efficient micro heat exchanger-reactors is observed (Figure 3.53) [115].

[GP 11] [R 19] Gas-exit temperatures ranging from ambient temperature to nearly 1200 °C were measured (Figure 3.54) as a function of the so-called equivalence ratio, a function of the H_2/O_2 ratio (0.5 slpm synthetic air, 0.1 slpm oxygen + 0.2 slpm nitrogen or 0.5 slpm oxygen + 0.75 slpm nitrogen; varying hydrogen content) [9]. A steep temperature increase was observed; a maximum was found at nearly stoichiometric conditions. For lower nitrogen dilutions, this maximum approaches nearly 1200 °C, whereas lower values are found when using air, less rich in oxygen. The maximum temperature also increases with increasing total flow rate. This is correlated with the heat losses, depending on flow rate and residence time.

[GP 11] [R 19] The gas-exit temperatures in a quartz micro reactor are higher than in a silicon micro reactor of similar design for reasons of strongly reduced heat losses, given the same process parameters (0.5 slpm synthetic air, 0.1 slpm oxygen + 0.2 slpm nitrogen or 0.5 slpm oxygen + 0.75 slpm nitrogen; varying hydrogen content) [9].

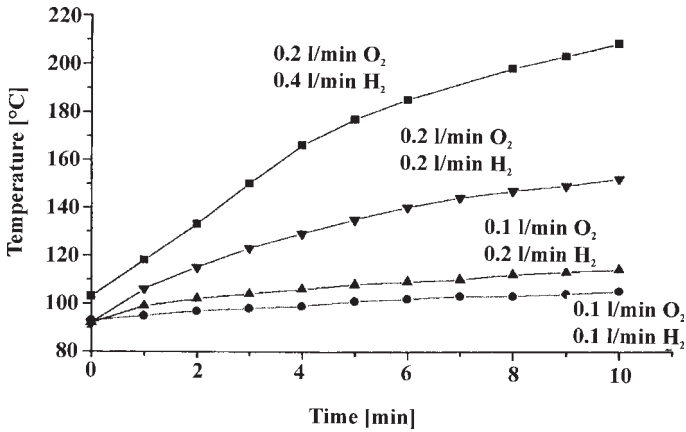


Figure 3.53 Temperature of the exiting reactant gas plotted against time on-stream for various operating conditions. N_2 as diluent, 1.0 l min^{-1} ; N_2 as coolant, 3.0 l min^{-1} [115].

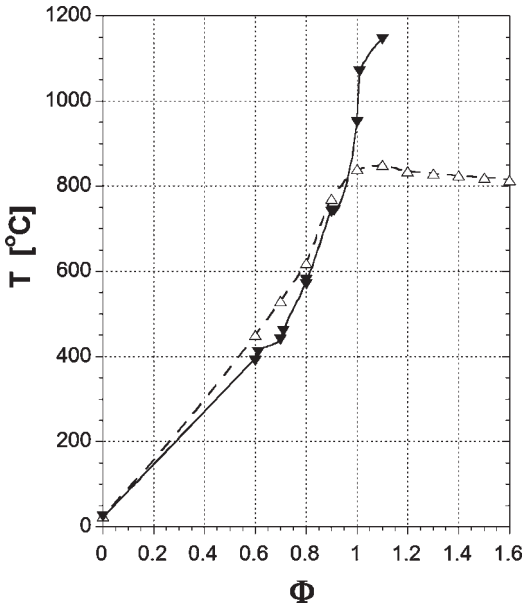


Figure 3.54 Measured gas exit temperatures for a catalytic H_2/O_2 reaction with varying H_2 content in 0.5 slpm synthetic air (Δ) and oxygen (∇) enriched air (0.1 slpm oxygen + 0.2 slpm nitrogen) [115].

Reactor material/type of micro reactor

[GP 11] [R 19] The gas exit temperatures in a quartz micro reactor are higher than in a silicon micro reactor of similar design for reasons of strongly reduced heat losses, given the same process parameters (0.5 slpm synthetic air, 0.1 slpm oxygen + 0.2 slpm nitrogen or 0.5 slpm oxygen + 0.75 slpm nitrogen; varying hydrogen content) [9].

[GP 11] [R 19] No qualitative differences between the reaction performance of a wire-based silicon-chip and a quartz-shell micro reactor were observed [9].

Wall material

[GP 11] [R 19] The influence of different wall materials on the ignition behavior of the hydrogen/oxygen reaction using air was studied in numerical simulations with a two-dimensional boundary-layer model of a micro-channel reactor [117]. The model incorporates balance equations for mass, energy and momentum. Detailed elementary-step kinetics for both surface reactions and homogeneous gas-phase reactions were used in the simulations. Based on prior experimental evidence, parameters were chosen. The walls were divided into three categories: catalytic, so-called radical combination and inert. Platinum was taken for the first; the second represents materials such as quartz-glass and silicon, and the third stands for 'un-hampered' homogeneous gas-phase reaction.

Strong wall effects were observed for the catalytic and radical-combination walls [9]. In addition to the ignition-inhibiting effect found for both types, the catalytic wall displays a further effect, being ignition-promoting, which is explained by higher reaction rates on the catalytic surface as for the homogeneous reaction. This means that whereas flames and explosions may be suppressed in a micro channel, conversion at the heterogeneous surface may be high and so the range of reactive conditions is considerably increased.

Novel reactor concepts/membrane reactor

[GP 11] [R 20] Investigations with a Pd membrane reactor relied on reaction of streams separated via a membrane (to prevent complete mixing of reactants, not to enhance conversion) [11]. A hydrogen/nitrogen stream is guided parallel to an oxygen stream, both separated by the membrane and water is thereby formed. The membranes, made by thin-film processes, can sustain a pressure up to 5 bar.

3.3.14

Oxidation of Formamides – Synthesis of Methyl Isocyanate

Proceedings: [71]; short mention of cyclohexyl and butyl isocyanate syntheses (no details): [71]; sections in reviews; [95, 97, 100].

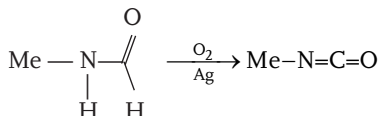
3.3.14.1 Drivers for Performing the Synthesis of Methyl Isocyanate

The corresponding industrial investigation had a truly pioneering character as it was the first industrial study on micro reactors to be published [71]. In the framework of this extended study, many catalytic gas-phase reactions were carried out in a micro structured reactor. The reactions were chosen according to selection criteria defined by the company owing to an extensive analysis of their suitability for micro flow processing. The following criteria were chosen: high temperature, dangerous, catalytic and photochemical. Concerning heterogeneous reactions, the catalyst was introduced in the form of solid particles as a mini fixed bed. For the synthesis of methyl isocyanate from methylformamide, similar conversions for the conventional synthesis could be determined, at low selectivities, however.

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 hydro-treating, 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.