

# Enhanced mass transfer using a novel polymer/carrier microreactor

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## Abstract

Microreactors have gained great interest in a large variety of chemical reactions due to two major advantages: excellent heat transfer in the case of highly exothermic or endothermic reactions and enhanced mass transfer. Considering an enhancement of mass transfer one has to distinguish between homogeneous liquid-phase reactions and heterogeneous reactions. Microreactors for homogeneous reactions are based on entwined microchannels in the range of 10–300  $\mu\text{m}$  within special micromixers. Heterogeneous applications cover the field of heterogeneous catalysis and solid-phase supported organic syntheses.

Since polymer supports have seen an increasing interest in the field of solid-phase supported organic syntheses and ion exchange applications in the last years, in this study the use of a novel polymer/carrier microreactor for these applications is presented. The microreactor consists of a megaporous inorganic carrier material with irregular shaped channels and an immersed polymer phase which is used as a solid support for organic reactions. Investigations on dynamic ion exchange were conducted for different exchanging ions and different reactor systems. Furthermore the solid-phase supported selective reduction of cinnamaldehyde is studied, a model reaction for the important class of reductions of aldehydes in organic chemistry.

All results show an enhanced mass transfer to the active sites of the polymer and higher effective rates using the novel microreactor in comparison to commercially available ion exchange resins.

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## 1. Introduction

The development of microreactor systems for chemical processes has become a major aspect in chemical engineering research throughout the last decade [1,2]. Due to the improvements of manufacturing processes it became possible to generate a great variety of miniaturised devices in micrometer dimensions, e.g. micromixers, microreactors or heat exchangers [3]. Microreactor systems, due to their small characteristic channel dimensions of several tenth to hundreds micrometers, show several advantages over conventional laboratory-scale reactor systems. The most considerable advantages of microreactor systems are enhanced mass transfer and excellent heat exchange [4]. The first is based on the small channel diameters, which results in a reduction of mixing times even at a laminar flow regime due to short diffusion path length [4], the latter is due to the large surface-to-volume ratio, which results in heat transfer rates of up to 25000 W/(m<sup>2</sup> h) [5]. Besides these striking advantages, benefits such as small reaction volumes, less consume

of space and material and the possibility of a modular integration of microreactors in complete systems favour the application of microreactors. Up to now microreactors have been mainly applied in the fields of fine chemistry, pharmaceuticals and chemical engineering, here as a tool in process development to obtain kinetic data using only small amounts of chemicals [3].

During the development process of new pharmaceuticals in small scale syntheses the use of polymer supports has become an interesting alternative to the classic organic chemistry in solution throughout the last years [6,7]. The use of functionalised polymers, which serve as supports for reagents or catalysts, in combination with reactants in a fluid phase yields the advantages of an easy purification of the desired product and the ability to drive reactions to completion [8]. Presently polymer beads with diameters up to 500  $\mu\text{m}$  are used to immobilise reagents or catalysts [6,7]. These large dimensions are due to the polymerisation process and are required to facilitate the separation of the resin from the reaction products. But a large number of chemical transformations and ion exchange applications are limited by mass transport within these large particles, resulting in long reaction times. The large dimension of the particles together with the necessity of several single filtration steps

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using the resin in classical batch operations mark the major drawbacks of this technique.

In our study a novel polymer/carrier microreactor is presented, which consists of a megaporous inorganic carrier material with pore diameters in the range of 50–200  $\mu\text{m}$ , which is comparable to the dimensions of micromachined reactor systems. These megapores contain a polymeric phase consisting of small interconnected particles with diameters of 1–5  $\mu\text{m}$ . These particles can be chemically functionalised to obtain acidic or basic ion exchange resins. The acquired ion exchange resins serve as polymer supports for ionic bonded reagents ensuring a high accessibility of the active sites [9]. The polymerised carrier material, shaped as a monolithic rod, is encapsulated in a pressure resistant casing and operated in a flow-through mode. In this study dynamic ion exchange experiments are conducted using the novel polymer/carrier microreactor and conventional ion exchange resins. Furthermore the reduction of cinnamaldehyde with immobilised borohydride ions as a model reaction for solid-phase supported organic syntheses is studied under a variation of temperature and reactant ratio to acquire kinetic data.

The results show that the novel polymer/carrier microreactor exhibits enhanced mass transfer properties compared to commercial ion exchange resins for different ion exchange applications as well as for solid-phase supported organic syntheses. These results, combined with the easy handling of the novel microreactor, make this system a versatile tool for laboratory use in solid-phase supported applications.

## 2. Fabrication of the microreactor

At the Institute for Chemical Process Engineering a new process for a precipitation polymerisation inside the void pore space of a megaporous inorganic carrier material has

been developed [10]. This technique enables the generation of either crosslinked poly(styrene-co-divinylbenzene) or crosslinked poly(vinylchlorobenzene-co-divinylbenzene).

Considering the necessary requirements of the carrier material, which are high porosity, large pore diameters and chemical resistance, porous glass carriers with a porosity of  $\varepsilon \approx 0.4$  and pore diameters of 50–200  $\mu\text{m}$  are the best choice [10]. Two different carrier materials differing in their fabrication process have been used and evaluated in this study. The first is characterised by a fractal glass structure, whereas the second is made up of sintered glass particles (Fig. 1).

The fractal glass structure contains pores with dead ends, whereas the sintered glass particles are free of dead end pores, resulting in different flow behaviour which can influence mass transport. To create flow-through microreactors the carrier material is preferably shaped as a monolithic rod that can be encapsulated in an appropriate way.

For the precipitation polymerisation the two monomers vinylbenzylchloride (VBC) and divinylbenzene (DVB; 65% ethylbenzene) were dissolved in C14–C17 *n*-paraffin. After dissolution of azoisobutyronitrile the porous glass rods (with a fractal structure as well as with a matrix of sintered glass particles) with a diameter of 5.3 mm and a length of 110 mm were immersed in this solution. Air was removed from inside the pore volume by applying a vacuum for a short time. After heating at 70 °C overnight, the rods were cleaned of any adhering polymer and rinsed with trichloromethane [11]. The result of this process are agglomerations of small polymeric particles with diameters of 1–5  $\mu\text{m}$ , which are mechanically fixed in the void pore space of the carrier material and interconnected by polymeric bridges. The degree of crosslinking of the polymer is 5%. Fig. 2 depicts the structure of the different polymerised carrier materials.

In a following step, a pressure resistant casing for the rods is created. Therefore, the rods, as the key components of the novel microreactor, are placed in between two

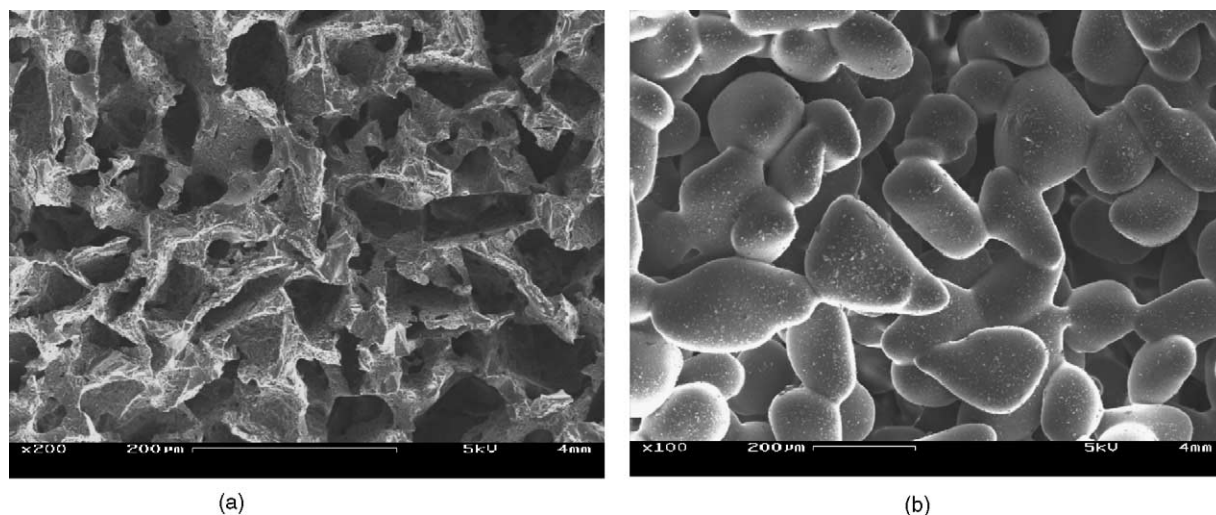


Fig. 1. SEM images of two different glass carrier materials: (a) fractal structure and (b) sintered glass particles.

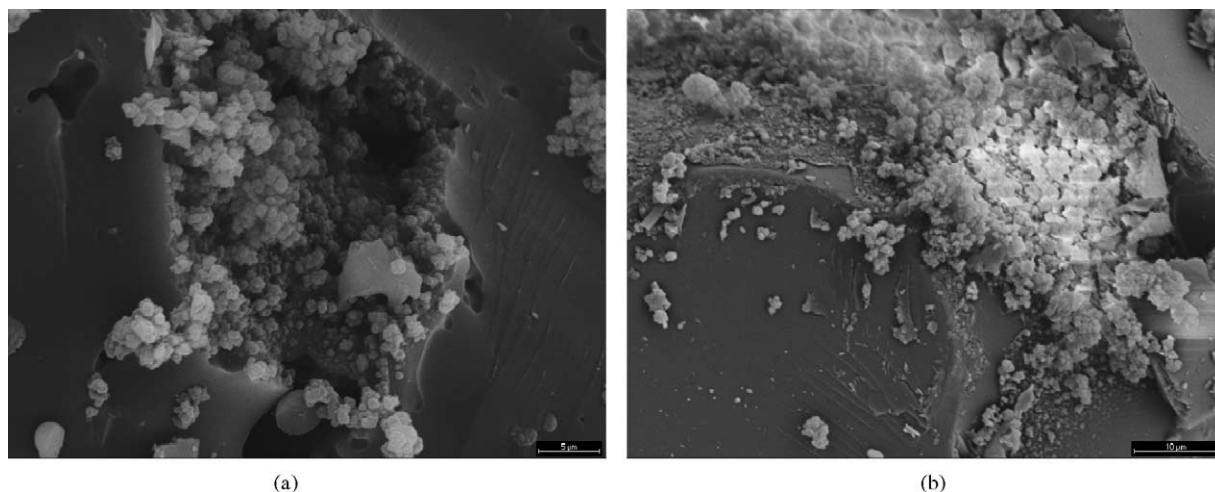


Fig. 2. SEM images of polymerised glass carrier materials: (a) fractal structure and (b) sintered glass particles.

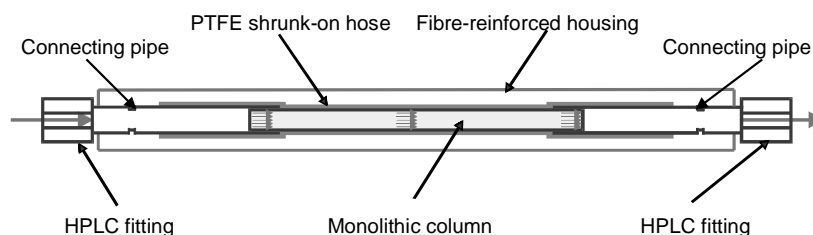


Fig. 3. Cross sectional drawing of the novel polymer/carrier microreactor system.

constructed stainless steel connecting pipes with an outer diameter of 6.35 mm. This system is sealed with a chemically resistant PTFE/FEP dual shrinking hose to avoid wall effects. Those semi-finished products are encapsulated with a fibre-reinforced epoxy-resin to create a pressure resistant reactor system. This is accomplished by winding glass or carbon fibre impregnated with epoxy resin under high traction around the semi-finished products. After curing, a fibre reinforced epoxy resin encases the monolithic rod. In the last construction step two conventional column end fittings are attached to the connecting pipes to create an inlet and outlet for the fluid phase reactants (Fig. 3).

After the formation of the mechanical reactor structure, the chemical modification of the interior polymeric phase is accomplished to obtain strongly basic ion exchange resins. A solution of dry toluene saturated with trimethylamine is continuously passed through the microreactor for at least 6 h. In the following step, the reactors are washed with ethanol for another 3 h and then dried in vacuum. The polymerised rods, now functionalised with quarternary ammonium cations, are treated with hydrochloric acid (5%) to obtain the stable chloride form of the corresponding ion exchange resin which can be used for ion exchange applications and solid-phase supported syntheses.

### 3. Experimental

#### 3.1. Preparation and characterisation of the reactor systems

Novel polymer/carrier microreactors with differently structured carrier materials (fractal structure and matrix of sintered glass particles) as well as reactor systems packed with commercial ion exchange resins were prepared for this study. These reactor systems were fabricated from a stainless steel tube with an inner diameter of 5.3 mm and a length of 110 mm corresponding to the size and geometry of the novel microreactors. The tubes are packed with an adequate amount of commercial ion exchange resins (a gel-type AMBERLITE® IRA 400 and a macroporous AMBERLITE® IRA 900) to attain the same capacity as the novel microreactor with fractal structure. As the polymer phase in the microreactors the commercial resins are strongly basic ion exchange resins with quarternary ammonium groups. IRA 400 is a gel-type resin without any macropores and typical particle diameters of 400–500 μm, whereas the IRA 900 contains macropores in the range of several 10 nm and an effective particle size of about 460 μm.

All four reactor systems are characterised with respect to their polymer content and their capacities, which means the number of ion exchange sites. The polymer content has

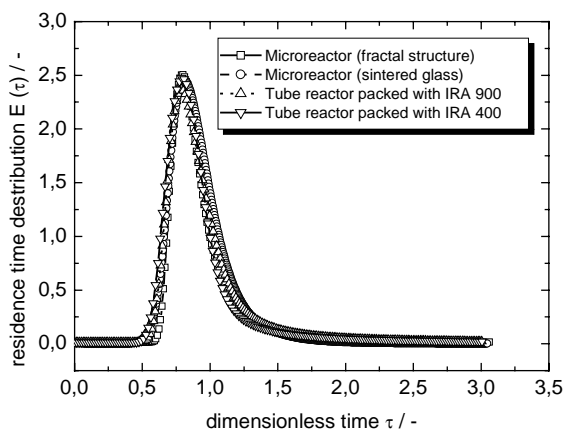


Fig. 4. Measured residence time distributions of the investigated reactor systems.

been determined by weighing the glass carriers before and after polymerisation to calculate the mass of the immersed polymer. The mass of the polymer is related to the absolute mass of the polymerised carriers resulting in the polymer content of the microreactors. The capacities of the different reactor systems have been determined by passing 250 ml of a 4 wt.%  $\text{Na}_2\text{SO}_4$  solution through the reactors ensuring a complete exchange of the chloride ions. The effluent solution is collected and titrated with a 0.1 M  $\text{AgNO}_3$  solution using potassium chromate as an indicator to calculate the amount of chloride ions in solution which marks the capacity of the reactor system. Knowing the capacity and the polymer content of each reactor the specific capacity of the polymer can be calculated.

The comparison shows that the polymer loading of the fractal carrier material is about twice as high as for the sintered glass material. This has a major effect on the achievable capacities per microreactor. Considering the specific capacities of the immersed polymer phase for both carrier materials, it can be seen that these values are comparable or even higher than those for commercial ion exchange resins.

The obtained packed tube reactors as well as the novel microreactors have the same size, capacity and comparable measured residence time distributions (cf. Fig. 4), which indicates comparable flow behaviour. Considering the bed porosity  $\varepsilon_b$  of the packed reactors (which can be estimated to  $\varepsilon_b \approx 0.25$  for swollen spherical particles in an ionic aqueous solution) and the total porosity  $\varepsilon_t$  of the microreactors (which is calculated from the porosity of the carrier material and the volume of the internal swollen polymer phase to be about 0.2), comparable mean residence times of 3 s for the microreactors and 3.5 s for the packed reactors are determined.

### 3.2. Experimental set-up

All experiments on the dynamic ion exchange and the solid-phase supported reduction of cinnamaldehyde were

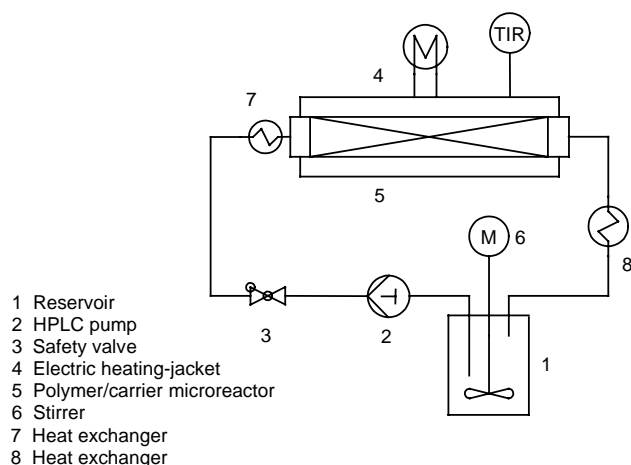


Fig. 5. Experimental set-up for investigations in batch-recycle mode.

carried out in a batch recycle-mode to determine kinetic data and differences in mass transfer. Fig. 5 depicts the experimental set-up for all investigations.

The different reactor systems were positioned in the heating oven and heated to the set temperatures. The incoming fluid was also heated to the set temperature by an additional heat exchanging device to avoid temperature gradients at the inlet of the reactors. The flow rate was set to high values to operate the reactor systems nearly free of temperature and concentration gradients, which results in isothermal conditions over the entire length of the reactor and in differential small conversions per pass through the reactor. This batch-recycle mode simulates a batch behaviour and can be used to compare the different reactor systems [12].

#### 3.2.1. Dynamic ion exchange experiments

The set-up for the experiments on dynamic ion exchange was modified by a bypass around the reactor connected to the main lines with two turnable valves. This modification was necessary to bypass the reactor with the solution of exchanging ions before the start of each experiment. The reactors were initially loaded with chloride ions to be exchanged with different anions. The lines and the reservoir were filled with 50 ml of a 0.1 M solution of different sodium salts at the beginning of each experiment and passed through the bypass. The starting point of each experiment is marked by turning the valves and passing the solution of exchanging ions through the reactor. The degree of ion exchange is monitored by measuring the increase of the chloride concentration in the solution. This is accomplished by using a chloride selective electrode with a corresponding reference electrode by METTLER-TOLEDO which are placed in the reservoir. The change of the electric potential between these two electrodes is related to the change of the chloride concentration in solution. Experiments were conducted for different exchanging anions, such as hydroxide, toluenesulphonate and borohydride ions and for different reactor systems.

### 3.2.2. Solid-phase supported reduction of cinnamaldehyde

The experiments on the solid-phase supported reduction of cinnamaldehyde imply three different steps: activation of the reactor with the reducing agent borohydride; reduction of cinnamaldehyde with the ionic bonded borohydride; and regeneration of the reactor. For the activation of the reactors, 100 ml of a 0.5 M sodium borohydride solution are passed through the reactor to ensure a complete exchange of the chloride ions. This is followed by a washing sequence of 100 ml distilled water and 50 ml methanol. The reactions are carried out for different concentrations of cinnamaldehyde ranging from 0.025 to 0.1 mol/l at various temperatures. During the regeneration sequence after the end of each reaction the reactors are successively washed with 50 ml methanol, 50 ml distilled water, 100 ml 1 m NaOH solution, 50 ml distilled water, 100 ml 2 m HCl solution and 200 ml distilled water.

To monitor the progress of reaction samples from the solution are taken and analysed by gas chromatography.

## 4. Results and discussion

The performed experiments were aimed to exhibit enhanced mass transfer properties using the novel polymer/carrier microreactor compared to reactors packed with commercial ion exchange resins under same conditions. Ion exchange processes are well suited applications to demonstrate differences in mass transfer because they solely depend on diffusion inside the polymeric particles [13]. To demonstrate the advanced mass transfer properties of the novel microreactors in the field of solid-phase supported syntheses a model reaction has been chosen which is mainly limited by mass transfer to the active sites. According to [14], the reduction of aldehydes by polymer bonded borohydride presents this type of reaction.

### 4.1. Dynamic ion exchange

As stated in Table 1 there are differences in the capacities of the polymer/carrier microreactors. To be able to compare the results of the dynamic ion exchange experiments the measured concentration of chloride ions has to be related to the maximum exchangeable amount of chloride ions, which means to the determined capacity of each reactor. Thus, the degree of ion exchange (conversion)  $Y$  is

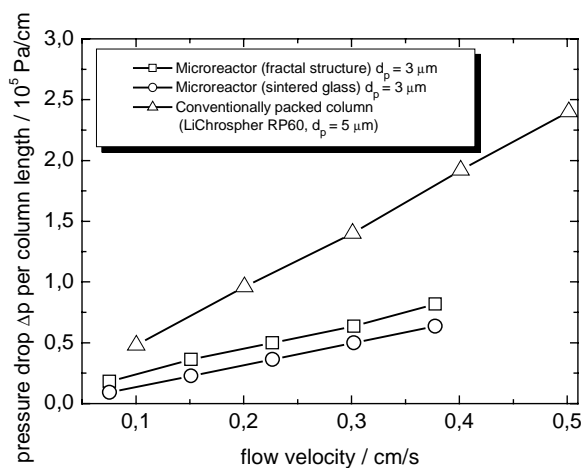


Fig. 6. Pressure drop of different columns filled with polymer particles of comparable diameters  $d_p$ .

calculated by:

$$Y = \frac{c_{\text{Cl}^-} V}{C} \quad (1)$$

with  $c_{\text{Cl}^-}$  being the measured concentration of chloride ions in solution (mol/l),  $V$  being the volume of the entire circular flow (ml) and  $C$  giving the measured capacity of each reactor (mmol).

All experiments on dynamic ion exchange revealed that the novel polymer/carrier microreactor is a very advantageous tool for ion exchange applications. Due to the morphology of the composite material it is possible to use very small polymeric particles, which ensure good mass transport properties, in a very convenient way. The large channel diameters of the megaporous carrier result in a much lower pressure drop compared to columns filled with polymeric particles with the size of 1–5  $\mu\text{m}$  [15], which is shown in Fig. 6.

On the other hand, the small particles in the porous carrier material ensure a very good mass transfer to the active sites compared to commercial resins as the conducted experiments document. Fig. 7 depicts the ion exchange of all investigated ions in the prepared microreactors.

As can be seen in Fig. 7, the ion exchange of toluenesulphonate ions and borohydride ions is comparable with respect to ion exchange kinetics and conversion. The obtained equilibrium conversions are in the range of about 0.8–0.85 and are reached for both microreactors and exchanging ions after about 500 s. A different behaviour is ob-

Table 1

Characteristic data of the prepared microreactors and tube reactors packed with commercial ion exchange resins

Reactor	Polymer content (mass%)	Total reactor capacity (mmol)	Specific polymer capacity (mmol/g <sub>polymer</sub> )
Microreactor (fractal structure)	7.51	1.05	5.81
Microreactor (sintered glass)	3.70	0.55	4.54
Tube reactor packed with IRA 400	100 (no carrier material)	1.0	3.86
Tube reactor packed with IRA 900	100 (no carrier material)	1.0	4.52

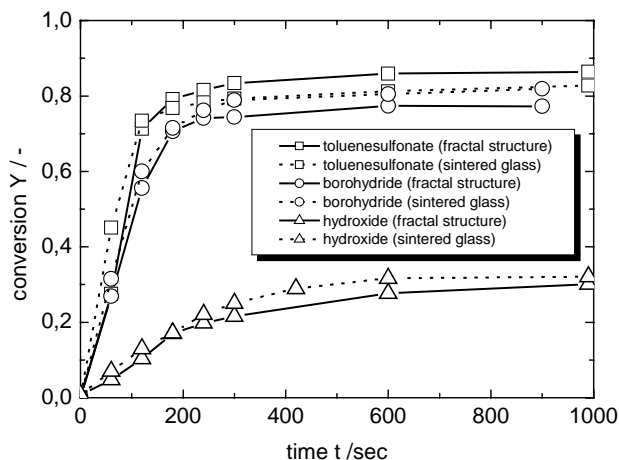


Fig. 7. Progress of ion exchange for 0.1 molar solutions in the novel polymer/carrier microreactors at 20 °C.

served for the ion exchange with hydroxide ions. Final conversions of about 0.3 are obtained for these ions, indicating a high affinity of the chloride ions to the ion exchangers. For all exchanging ions no distinct difference between the two applied carrier materials has been observed.

Considering the exchange of toluenesulphonate and borohydride ions, significant differences in the ion exchange kinetics have been observed for the applied reactor systems. Fig. 8 shows the experimental results for the ion exchange of toluenesulphonate and borohydride ions at 20 °C in the different reactor systems.

Toluenesulphonate ions, which are comparable in size to many organic molecules, as well as borohydride ions, which act as immobilised reagents for reductions, are exchanged faster applying the novel polymer/carrier microreactors, indicating an enhanced mass transfer in the small polymeric particles due to shorter diffusion paths. Both, AMBERLITE® IRA 400 and 900, have diameters in the range of 400–500  $\mu\text{m}$  which marks a major mass transport resis-

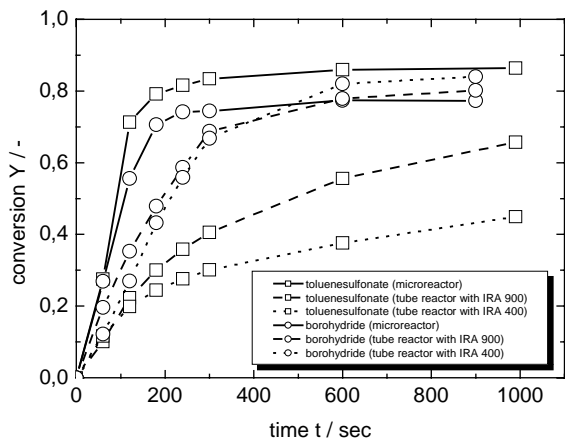


Fig. 8. Progress of ion exchange for 0.1 molar sodium toluenesulphonate and sodium borohydride solutions in different reactor systems at 20 °C.

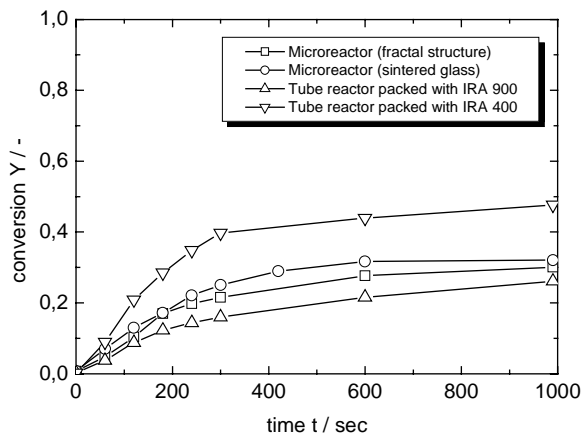


Fig. 9. Progress of ion exchange for a 0.1 molar sodium hydroxide solution in different reactor systems at 20 °C.

tance. Considering the macroporous structure of the IRA 900, which allows mass transport to the active sites via diffusion in the fluid phase inside the macropores, the higher rate of exchange compared to the gel-like IRA 400 can be explained for both investigated ions.

The ion exchange equilibrium is about 0.85 for toluenesulphonate ions and 0.8 for borohydride ions applying the novel polymer/carrier microreactors. These values are obtained after about 500 s for both investigated ions. Considering the exchange of toluenesulphonate ions in the packed tube reactors, similar equilibrium values compared to the microreactors have been measured, but it takes more than 3000 s for the commercial resins to reach equilibrium. Considering the exchange rate of borohydride ions the differences between the microreactors and the packed tube reactors systems are less significant. Comparable equilibrium values of about 0.8 are obtained for all considered reactor systems, whereas these values are reached after about 500 s for the microreactors and after about 700 s for the packed tube reactors.

The experimental results for the exchange of chloride ions with hydroxide ions are different to some degree compared to the exchange with toluenesulphonate and borohydride ions.

As depicted in Fig. 9, the application of the polymer/carrier microreactor results in a slightly higher rate of ion exchange than in the tube reactor packed with IRA 900. The difference between the microreactor and the reactor packed with IRA 900 is in the same range as for the exchange with borohydride ions. In contrast to all results obtained from the previous experiments, the use of the tube reactor packed with the gel-like IRA 400 enables a faster exchange of hydroxide ions compared to the polymer/carrier microreactors. This is likely due to the fact of having a basic solution with a pH-value of 13 which swells the large gel-type resin to higher degree than the macroporous IRA 900 and the small polymer particles in the microreactors. The higher swelling caused by the drastic shift of the pH

value may allow better gel-diffusion in the large particles which can exceed the properties of mass transport in small particles, that do not swell so dramatically, or in liquid filled macropores. As can be seen in Fig. 9, the ion exchange equilibrium for hydroxide ions is in the range of 0.3 for the polymer/carrier microreactor and the tube reactor packed with IRA 900 and reaches a value of about 0.5 for the reactor packed IRA 400. This also indicates the fact of a higher swelling of the large gel-type particles by sodium hydroxide solution resulting in a higher accessibility of the ion exchange sites.

Even though ion exchange is not a chemical process itself, a kinetic model derived from chemical reactions can be used to describe the progress of ion exchange. The amount of exchanging ions in solution exceeds the capacities, which means the amount of chloride ions, by a factor of at least 10. Thus, the concentration change of the exchanging ions in solution is negligible so that their concentration can be considered constant and does not influence the kinetic in this case. A simple model for a first order reversible reaction considering only the concentration of the chloride ions is sufficient enough to describe the process of ion exchange. The application of this simple model to determine rate constants for the ion exchange process is necessary to estimate optimised loading times of the resin with different ions which serve as immobilised reagents in solid-phase supported reactions (e.g. borohydride ions). An optimisation of the loading times saves material resources as well as laboratory time. Furthermore, a quantitative description of the efficiency of the novel microreactors in comparison to traditionally packed tube reactors can be given.

Eq. (2) gives the time depend progress of ion exchange

$$\frac{dc_{\text{Cl}^-}}{dt} = k_+ \bar{c}_{\text{Cl}^-} - k_- c_{\text{Cl}^-} \quad (2)$$

with  $k_+$  being the rate constant for the forward reaction,  $k_-$  being the rate constant for backward reaction and  $\bar{c}_{\text{Cl}^-}$  being the concentration of chloride in the polymer phase. Knowing the initial concentration of chloride in solution, which is zero, in the polymer phase, which corresponds to the capacity, and the equilibrium concentration in solution, which is determined experimentally, Eq. (2) can be integrated easily. Introducing the conversion  $Y$ , the equilibrium conversion  $Y_{\text{eq}}$  and an overall rate constant  $k$ , which is described by:

$$k = k_+ - k_- \quad (3)$$

the following equation is obtained for an equimolar exchange of equivalently charged ions:

$$\ln \left( \frac{Y_{\text{eq}} - Y}{Y_{\text{eq}}} \right) = kt \quad (4)$$

The values for  $k$  were optimised by minimising the root mean square values of the conversion  $Y$ . Exemplarily the experimental results and the modelling for the exchange of toluenesulphonate are shown in Fig. 10. A good description

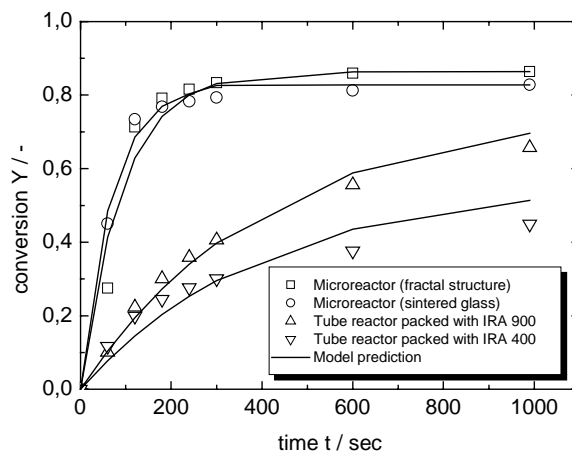


Fig. 10. Measured and calculated conversions  $Y$  for the exchange of toluenesulphonate ions applying different reactor systems.

of the experimental values is given by the model. Comparable fittings have been obtained for the other exchanging ions.

Table 2 gives a summary of all determined rate constants, which in fact reflect a mixture of mass transfer and reaction kinetics. Due to the fact that the ion exchange itself can be considered a spontaneous reaction [13], the determined rate constants mainly quantify the mass transfer to the active sites. The obtained constants for the novel polymer/carrier microreactors are higher by a factor of about 2 for the exchange with borohydride ions and even higher by the factor of 4 for the exchange with toluenesulphonate, indicating the enhanced mass transfer applying this new microreactor for different ion exchange applications.

#### 4.2. Solid-phase supported reduction of cinnamaldehyde

Ion exchange resins loaded with borohydride have been widely used and investigated for reductions of azides [16], nitrocompounds [17] and carbonyl compounds [18]. Especially selective reductions of  $\alpha,\beta$ -unsaturated carbonyl compounds without effecting the carbon–carbon double bond are

Table 2  
Determined effective reaction rate constants  $k \times 10^3$  ( $\text{s}^{-1}$ ) for  $\vartheta = 20^\circ\text{C}$

	Toluenesulphonate	Borohydride	Hydroxide
Microreactor (fractal structure)	10.9	9.3	4.0
Microreactor (sintered glass)	14.7	9.9	4.7
Tube reactor packed with IRA 900	2.5	5.6	2.8
Tube reactor packed with IRA 400	2.5	4.9	4.5

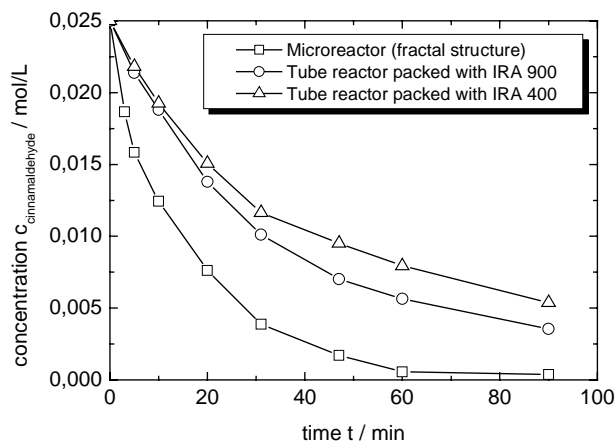


Fig. 11. Concentration profiles of cinnamaldehyde as a function of time for different reactor systems ( $\kappa = 0.5$ ,  $\vartheta = 25^\circ\text{C}$ ).

frequent problems in organic chemistry [18]. The use of basic ion exchange resins loaded with borohydride marks an interesting solution of this problem.

The obtained results of the reduction of cinnamaldehyde with immobilised borohydride using the novel polymer/carrier microreactor verify these results. No side products are detected by gas chromatography and a full conversion of cinnamaldehyde to cinnamyl alcohol is observed. According to the observed reaction mechanism [19] 1 mol of borohydride is able to reduce 4 mol of aldehyde. The solvent is involved in the reaction mechanism acting as a hydrogen donor. The type of solvent influences the reaction greatly, resulting in high reaction rates using methanol and very low reaction rates using ethanol [18].

The performed experiments with the novel polymer/carrier microreactors and the packed tube reactors show great differences in the rate of reaction depending on the type of reactor. Only fractal structured carrier material has been used for the preparation of the polymer/carrier microreactor and compared to commercial resins in experiments. Different reactant ratios  $\kappa$ , indicating the initial concentration of cinnamaldehyde related to the initial concentration of immobilised borohydride, have been studied at different temperatures. Fig. 11 depicts the concentration profiles of cinnamaldehyde as a function of time for a ratio of  $\kappa = 0.5$  at a temperature of  $25^\circ\text{C}$  for the investigated reactor systems.

It can clearly be seen that the use of the polymer/carrier microreactor leads to a faster conversion of cinnamaldehyde for low temperatures and an excess of polymer-bonded reducing agent. A complete conversion is attained after 60 min applying the microreactor, whereas a conversion of only 70% is reached using tube reactors packed with commercial resins. Even after 90 min no full conversion is observed using these reactors.

Similar results are obtained for high temperatures and an excess of the fluid phase reactant cinnamaldehyde (Fig. 12). With a 2:1 excess of cinnamaldehyde it is possible to ac-

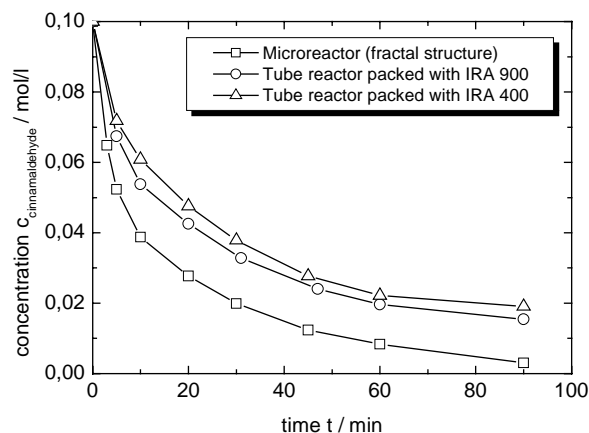


Fig. 12. Concentration profiles of cinnamaldehyde as a function of time for different reactor systems ( $\kappa = 2$ ,  $\vartheta = 60^\circ\text{C}$ ).

complish almost complete conversion after 90 min using the polymer/carrier microreactor. Considering the curves for the tube reactors packed with IRA 400 and IRA 900 it is obvious that a full conversion for a 2:1 excess of cinnamaldehyde can not be reached. This can be explained by the fact that the commercial particles, due to their size, are not entirely penetrated with the cinnamaldehyde–methanol–solution and only a partial amount of the borohydride and the intermediates can be used for reaction resulting in incomplete conversions for an excess of fluid phase reactant.

Comparable results have been attained for all other reactant ratios and temperatures pointing out the enhanced mass transfer to the polymer bonded reagents by fluid phase reactants using the novel microreactor.

Experiments with the microreactor at different temperatures and reactant ratios have been used to determine intrinsic kinetic parameters of this solid-phase supported synthesis in a very easy way [20] minimising mass transfer resistances.

## 5. Conclusions

The preparation of a novel polymer/carrier microreactor and its applications for ion exchange processes and solid-phase supported syntheses have been presented. Thanks to a precipitation polymerisation in an inorganic carrier material very small polymeric particles can be generated and handled in a very convenient way. A pressure resistant casing of the rod shaped composite material allows convective flow through the material, operating the microreactor in a batch-recycle mode.

Experiments on diffusion limited ion exchange processes with anions of different sizes exhibit an enhanced mass transfer using the novel microreactor compared to tube reactors packed with commercial ion exchange resins. The advantages of the microreactor become more obvious using large exchanging ions (toluenesulphonate), which are comparable



in size to organic molecules, resulting in a dramatic decrease in time needed to reach equilibrium. Even for smaller ions, like borohydride, exchanging times are shorter compared to commercial resins.

The application of the novel polymer/carrier microreactor for solid-phase supported reactions confirms the results obtained from ion exchange investigations. The studied reduction of cinnamaldehyde with polymer bonded borohydride proceeded faster for all examined conditions using the microreactor.

These experimental results demonstrate the ability of this novel polymer/carrier microreactor in applications which are mainly limited by mass transfer resistance. The microreactors combine the advantages of a megaporous carrier material, resulting in a low pressure drop and easy handling, and of small polymeric particles (1–5  $\mu\text{m}$ ), enabling an enhanced mass transfer to the active sites. It is well suited for laboratory applications generating small amounts of fine chemicals in shortened times, thus improving the productivity of a laboratory.

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