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Mass transfer limitations in microchannel reactors

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Abstract

The mass transfer in microchannel reactors with catalyst-coated walls is investigated. A limitation by internal mass transfer can be tested by the variation of the temperature or the thickness of the catalyst layer. Due to the laminar flow in the microchannels the external mass transfer relies solely on the molecular diffusion. Suitable test methods for the external mass transfer are: variation of temperature, channel diameter at constant residence time, total pressure at constant partial pressures of the reactants, or change of the inert gas. For the selective oxidation of isoprene in a microchannel reactor mass transfer limitations are experimentally excluded by the variation of catalyst particle diameter and the change of the inert gas nitrogen to helium. Using a two-dimensional model the radial profiles of the reactants in the microchannels are simulated. Two different criteria to distinguish between the kinetically and the mass transfer controlled regime are presented.

Keywords: Microreactor; Microchannel; Mass transfer limitation; Two-dimensional simulation; Selective oxidation of isoprene

1. Introduction

Microchannel reactors represent a new type of structured reactors. Since the early nineties the attraction of microchannel reactors has been increasing continuously (see recent reviews [1–4]). Small channels with dimensions below 1 mm are the common feature of the majority of microchannel reactor designs. The chemical reactions take place either in a single or in many parallel microchannels. The outstanding characteristic of microchannel reactors is the high transfer rate for the heat of reaction. Hence, in microchannel reactors the controlled conversion of explosive reaction mixtures is possible [5–9]. Even for extremely exothermic or endothermic reactions, near isothermal conditions can be realized in microchannel reactors [10–13]. Consequently, the use of microchannel reactors is suggested for kinetic and mechanistic investigations of reactions with high positive or negative reaction enthalpies [14–16].

When microchannel reactors are used for kinetic experiments it is imperative to ensure the absence of heat transfer and mass transfer influences to obtain the intrinsic rates. In microchannel reactors used for heterogeneously catalyzed reactions the catalyst is generally deposited onto the walls of the microchannels. Therefore, the reactants have to be transported – in the worst case – from the center of the channel to the catalyst-coated walls. This mass transfer has to be faster than the reaction, otherwise the reactant and product concentrations at the catalyst surface are lower respectively higher than at the center of the channel. The reaction becomes mass transfer controlled. Due to the laminar flow profile the mass transfer of molecules perpendicular to the flow direction relies solely on the molecular diffusion.

Before starting kinetic measurements in conventional fixed bed reactors, the absence of mass transfer influences is excluded by standard test methods. Due to the analogy of heat and mass transfer the latter is expected to be very fast in microchannel reactors. However, for extreme high temperatures an influence on the reaction rate by mass transfer cannot be fully excluded. Suitable test methods are requested [17] and will have to be developed, as there are no established standard methods so far. Therefore, a comprehensive summary of examples in the literature is given in the present study. The examples are reviewed critically. All possible methods are described and evaluated carefully. Methods used for monolithic reactors are also considered. With respect to the mass transfer, monolithic reactors are very close to microchannel reactors. Merely the dimensions of the channels in monolithic reactors are larger in general by a factor between 2 and 10. For more theoretical work on mass transfer in catalytic monoliths, see e.g. [18].

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Nomenclature

A, B, C	constants
d	channel diameter (m)
d_h	hydraulic diameter $d_h = 4$(cross-section/circumference) (m)
d_p	particle diameter (m)
D_M	molecular diffusion coefficient (m^2/s)
E_a	activation energy (J/mol)
k_s	surface related reaction rate constant (m/s)
k'_s	surface related reaction rate constant (isoprene oxidation) (m/s)
$k'_{s,0}$	surface related frequency factor (isoprene oxidation) (m/s)
$k_{s,eff}$	effective surface related reaction rate constant (m/s)
l	channel length (m)
M	molar mass (g/mol)
$n_{channel}$	number of channels in microchannel reactor
p	absolute pressure (bar)
r	radial coordinate (m)
r_s	surface related reaction rate (mol/s m^2)
R	general gas constant (J/mol K), channel radius (m)
Re	Reynolds number ($Re = u_{av}d/\nu$)
Re_p	Reynolds number of a particle ($Re_p = u_{av}d_p/\nu$)
R_{max}	maximum distance to catalyst surface (m)
S	molar selectivity (%)
Sc	Schmidt number ($Sc = \nu/D_M$)
Sh	Sherwood number ($Sh = \beta d/D_M$)
T	temperature (K)
u	flow velocity (m/s)
u_{av}	radial averaged flow velocity (m/s)
u_{nom}	nominal linear flow velocity (m/s)
$\dot{V}_{tot}$	total volumetric flow rate at 1.01325 bar, 0 °C (N ml/min)
x	mole fraction
x_{av}	radial averaged mole fraction
x_{wall}	mole fraction at channel wall $r = R$
x_0	mole fraction at channel entrance
X	molar conversion (%)
z	axial coordinate (m)

Greek letters

β	mass transfer coefficient (m/s)
δ_{cat}	thickness of catalyst layer (m)
ν	kinematic viscosity (m^2/s)
$\nu_{i,j}$	stoichiometric coefficient of component i in reaction j
ρ_n	molar density (mol/m^3)
$\rho_{m,cat}$	mass density of catalyst (g/m^3)
Ω	collision integral
τ_{hydr}	hydrodynamic residence time (s)
τ_{mod}	modified residence time (catalyst mass/total molar flow rate) (min g/mol)

Using a model reaction, the present study shows how the absence of mass transfer influences in a microchannel reactor is demonstrated experimentally. The selective oxidation of isoprene (2-methyl-1,3-butadiene) to citraconic anhydride (3-methyl-2,5-furandione) was chosen as model reaction [16,19]. A simulation study on the basis of a two-dimensional model was performed and helped to identify the main influencing parameters. Both the qualitative and quantitative influence of these parameters and criteria for the discrimination between the kinetic and the mass transfer controlled regimes are shown in this study.

2. Experimental

2.1. Reactors and setup

The metallic microchannel reactor used in this study was constructed by the Institut für Mikrotechnik Mainz (IMM) [20–22]. The reactor consisted of a stack of six microstructured aluminum plates (4 cm × 4 cm × 0.5 cm), each containing 34 microchannels and two stainless steel housing plates. The plates were microstructured by an isotropic wet chemical etching process. They were stacked together using graphite sealing. This etching process leads to almost semi circular microchannels with a rough surface and a resulting hydraulic diameter (d_h) of about 280 μm (Fig. 1). The length of the channels was 20 mm.

The ceramic fixed bed reactor consisted of one ceramic tube (α-Al_2O_3, length: 300 mm, inner diameter: 10 mm) with three heating zones. In the center of the tube a stainless steel capillary was inserted to monitor the axial temperature profile. The isothermal zone was 80 mm long. The catalyst pellets (ca. 0.2 ml) were diluted by nonporous inert spheres (Al_2O_3/SiO_2, 0.75–1 mm diameter) to a total of 3 ml.

The catalytic measurements were carried out in a conventional flow apparatus at atmospheric pressure. The gases were dosed by mass flow controllers, as was the liquid isoprene

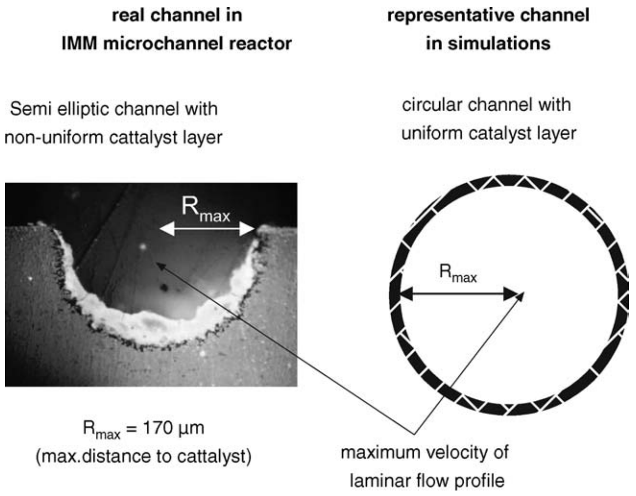


Fig. 1. Real geometry of the microchannel cross-section in experiment and simplified geometry in simulations.

(Fluka), which was subsequently evaporated using nitrogen as carrier gas.

The analysis of the organic products and permanent gases was carried out online with a GC, which was equipped with three columns (HP-5, PoraPlotQ and molecular sieve 5 Å) and two detectors (FID and TCD).

For temperature variations, it was found beneficial to decrease temperature starting from a high value, rather than increasing temperature. Prior to every experiment the catalyst was activated in air for 1 h at 500 °C. A more detailed description is given in [16].

2.2. Catalysts

The $V_{75}Ti_{25}O_x$-catalyst was prepared by wet impregnation of TiO_2-anatase (Fluka; BET-surface area about 9 m^2/g) with an aqueous solution of V_2O_5 (GfE, Nuremberg) in oxalic acid, which was stirred and evaporated. The remaining precursor was dried at 120 °C overnight followed by calcination at 500 °C for 4 h. The obtained catalyst had a BET-surface area of about 11 m^2/g. The V/Ti molar ratio was 3:1, which was verified through ICP-analysis. This catalyst powder was used in the fixed bed reactor in form of pressed pellets without the addition of any binders.

In order to be able to use the catalyst in the microchannel reactor, the catalyst had to be fixed onto the channel walls. The following coating procedure was developed [23]: 2.2 g sodium silicate solution (27 wt.% SiO_2, 10 wt.% Na) is diluted in 10 ml distilled water. The sodium is removed by ion exchange with Dowex® cation exchanger (H^+-form). The conventionally prepared catalyst (2 g) is ground, sieved (<100 μm) and suspended in the filtered silicate solution. The suspension is stirred for 1 h and then applied onto the channel walls using a fine brush. In the channels the suspension is distributed by capillary forces. The microstructured plates are dried for 1 h at 120 °C, then a second layer is applied. The plates are again calcined in air for 1 h at 450 °C. The plates are weighed before and after the coating to determine the catalyst mass. The average weight-loading of the plates is 13 mg catalyst.

2.3. Simulations

Based on the facts that the flow in the microchannel reactor is equally distributed on the channels [24] and that near isothermal conditions are reached [16], the simulation of a single representative microchannel is sufficient to describe the behavior of the microchannel reactor.

For the simulations the real geometry of the microchannel cross-section had to be simplified (Fig. 1). In the real microchannel reactor, only the circular circumference of the etched semi elliptic microchannels is coated with a catalyst. The top cover is not coated. For the simulation of the mass transfer in these channels with hydraulic diameters of 280 μm, a complex three-dimensional model would be required. To reduce complexity and calculation time the geometry was simplified. The circular channel in the simulations can be fully described by a two-dimensional model. The maximum distance R_{max} of the reactant molecules to the catalyst of 170 μm representing the characteristic length for the external mass transfer is kept constant. With 170 μm R_{max} is even greater than half of the hydraulic diameter. This is not the case when comparing mass transfer in rectangular and circular channels with same hydraulic diameters. In rectangular channels the effect of the sharp edges on the mass transfer cannot be neglected. The position of the maximum flow velocity in the semicircular and the circular channel is different. So in the simulations, the distance of the reactant molecules with the highest flow velocity and hence the shortest residence time in the circular channel is even greater than in the real channels. Consequently, a possible mass transfer influence is rather overestimated than underestimated in the simulations. The length (20 mm) of the simulated channel and the dimensions of the real microchannels are identical.

Due to the isothermal conditions, the heat balances can be neglected. Using the analytical solution for the laminar flow profile, the system can be fully described by the solution of the two-dimensional species balances. In the partial differential equation (1), in flow direction (z-coordinate) transport by convection and molecular diffusion and in transversal direction (r-coordinate) transport solely by molecular diffusion is considered:

$$-u(r)\frac{\partial x_i(r,z)}{\partial z} + D_{M,i}\frac{\partial^2 x_i(r,z)}{\partial z^2} + D_{M,i}\frac{\partial^2 x_i(r,z)}{\partial r^2} + D_{M,i}\frac{1}{r}\frac{\partial x_i(r,z)}{\partial r} = 0$$

$$\text{with } u(r) = 2u_{av}\left[1-\left(\frac{r}{R}\right)^2\right] \quad (1)$$

u is the flow velocity in axial direction, u_{av} the average flow velocity, x_i the molar fraction of component i, $D_{M,i}$ the molecular diffusion coefficient of i and R is the channel radius.

Assuming the absence of any influences by internal mass transfer in the catalyst layer, the chemical reaction is easily integrated by one of the boundary conditions. All the reactant molecules transferred to the wall are consumed by the reactions. The reaction rates $r_{s,j}$ are defined as molecules reacting per time and surface of the channel wall, and not per volume or mass of catalyst:

$$\frac{p}{RT}D_{M,i}\left.\frac{\partial x_i(r,z)}{\partial r}\right|_{r=R} = \sum_{j=1}^{m}\nu_{i,j}r_{s,j}, \quad r=R \quad (2)$$

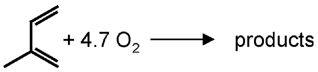
The other boundary conditions consider the symmetry at the channel center (Eq. (3)), the conditions according to [25] at the channel entrance (Eq. (4)) and the absence of any gradients at the channel outlet (Eq. (5)):

$$\left.\frac{\partial x_i(r,z)}{\partial r}\right|_{r=0} = 0, \quad r=0 \quad (3)$$

$$u(r)(x_{0,i} - x_i(r,z=0)) = -D_{\mathrm{M},i} \left.\frac{\partial x_i(r,z)}{\partial z}\right|_{z=0}, \quad z=0 \tag{4}$$

$$\left.\frac{\partial x_i(r,z)}{\partial z}\right|_{z=1} = 0, \quad z=1 \tag{5}$$

As no detailed reaction kinetics are available for the isoprene oxidation, a simple description for the effective isoprene consumption was used. Isoprene is reacting with oxygen to yield products according to Eq. (6):



(6)

Here, parallel or consecutive reactions leading to different products (as for example citraconic anhydride or carbon oxides) and hence different numbers of moles are neglected. This is possible as the reactant isoprene with 0.6 vol.% is highly diluted. The reaction rate r_{s} of the isoprene consumption is described in Eq. (7):

$$r_{\mathrm{s}} = k'_{\mathrm{s}} x_{\mathrm{isoprene}} x_{\mathrm{oxygen}}^{0.2} = k'_{\mathrm{s},0} \exp\left(-\frac{E_{\mathrm{a}}}{\mathrm{RT}}\right) x_{\mathrm{isoprene}} x_{\mathrm{oxygen}}^{0.2} \tag{7}$$

A power law model for the isoprene consumption was assumed where the orders in isoprene and oxygen were set to 1 and 0.2, according to experimental results. Consecutively, the frequency factor $k'_{\mathrm{s},0}$ and the activation energy E_{a} were determined based on the experimental results in the microchannel reactor [26]. The parameters were estimated with the software package gProms® assuming a kinetic control of the isoprene oxidation and a plug flow behavior of the microchannel reactor. The validity of these assumptions could be verified in the subsequent two-dimensional simulations (see Section 5). Using the estimated parameters, the dependence of the isoprene conversion on temperature, isoprene and oxygen concentration, and residence time can be described.

For the two-dimensional simulation with gProms®, it was found that a resolution of 400 equidistant grid points in axial direction and 20 equidistant grid points in radial direction was sufficient. For the spatial discretisation a second order centered finite difference method was used.

3. Test methods for mass transfer limitations

The vast majority of microchannel reactors used for heterogeneous catalyzed gas phase reactions consists of a single or mostly several parallel channels coated with catalyst. Microfixed beds are rarely used. Consequently, the mass transfer in microchannel reactors is fundamentally different from the mass transfer in conventional fixed bed reactors.

In fixed bed reactors, the catalyst particles are surrounded by the reactant flow. The *external mass transfer* to the surface of the catalyst particle is described by the film model, according to which the bulk phase is perfectly mixed and the whole resistance is located in the film surrounding the catalyst particle. In this film, the molecules are transported by molecular diffusion. The film thickness acts as a model parameter that is mainly influenced by the flow velocity and the flow regime. The transport is enhanced by the (generally random) flow through the fixed bed. The *internal mass transfer* depends on the effective diffusion coefficient in the porous catalyst particle. In contrast to the external mass transfer, diffusion and reaction in the catalyst particle take place at the same time. For mass transfer limited reactions, the reactant concentration is reduced and the effectiveness factor can drop below unity.

In microchannel reactors the flow through the channels is generally laminar. The catalyst is deposited at the channel walls. From the gas phase to the catalyst, the reactant molecules have to be transported normal to the flow direction. Due to the laminar flow regime, this *external mass transfer* relies on molecular diffusion driven by the concentration gradients. Molecules at the center of the channel with the longest distance to the wall have the highest flow velocity hence the shortest residence time. In contrast to a fixed bed reactor, the assumption of a perfectly mixed bulk phase and a stagnant film is not reasonable here. Furthermore, the thickness of the film surrounding the catalyst particle and the hydrodynamic radius of a microchannel are not comparable at all. Consequently, the film model is not applicable for catalyst-coated microchannels. In contrast, the *internal mass transfer* in the catalyst layer is similar to the transfer in the catalyst particles of a fixed bed. It is described by the pore diffusion in the catalyst layer. In case of an internal mass transfer limitation, the reactant concentration in the layer is lower than at the catalyst surface. Analogous to the center of a catalyst particle, the lowest concentration is located at the channel wall.

A limitation by internal rather than by external mass transfer is more likely in fixed bed reactors. This is due to low effective diffusion coefficients and the enhanced external mass transfer by turbulent flow. For microchannel reactors, the situation is different. The external mass transfer depends solely on molecular diffusion. Additionally, the maximum distance for reactant molecules to the catalyst at the wall, which is equal to the channel radius, is much larger than the thickness of the catalyst layer. Therefore, the external mass transfer in microchannel reactors gains importance. The invalidity of the film model calls for a different model and also new experimental test methods. In the following, it is shown how a limitation by internal and external mass transfer in microchannel reactors can be experimentally excluded.

3.1. Internal mass transfer

3.1.1. Variation of the temperature

For heterogeneously catalyzed reactions in fixed bed reactors, a common test procedure regarding internal mass transfer is to measure the conversion with increasing temperature. The slope in the Arrhenius diagram indicates whether the reaction is mass transfer or kinetically controlled. With increasing temperatures, the reaction changes from the kinetically controlled regime to the mass transfer controlled regime. At the same time the apparent activation energy drops to half of the activation energy for the chemical reaction.

Tronconi and Beretta showed how this test method can be adapted to monolithic reactors [27]. They used a monolith reactor with walls consisting of catalyst material. This wall material was ground and used in a fixed bed reactor. Investigating the oxidation of NO they could compare the slopes in the Arrhenius diagram for the reaction in the monolith reactor and in the fixed bed reactor with the same catalyst in powder form. The activation energy for the powder catalyst was twice the value derived from the measurements in the monolith, which indicates an internal mass transfer control in the monolith.

This method can also be adapted to microchannel reactors. Either the temperature in the microchannel reactor is varied to observe the change between the kinetic and the mass transfer regime, or the catalyst of the microchannel reactor is tested in powder form in a fixed bed reactor and the activation energies are compared.

The advantage of this test procedure is that in most experimental setups the temperature can easily be varied. However, it is not always possible to vary the temperature over a sufficiently broad range to observe the transition from kinetic to mass transfer control. When the catalyst is used in powder form, an additional fixed bed reactor is required. Sometimes differences in activation energies do not clearly indicate the transition. Particularly for complex reaction networks with consecutive and parallel reactions, a change in the mechanism, or transformations of the catalyst may also lead to a change in activation energy and consequently have a negative influence on the results.

3.1.2. Variation of the catalyst layer thickness

In heterogeneous catalysis the variation of the particle diameter is favored to check for an internal mass transfer limitation. The conversion with reduced particle diameters is measured. As the mass transfer is linearly dependent on the particle radius and the kinetics are independent of the radius, an increase in conversion indicates the mass transfer controlled regime. Pfeifer adopted this method for microchannel reactors [28]. Catalyst coatings of different thickness but same compositions were prepared. For a constant reactant flow, a linear dependence on the conversion on the catalyst mass was observed. This dependence is expected for a kinetically controlled reaction. Therefore, an internal mass transfer limitation was excluded for all prepared catalyst coatings with a thickness varying between 5 and 20 μm.

The variation of the catalyst layer thickness is an unambiguous proof for internal mass transfer influence when the other reaction conditions are kept constant. However, a reproducible preparation method for the catalyst coating is required, to ensure a constant and adjustable layer thickness and therefore an equal hydrodynamic residence time in all channels. If microchannels with constant channel radius are used, an influence of the different hydrodynamic residence times has to be excluded. The different residence times result from the different free cross-sections due to the different thicknesses of the catalyst layers (see Section 3.2.2).

3.2. External mass transfer

3.2.1. Variation of the temperature

In fixed bed reactors the variation of the temperature can be applied to investigate an influence of the internal and of the external mass transfer. For this purpose, the different temperature dependence of diffusional processes and reaction kinetics is made use of. For reactions controlled by external mass transfer the slope in the Arrhenius diagram is very flat. Eq. (8) shows the dependence of the effective reaction rate constant $k_{\mathrm{s,eff}}$ on the temperature [27]. The rate constant is linearly dependent on the molecular diffusion coefficient D_{M} and the molar density ρ_n due to the volume expansion with increasing temperature, which in turn increases the flow velocity

External mass transfer control:

$$k_{\mathrm{s,eff}} \sim D_{\mathrm{M}}\rho_n \sim T^{1.75}T^{-1} = T^{0.75} \tag{8}$$

The variation of the temperature is also used in monolithic reactors. Tronconi and Beretta measured the temperature dependence of the NO oxidation in two different monolithic reactors [27]. For both monolithic reactors with different catalysts the slopes in the Arrhenius diagram corresponded to the slope of a function proportional to $T^{0.75}$ indicating a fully mass transfer controlled regime in these reactors.

When mass transfer coefficients in monolithic reactors have to be measured, this method is often used to determine the minimum temperature for the fully mass transfer controlled regime. Only at higher temperatures, correct mass transfer coefficients are measured [29,30].

This test method is very easy to apply. However, as already discussed before (Section 3.1.1), the slope in the Arrhenius diagram sometimes does not clearly indicate the transitions between the kinetic, the external and internal mass transfer controlled regimes.

3.2.2. Variation of the channel diameter

An alternative experimental test method is to selectively enhance the external mass transfer in the microchannels without affecting the kinetics. Then the conversion for reactions influenced by external mass transfer increases, whereas for kinetically controlled reactions the conversion remains constant.

One possibility here is to reduce the maximum distance for the reactant molecules to the catalyst. This is realized by reducing the diameter of the microchannels. For the same conditions, the rate of a reaction controlled by external mass transfer increases with decreasing channel diameter. The challenge is to ensure the same reaction conditions. The variation of the channel diameter does not influence the kinetics, the reaction conditions such as pressure, temperature or concentrations, and the chemical and physical properties. However, the modified residence time τ_{mod} is affected. The modified residence time is the reciprocal of molar reactant flow per catalyst mass. For a microchannel reactor with circular channels the modified residence time is calculated according to following equation (9):

$$\tau_{\mathrm{mod}} = \frac{\text{catalyst mass}}{\text{reactant flow}} = \frac{(n_{\mathrm{channel}}\pi d l \delta_{\mathrm{cat}})\rho_{m,\mathrm{cat}}}{(n_{\mathrm{channel}}\pi/4\, d^2)u_{\mathrm{av}}(p/(RT)x_i)} = \frac{4l\delta_{\mathrm{cat}}\rho_{m,\mathrm{cat}}}{d u_{\mathrm{av}}(p/(RT)x_i)} \qquad (9)$$

The reactant flow decreases quadratically with the diameter due to the reduced cross-section. However, the catalyst mass decreases linearly with the diameter since the wall surface coated with a constant catalyst layer thickness δ_{cat} and a density $\rho_{m,\mathrm{cat}}$ depends on the circumference of the channel. The modified residence time is therefore linearly dependent on the reciprocal channel diameter. To compensate this, the channel length l or the average flow velocity u_{av} can be adjusted. This leads to a different hydrodynamic residence time ($\tau_{\mathrm{hydr}} = l/u_{\mathrm{av}}$). For an ideal reactor, the conversion is solely dependent on the modified residence time and independent of the hydrodynamic residence time. However, an influence of the hydrodynamic residence time on the residence time distribution has to be excluded for the real reactor used in experiments. For a constant modified and hydrodynamic residence time the thickness of the catalyst layer has to be adjusted.

This problem of keeping the two different residence times constant for varying channel diameters is not restricted to channels with a circular cross-section. It is the same for quadratic, rectangular or triangular channels.

There are examples in literature where the results of experiments in microchannel reactors with different channel diameters were compared. The partial oxidation of methane to syngas was investigated in two microchannel reactors with different hydraulic diameters [31]. No influence of the hydraulic diameter on the conversion was found. However, the conversions were compared at identical hydrodynamic but different modified residence times.

The second example is the 1-butene oxidation to maleic anhydride [11]. A higher 1-butene conversion was measured in the reactor with the smaller microchannels. In these experiments, the hydrodynamic residence time, the channel length, and the total inner wall surface were constant, but the total cross-section decreased with the channel diameter. Hence, a higher conversion is expected for the smaller channels due to the smaller reactant flow per catalyst deposited on the inner wall surface. The higher conversion measured can therefore not be attributed solely to an enhanced mass transfer.

The variation of the channel diameter is a valid test method for external mass transfer limitations as long as the results for reactors with different channel diameters are compared at the same reaction conditions. The reactor design and conditions have to be chosen carefully to realize especially a constant modified residence time, i.e. reactant flow per catalyst mass.

3.2.3. Variation of the inert gas

Another possibility to enhance the external mass transfer is to increase the molecular diffusion coefficient. The molecular diffusion coefficient depends on temperature, total pressure, and inert gas. As the inert gas has no impact on the kinetics, it can easily be exchanged to increase the diffusion coefficients and thus accelerate the mass transfer. The diffusion coefficient of oxygen in helium is for example higher than in nitrogen by a factor of about 3.4. For reactions limited by mass transfer, the change of the inert gas to helium should increase the conversion due to the enhancement of the mass transfer. Bruno et al. investigated the CO oxidation in monolithic reactors in different inert gases [32]. In nitrogen and helium higher conversions were found than in argon and CO_2.

The change of inert gas is a simple experimental test method. However, the influence of inert gas on the heat transfer has to be evaluated carefully. Beside the molecular diffusion coefficient, the heat capacity and the heat conductivity of the gas is changing. However, for microchannel reactors in which near isothermal conditions are attainable, the impact on the reaction temperature is of minor importance. For the choice of the inert gas it is important that any interactions of the inert gas with the catalyst surface can be excluded.

Two-dimensional simulations illustrate the different behavior of the conversion for any first order reaction in nitrogen or helium. In Fig. 2, it is shown how the conversion for a first order reaction in a circular microchannel depends on the reaction rate at the channel wall. For low reaction rates the conversion is small and identical for both inert gases. Thus, the reaction is kinetically controlled. For higher reaction rates the conversion increases, and so does the difference between the conversion in helium and nitrogen. The influence of the mass transfer on the reaction increases. At high reaction rates the conversion is independent of the kinetics. It is fully mass transfer controlled and depends on the molecular diffusion coefficient determining the mass transfer.

3.2.4. Variation of the total pressure

Beside the influence of the inert gas on the molecular diffusion coefficient, the diffusivity is also dependent on the temperature and the total pressure [33]:

$$D_{\mathrm{M}} \sim \frac{T^{3/2}[(M_1 + M_2)/(M_1 M_2)]^{0.5}}{p\Omega} \qquad (10)$$

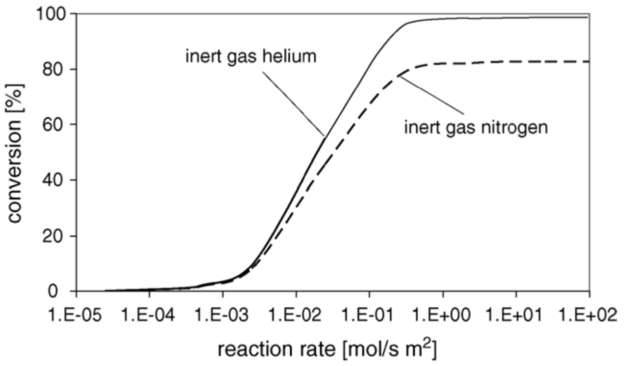


Fig. 2. Comparison of the simulated conversion depending on the surface related reaction rate for the inert gases helium and nitrogen, two-dimensional simulation: $R = 170\ \mu\mathrm{m}$, $z = 500\ \mu\mathrm{m}$, $u_{\mathrm{av}} = 1.5$ m/s, $D_{\mathrm{M,nitrogen}} = 3.8 \times 10^{-5}\ \mathrm{m^2/s}$ and $D_{\mathrm{M,helium}} = 1.4 \times 10^{-4}\ \mathrm{m^2/s}$.

The temperature influences both the diffusivity and the reaction kinetics. In contrast, a reduction of the total pressure while the partial pressures of the reactants remain constant, increases the mass transfer without affecting the kinetics. Thus, the decrease of the total pressure may be used to check for mass transfer limitations. Grass [34] and Hahn [35] showed how in CO-oxidation the system moves into the mass transfer limited regime with increasing pressure. This method was also applied to the methanol steam reforming in a microchannel reactor [36]. Here it was found that the reaction was sufficiently slow and hence kinetically controlled.

The reduction of the total pressure to test for mass transfer limitation is a reliable method. The disadvantage of the method is the high experimental effort to reduce the pressure, as in most cases vacuum conditions are required.

3.2.5. Variation of the flow velocity

In fixed bed reactors an external mass transfer limitation is typically tested through the variation of the flow velocity. For constant residence times realized by adjusting the bed length and/or catalyst mass higher flow velocities lead to an enhanced mass transfer. This is due to the increased turbulence and thus reduced thickness of the stagnant layer in the film model. For the calculation of external mass transfer coefficients in fixed bed reactors, various correlations exist for the Sherwood number Sh. The Sherwood number depends on the Schmidt number Sc and the Reynolds number of a particle Re_p. Eq. (11) shows the dependence of the mass transfer on the nominal linear flow velocity u_{nom} where A, B and C denote constants (see e.g. [37]):

$$Sh = ARe_p^B Sc^C = A\left(\frac{u_{nom} d_p}{\nu}\right)^B \left(\frac{\nu}{D_M}\right)^C \tag{11}$$

Following the heat-mass analogy, Eq. (12) [38] shows that the mass transfer in channels with laminar flow depends on the reciprocal hydrodynamic residence time u/l. For constant residence times, an increased flow velocity has no effect on the mass transfer. Therefore, the variation of the flow velocity in microchannel reactors where laminar flow prevails is no suitable test method to check for external mass transfer limitations.

$$Sh = \begin{cases} A & \text{small}\, ReSc\dfrac{d}{l} \\ B\left(ReSc\dfrac{d}{l}\right)^{1/3} = B\left(\dfrac{u}{l}\dfrac{d^2}{\nu}Sc\right)^{1/3} & \text{large}\, ReSc\dfrac{d}{l} \end{cases} \tag{12}$$

Nevertheless, there are examples in literature where mass transfer limitations in microchannel reactors were tested by the increase of flow velocities. Rebrov et al. increased the flow velocity at constant channel length and reduced reactant concentrations [39]. The reduced reactant concentrations were necessary to compensate the shorter residence time and to retain the reactant feed per time and catalyst mass. No influence of the flow velocity on the reaction was found. Therefore, the reaction was assumed to be kinetically controlled. However, the authors did not discuss the effect of the reduced partial pressure of the reactants on the kinetics.

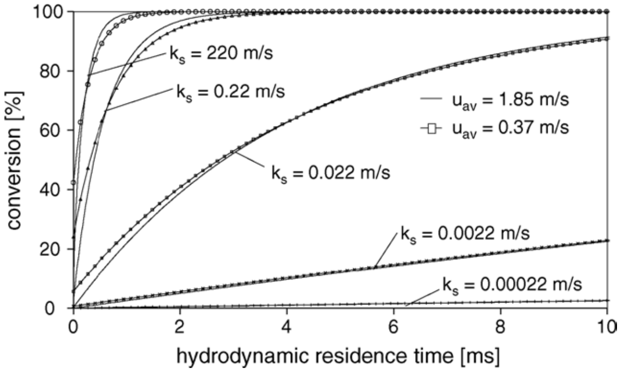


Fig. 3. Simulated dependence of the reactant conversion on the hydrodynamic residence time for different combinations of flow velocities u_{av} (denoted by lines with symbols for u_{av} = 0.37 m/s and by lines without symbols for u_{av} = 1.85 m/s) and reaction rate constants k_s for a first order reaction at the channel wall, two-dimensional simulation: $R = 170\ \mu$m, $l = 20$ mm, $D_M = 3.8 \times 10^{-5}$ m^2/s, $r_s = k_s xp/RT$, k_s = 0.00022–220 m/s, x_0 = 0.52 vol.%.

For the methanol steam reforming, the influence of an increased flow velocity was investigated by Pfeifer et al. [40]. Here the hydrodynamic residence time was kept constant by reducing the channel length. No influence on the conversion was found. The conclusion of the absence of external mass transfer limitation is not convincing, as according to Eq. (12) this result is expected. Additional questions concerning this method arise when the increased importance of entrance effects in short channels on the mass transfer have to be considered [30,41,42].

Simulations confirm the unsuitability of this test method. Fig. 3 displays the conversions of a first order reaction in a circular microchannel with laminar flow regime for different flow velocities and different reaction rates at the channel wall. The simulations indicate a small influence of the flow velocity on the conversion. This can be explained by dispersion effects and is not due to an improved mass transfer. In general the axial transport relies on the convection, but especially for low flow velocities the axial dispersion contributes to this transport. This leads to slightly smaller residence times and hence reduced conversions. In Fig. 3, the interplay between reaction, convection, and dispersion is shown. For low reaction rates the conversion is almost independent of the flow velocity. Thus, for high reaction rates and therefore excessive consumption of reactants at the channel walls the inlet concentration of the reactants drops according to Danckwerts' boundary condition. The average concentrations have been calculated with the so-called cup mixing method. With increasing residence time, the curves for the different flow velocities cross. At high flow velocities the conversion increases due to the reduced importance of the dispersion.

4. Isoprene oxidation

4.1. Test for internal mass transfer limitation by varying the particle diameter in a fixed bed reactor

A fixed bed reactor was used to check for an internal mass transfer limitation in the isoprene oxidation. The isoprene conversion was measured at constant conditions but at three different average particle diameters (see Section 3.1.2). In Fig. 4, the conversions depending on the temperature are shown. At temperatures below 360 °C, there are only minor differences in conversion for all particle diameters. For temperatures higher than 360 °C and hence increased reaction rates, the conversion for an average particle diameter of 1 mm is significantly lower than for the smaller particles. Here the influence of pore diffusion sets in. With these particles full conversion cannot be reached even at a temperature of 500 °C. With particle diameters below 0.63 mm and temperatures up to 390 °C, a negative influence of pore diffusion on the reaction rate can be excluded. Nevertheless an internal mass transfer limitation cannot be ruled out for even higher temperatures when full conversion is reached.

These results can be transferred to the microchannel reactor. Therefore, the behavior of the SiO_2-containing $V_{75}Ti_{25}O_x$ catalyst used in the microchannel reactor and the SiO_2-free $V_{75}Ti_{25}O_x$ catalyst used in the fixed bed reactor were compared in additional experiments. Both catalysts were tested in the fixed bed reactor and no differences were observed when the same mass of catalytically active $V_{75}Ti_{25}O_x$ was used [26].

The catalyst layer in the microchannel reactor has a maximum thickness of 80 μm. This corresponds to a catalyst particle in a fixed bed with a diameter of 160 μm. Therefore, no internal mass transfer influence in the microchannel reactor is expected. In the fixed bed reactor, even larger particles do not show any internal mass transfer limitations for conversions below 100%.

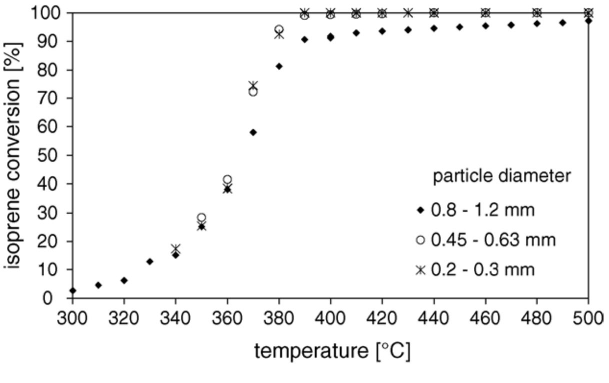


Fig. 4. Measured isoprene conversion for catalyst particles with various diameters depending on the temperature, reaction conditions: 0.6 vol.% isoprene in air, $\dot{V}_{tot} = 300$ N ml/min, $p = 1.2$ bar, $\tau_{mod} = 7.9$ min g/mol, 106 mg $V_{75}Ti_{25}O_x$, fixed bed reactor.

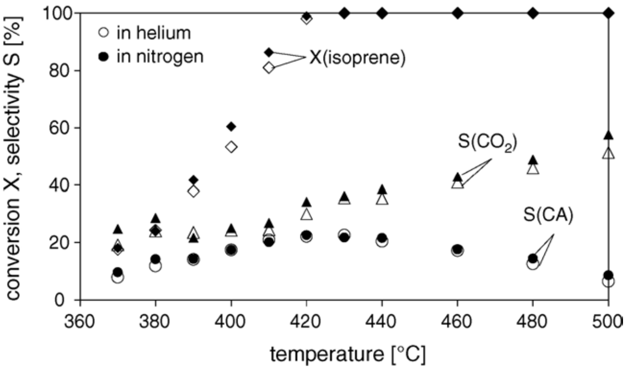


Fig. 5. Isoprene conversion and selectivity to CA and CO_2 as a function of temperature for the inert gases helium and nitrogen, reaction conditions: 0.4 vol.% isoprene and 20 vol.% O_2 in nitrogen resp. helium, $\dot{V}_{tot} = 300$ N ml/min, $p = 1.2$ bar, $\tau_{mod} = 5.9$ min g/mol, 79 mg $V_{75}Ti_{25}O_x$–SiO_2, microchannel reactor.

4.2. Test for external mass transfer limitation by changing the inert gas from nitrogen to helium

According to Section 3, one suitable method to test for external mass transfer limitations is to change the inert gas to helium. This increases the molecular diffusion coefficients of isoprene by a factor of about 3.7 and oxygen by a factor of about 3.4. For constant reaction conditions, the behavior of the isoprene oxidation in the microchannel reactor with the inert gases nitrogen and helium was compared. The result is shown in Fig. 5. No systematic differences in the isoprene conversion and the selectivities to CA and CO_2 are observable. There are small differences for the isoprene conversion at temperatures between 370 and 410 °C. Here, the conversion for the experiment in helium is below that in nitrogen. For a mass transfer limited reaction this is expected to be the opposite, as the diffusivity in helium is larger. It is concluded that these differences stem from inaccuracies in the measurement of the reactor temperature. Due to the steep increase of conversion with temperature, a deviation in the measured temperature of 1 K causes an absolute error in the conversion of about 3%. It is possible that the higher heat conductivity of helium enhances the heat transfer and leads to a lower catalyst temperature. These experiments, together with the results of the simulations in Section 5, lead to the conclusion that the isoprene oxidation in the microchannel reactor is free of external mass transfer influences. There are no influences on the reactants and on the products, as an external mass transfer limitation concerning the target product CA is expected to lead to reduced selectivities. The CA would preferably be consumed by consecutive reactions if an enrichment of the product due to a slow mass transfer from the catalyst surface occurs.

5. Two-dimensional simulations of external mass transfer in microchannels

In addition to the experimental tests, the external mass transfer behavior of the isoprene oxidation in the microchannel reactor was simulated. Due to the small dimensions of the microchannels, simulations are the only means to determine the radial concentration profiles in the channels. The real dimensions of the microchannels, the conditions during the experiments (molecular diffusion coefficients of oxygen and isoprene, total flow and flow velocity dependent on pressure, temperature), and the kinetics of the isoprene oxidation were used to simulate the concentration profiles. Therefore, the species balances for isoprene and oxygen in the channel were solved. Here the convection by the laminar flow and the molecular diffusion in radial and axial direction was taken into account. The chemical reaction was integrated by the boundary condition at the channel wall. For further details see Section 2.3.

In Fig. 6, the radial concentration profiles of both reactants isoprene (a) and oxygen (b) near the channel entrance ($z = 500$ μm) and at the channel outlet ($z = 20$ mm) are shown. The concentrations are nearly constant along the radial coordinate. There is no depletion of reactants at the channel wall. The simulations confirm the experimental results. The reaction is kinetically controlled. The consumption by the reaction at the channel wall is much slower than the radial mass transfer by molecular diffusion.

Analogous to the mass transfer in fixed bed reactors, criteria to delimit the regime of mass transfer control and the regime of kinetic control are desirable. The ratio between the rate of the chemical reaction at the wall and the radial mass transfer by molecular diffusion determines the rate of the process. For circular channels with plug flow behavior and a first order reaction, Damköhler defined limits for the various regimes [43]:

$$\begin{aligned} &\frac{k_s R}{D_M} < 0.1 \quad \text{(kinetic regime)} \\ &0.1 \leq \frac{k_s R}{D_M} \leq 100 \quad \text{(transient regime)} \\ &\frac{k_s R}{D_M} > 100 \quad \text{(mass transfer controlled regime)} \end{aligned} \tag{13}$$

Damköhler did point out that these boundaries would be lower for a laminar flow regime. Due to the laminar flow the molecules at the center of the channel with the longest distance to the wall have the lowest residence time in the channel. Therefore, the probability of these molecules getting into contact with the catalyst at the wall is reduced and they might leave the channel without being converted.

Despite this restricted validity of Damköhler's boundaries for laminar flow, they are used here for the classification of the isoprene oxidation (Fig. 7). The isoprene oxidation in the used microchannel reactor is located in the kinetic regime far from the boundary to the transient regime.

Hayes and Kolaczkowski suggested the use of the simulated radial concentration profiles to delimit the mass transfer controlled regime [44]. The reactions are fully mass transfer controlled for extremely low reactant concentrations at the wall. If the ratio between the mole fraction of the reactant at the wall $x_{\mathrm{wall},i}$ and the average mole fraction for the cross-section $x_{\mathrm{av},i}$ (cup mixing method) is below 0.03, the process is mass transfer controlled. In Fig. 8, this ratio of the simulated mole fractions is shown as a function of the reaction rate at the channel wall. When transferring the boundary limit of Hayes and Kolaczkowski [44] for the mass transfer controlled regime to the kinetic regime, the ratio of the mole fractions has to be greater than 0.97. Using this new criterion, the kinetic control of the isoprene oxidation in this microchannel reactor at these experimental conditions is again confirmed.

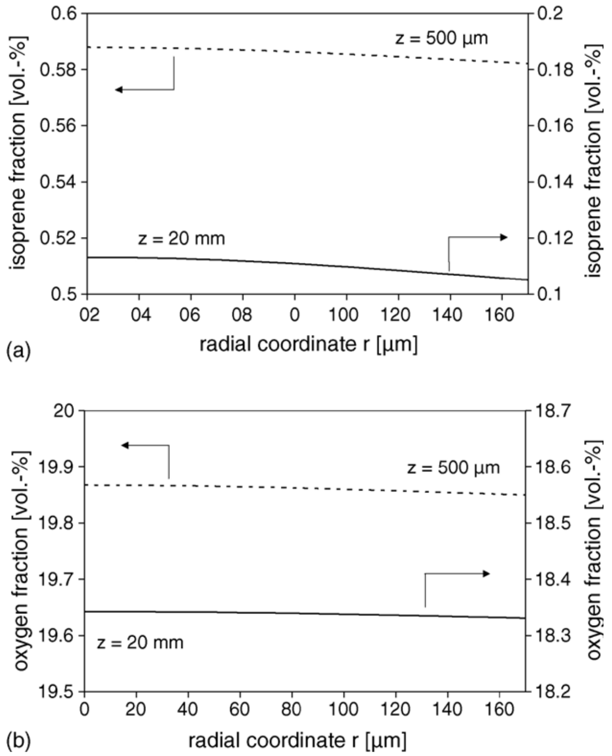


Fig. 6. Simulated radial concentration profiles of the reactants isoprene (a) and oxygen (b) at two different axial positions z, two-dimensional simulation model: $R = 170$ μm, $l = 20$ mm, $D_{\mathrm{M,isoprene}} = 3.8 \times 10^{-5}$ m^2/s, $D_{\mathrm{M,oxygen}} = 8.3 \times 10^{-5}$ m^2/s, $u_{\mathrm{av}} = 1.5$ m/s, $r_s = k'_s x^{0.2}_{\mathrm{isoprene}} x_{\mathrm{oxygen}}\, p/RT$, $k'_s = 3.5 \times 10^{-4}$ m/s, $x_{0,\mathrm{isoprene}} = 0.52$ vol.%, $x_{0,\mathrm{oxygen}} = 19.91$ vol.% (all conditions according to experiment with $\tau_{\mathrm{mod}} = 7.4$ min g/mol and $T = 400$ °C, $p = 1.2$ bar).

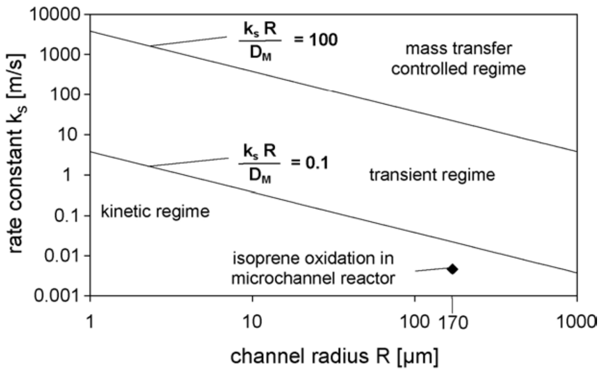


Fig. 7. Kinetic, transient and mass transfer controlled regime according to Damköhler [43] depending on the channel radius R and the rate constant k_s (first order) for a molecular diffusion coefficient $D_M = 3.8 \times 10^{-5}$ m^2/s, conditions for the isoprene oxidation: $R = 170$ μm, $D_{\mathrm{M,isoprene}} \times 3.8 \times 10^{-5}$ m^2/s, determination of k_s according to $r_s = k_s x\, p/RT = k'_s x^{0.2}_{\mathrm{isoprene}} x_{\mathrm{oxygen}}\, p/RT$ with $k'_s = 3.5 \times 10^{-4}$ m/s, $x_{0,\mathrm{isoprene}} = 0.52$ vol.% and $x_{0,\mathrm{oxygen}} = 19.91$ vol.%.

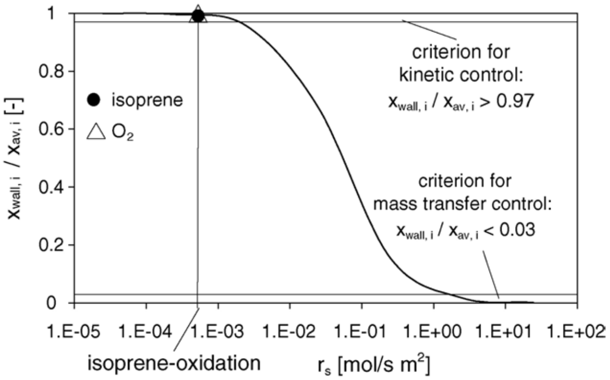


Fig. 8. Classification of regimes for the oxidation of isoprene with the extended criteria according to Hayes and Kolaczkowski [44]: ratio of the concentration at the channel wall x_{wall} and the average radial concentration x_{av} depending on the surface related reaction rate at the axial position of $z = 500\ \mu\mathrm{m}$, solid line: simulated concentrations profiles for $R = 170\ \mu\mathrm{m}$, $l = 20\ \mathrm{mm}$, $D_{\mathrm{M}} = 3.8 \times 10^{-5}\ \mathrm{m^2/s}$, $u_{\mathrm{av}} = 1.5\ \mathrm{m/s}$, $r_{\mathrm{s}} = k_{\mathrm{s}}xp/RT$, $k_{\mathrm{s}} = 0.00022–220\ \mathrm{m/s}$, $x_0 = 0.52$ vol.%, symbols: simulated concentration profiles of the isoprene oxidation: $R = 170\ \mu\mathrm{m}$, $l = 20\ \mathrm{mm}$, $D_{\mathrm{M,isoprene}} = 3.8 \times 10^{-5}\ \mathrm{m^2/s}$, $\mathrm{D}_{\mathrm{M,oxygen}} = 8.3 \times 10^{-5}\ \mathrm{m^2/s}$, $u_{\mathrm{av}} = 1.5\ \mathrm{m/s}$, $r_{\mathrm{s}} = k'_{\mathrm{s}} x^{0.2}_{\mathrm{isoprene}} x_{\mathrm{oxygen}}\, p/RT$, $k'_{\mathrm{s}} = 3.5 \times 10^{-4}\ \mathrm{m/s}$, $x_{0,\mathrm{isoprene}} = 0.52$ vol.%, $x_{0,\mathrm{oxygen}} = 19.91$ vol.% (conditions according to experiment with $\tau_{\mathrm{mod}} = 7.4$ min g/mol and $T = 400\ ^{\circ}\mathrm{C}$, $p = 1.2$ bar).

6. Conclusion

Regardless of the reactor type used, it is necessary to consider not only the influence of heat transfer but also the influence of mass transfer on chemical reactions. This is particularly important when reaction kinetics are studied. Due to the nearly isothermal conditions even at extreme conditions, microchannel reactors are of interest as reactors for kinetic and mechanistic investigations. Compared to the conventional fixed bed reactors that are widely used for kinetic studies, the mass transfer behavior in microchannel reactors with catalyst-coated channel walls is fundamentally different. Due to the laminar flow regime, the external mass transfer relies solely on the molecular diffusion perpendicular to the convection. Compared to fixed bed reactors, there are no mixing effects due to turbulence or the resistance of a catalyst bed. In consequence, the modeling and the experimental test methods to investigate external mass transfer limitations in microchannel reactors are different.

The variation of the inlet temperature can be used in fixed bed reactors and microchannel reactors to distinguish between the regimes of internal and external mass transfer and kinetic control. To test for internal mass transfer limitations, the variation of the catalyst layer thickness or the variation of the particle diameter in a fixed bed reactor seems to be more appropriate. The existence of external mass transfer limitations is demonstrated by selective enhancement of the mass transfer without affecting the reaction kinetics. For mass transfer limited reactions, the conversion increases with smaller channel diameters at constant residence times, with a reduced total pressure but constant partial pressures, or with an appropriate change of the inert gas to increase the molecular diffusion coefficients. The change of the inert gas is the preferred test method due to its relatively small experimental effort. For fixed bed reactors the increase of the flow velocity at constant residence times is a widely used test method. This method is unsuitable for microchannel reactors, as the flow velocity at constant residence times does not affect the external mass transfer behavior.

The selective oxidation of isoprene in a microchannel reactor was tested for internal and external mass transfer limitations. The average particle diameter in a fixed bed reactor was varied and the inert gas nitrogen was replaced by helium. Both experiments revealed that the isoprene oxidation in the microchannel reactor is free from any mass transfer limitations. A model to describe the external mass transfer in a microchannel was presented. In the model, the convective transport by the laminar flow, the molecular diffusion in radial and axial direction, and the chemical reactions at the channel walls were considered. The simulations of the isoprene conversion applying the geometry of the utilized microchannel reactor confirmed the experimental results. Criteria were presented to delimit the regimes of external mass transfer and kinetic control. For both criteria the kinetics of the investigated reaction have to be known.

The investigations confirm the suitability of microchannel reactors for kinetic measurements. For the selective oxidation of isoprene, as a representative selective oxidation, a mass transfer limitation in microchannel reactors with similar dimensions is excluded. Suitable experimental test methods and simulation models are available.

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