Improvement of active site accessibility of resin catalysts by polymer/carrier composites: development and characterisation of monolithic catalytic chromatographic reactors

U. Kunz*, C. Altwicker, U. Limbeck, U. Hoffmann

Institut für Chemische Verfahrenstechnik, Leibnizstr. 17, Technische Universität Clausthal, D-38678 Clausthal-Zellerfeld, Germany

Abstract

Synthetic resins are one of the most used catalysts in the production of additives for gasoline fuelled cars. Ethers like MTBE (methyl-*t*-butylether), TAME (*t*-amylmethylether) or ETBE (ethyl-*t*-butylether) are now widely used to enhance the anti-knock performance of the fuels. Now more than 14,000,000 t per year of the above-mentioned ethers are produced world-wide. On the other hand there is much less use of catalytic ion exchange resins in the production of fine chemicals. Reasons might be selectivity aspects, the availability of resins in a shape which is well suited for technical reactors and a lack of knowledge with respect to the accessibility and stability of the active sites.

In this study the preparation and characterisation of polymer/carrier composite components for catalytic applications is described. Monolithic rods for chemical reactions with simultaneous separation were prepared by a precipitation polymerisation process and investigated. The distribution of the cross-linker concentration across the particle radius is calculated based on co-polymerisation parameters and discussed. The active sites are sulfonic acid groups. The distribution of the active sites was measured by scanning electron microscopy. For the cyclisation reaction of 1,4-butanediol to tetrahydrofuran and water the application of rods as a monolithic chemical reactor was demonstrated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Monolithic column; Polymer/carrier composite; Catalysis; Chromatography; Multifunctional reactor

1. Introduction

In the past there were several approaches to rise the accessibility of active sites in resins for catalytic or chromatographic applications. One route was the development of macroporous resins nearly 50 years ago. Sulfonated resins of this type are now widely used in reactive distillation processes for the production of ethers as components for gasoline to enhance the anti-knock performance of the fuel. Early work to enhance the accessibility of active sites by preparing monolithic materials was done by Spes, who prepared shaped bodies of sintered polymers with resin particles with an open pore structure [1–3]. Chaplits prepared moulded catalysts which were used in reactive distillation processes [4]. The production and use of fibres with ion exchange properties is described by Yoshioka [5,6]. Today state of the art is wrapping resin beads with glass fibres clothing and forming bales. The bales are put into a column to perform the catalytic reaction of alcohols and olefines to form ethers with simultaneous separation by distillation. This technique was introduced by the CDTECH company [7–9]. A similar approach is the wrapping of resins inside stainless

* Corresponding author. Tel.: +49-5323-72-2187;
fax: +49-5323-72-2182.
E-mail address: kunz@icvt.tu-clausthal.de (U. Kunz).

Nomenclature

c_{M1}/c_{M2}	ratio of the monomer concentrations
dc_{M1}	change of monomer 1 concentration
dc_{M2}	change of monomer 2 concentration
r_K	radius of the first spherical polymer particle
r_n	radius of the spherical polymer particle enlarged by one shell
$r_1 = k_{11}/k_{12}$	co-polymerisation parameter
$r_2 = k_{22}/k_{21}$	co-polymerisation parameter
V_K $= (4/3)\pi r_K^3$	volume of the first spherical particle
V_{KS_n} $= (4/3)\pi r_n^3 - V_K$	volume of "onion-like" first shell of the particle
$V_{KS_{n+1}}$ $= (4/3)\pi r_{n+1}^3 - V_{KS_n}$	volume of "onion-like" following shells of the particle

steel wire sieves as performed by the SULZER company [10] or others [11]. At our institute composite materials in the shape of Raschig-rings of inorganic supports and sulfonated resins were developed and successfully used for the synthesis of ethers by Kunz et al. [12–14]. An other approach for chromatographic applications to rise active site accessibility is the development of perfusion resins with very large pores, e.g. by Afeyan et al. [15]. The improvement of active site accessibility inside resins for catalysis is described in detail by a recent review of Hudson [16,17].

As an extension in this paper the use of polymer/carrier monolithic composites for chromatographic reactors is demonstrated. Commercially available beads with diameters in the millimetre range are not well suited for this intended application. A pure polymer phase will not have stable mechanical dimensions when the solvent changes its polarity. The diffusion path length of millimetre sized particles is long, causing a separation of the reactants inside the particles

by different transport velocities. This may lead to selectivity problems. On the other hand micrometer particles will have a high pressure drop and thus a low productivity of the reactor. With regard to Pfeiffer et al. [18] the use of perfusion resins does not solve the problem because only a small amount of the fluid phase passing a chromatographic column is forced to flow through the pores of the polymer particles. So it is necessary to start the preparation of a new material with better accessibility of the active sites by decreasing the polymer particle size that also ensures low pressure drop. This seems to be contradictory but can be solved by the technique developed by us.

Our approach to enhance the accessibility of active sites is the preparation of monolithic polymer/carrier composites with very small but interconnected polymer particles within the pore system of a carrier material which allows a convective flow and an enhanced mass transfer. The choice of appropriate carrier materials in different shapes in combination with a precipitation polymerisation process (dispersion polymerisation) allows us to produce monolithic components with improved accessibility of active sites and simultaneously a low pressure drop in flow-through applications like chromatographic or membrane reactors. In contrast to existing approaches a forced convective flow involving the whole polymer phase can be achieved.

Before the preparation procedure was started requirements for the polymer/carrier composites were defined:

- material should be a strong acid catalyst;
- active sites should be sulfonic acid groups;
- shape of the catalyst should be rod, plate and tube;
- pore size of the carrier should be in the micrometer range;
- polymer particle size should be small (in the micrometer range).

As monomers styrene and divinylbenzene were chosen. These monomers were successfully used in the production of commercial resins and can easily be activated by sulfonation. The preparation of a monolithic composite material requires a carrier material with the following properties:

- available in different shapes (rod, disc, tube);
- large pore volume;

- open, interconnected pores;
- high mechanical strength;
- free of substances influencing the polymerisation process;
- chemical stability during all preparation steps.

2. Experimental

2.1. Preparation of the samples

2.1.1. Polymerisation
Based on our previous work an adopted procedure for the preparation of reactive chromatographic columns was developed. As well suited, porous glass carriers with pore diameters ranging from 50 to 300 μm were chosen. The preparation of the desired catalytic composite components was done by a precipitation polymerisation process (dispersion polymerisation). A solution of the monomers styrene and the cross-linker divinylbenzene (43.2 g styrene, 3.86 g divinylbenzene; concentration of divinylbenzene 65%, rest is ethylstyrene) in a hydrocarbon solvent (C14–C17 *n*-alkane, 300 ml) was prepared. After the addition of a radical initiator (azoisobutyronitril, 330 mg) the carrier material in the shape of monolithic rods (porous glass, 110 mm length, 5.3 mm diameter) was immersed in the solution and air bubbles were removed by vacuum (20 min at room temperature). Then the polymerisation process is started by rising the temperature to 70°C. After 12 h, the carrier rods were removed from the polymerised mixture and rinsed with trichloromethan to remove the high boiling solvent and residues from the polymerisation process. The rods were dried in vacuum at 70°C for 1 day.

2.1.2. Sulfonation
After the polymerisation step the copolymer particles were activated by sulfonation with chlorosulfonic acid. The 100 ml of trichlormethane were mixed with 10 ml chlorosulfonic acid. Then the dried polymer filled monolithic rods were added. For 24 h the mixture was kept at room temperature. Then the excess of sulfonating agent was discarded and the rods treated with cold water. After washing with methanol the rods were dried in vacuum. The result is a polymer/carrier composite with strong acid properties, suited as a catalytic component for chemical reactions. The activity per volume can be adjusted by changing the monomer concentration during the polymerisation step.

The polymer load of rods prepared this way is 9–10 wt.%, the capacity based on the resin mass is 4.5 meq. g^{-1}.

3. Theory

3.1. Calculation of cross-linker profiles inside single polymer particles

The swelling behaviour of ion exchange resins depends on the cross-linker concentration. Correlated with the swelling behaviour is the mechanical stability. A model for the growth of the cross-linked particles is suggested. Based on the co-polymerisation equation and on the assumption that the particles are growing like the shells of an onion it is possible to calculate the cross-linker concentration profile across the polymer particle diameter.

The following assumptions were made:

- At the first moment of precipitation (separation of phases) the polymer particle has the shape of a sphere caused by surface tension. In addition, the shape of a sphere is probable because the polymer chains are flexible and form a coiled tangle.
- The cross-linker concentration inside the polymer can be described by the co-polymerisation equation. The co-polymerisation equation is independent of the polymer forming mechanism, so it is adequate to use it for this case.
- The particles grow in spherical shells like an onion. This seams reasonable because the monomers diffuse to the outer surface of the particles where they are bound to the existing polymer phase.
- No concentration gradients in the monomer phase were assumed. The diffusive mass transport of monomers is faster than the polymerisation reaction.

The monomers used for the preparation of polymer/carrier-components are styrene and divinylbenzene. The reactivity of the two monomers in the radical polymerisation reaction is different, divinylbenzene has the higher reactivity. That means that during the

polymerisation process divinylbenzene is built into the polymer at a higher rate than styrene. This leads to a non-uniform distribution of the cross-linker divinylbenzene in the polymer phase.

The different reactivity of the monomers is expressed by the ratios r_1 and r_2 of two rate constants. The rate constant k_{11} describes the speed of monomer 1 molecules to be added to the growing polymer chain terminated by the same monomer molecule, whereas the rate constant k_{12} describes the speed of monomer 2 to be added to the growing chain terminated by monomer 1. The constants k_{22} and k_{21} are the constants for the vice versa case. The values for the co-polymerisation parameters r_1 and r_2 for styrene and p-divinylbenzene are $r_1 = 0.14$ and $r_2 = 0.50$, for styrene and m-divinylbenzene the values are $r_1 = 0.65$ and $r_2 = 0.60$ (values taken from [19]).

With these data the co-polymerisation diagram can be calculated, as it is shown in Fig. 1 for the co-polymerisation of styrene with p-divinylbenzene. Most commercial ion exchange resins produced have cross-linker concentrations in the range of 2–20 mol% DVB (divinylbenzene). This means, that the co-polymerisation diagram is valid for these products in the upper right corner of the co-polymerisation diagram. In a batch polymerisation the cross-linker concentration in the actually formed polymer phase moves along the curve until it stops at the upper right corner when all monomers have been consumed.

Commercial ion exchange resins are produced by suspension polymerisation. In this industrial process droplets of the monomers are dispersed in water. In the case of macroreticular resins a pore forming agent is added. Each droplet behaves as a batch reactor. The concentration of the pore forming agent inside the droplets is low, so during particle growth the pore forming agent is included in the polymer phase. Each droplet forms one polymer particle. The size of the particles is in the millimetre range. After the polymerisation the pore forming agent is removed by evaporation or by solvents. This creates the pores of macroreticular resins. The concentration of the cross-linker inside the particles of commercial resins is uniform across the diameter, because the polymer growth starts at many locations inside the whole droplet. The final particle is an agglomerate of many smaller particles.

In our precipitation polymerisation (dispersion polymerisation) the solvent for the monomers is in a large excess compared to suspension polymerisation. This leads to a separation of the particles at an early state of growth. Particle formation begins when the polymer chains formed are no longer soluble in the
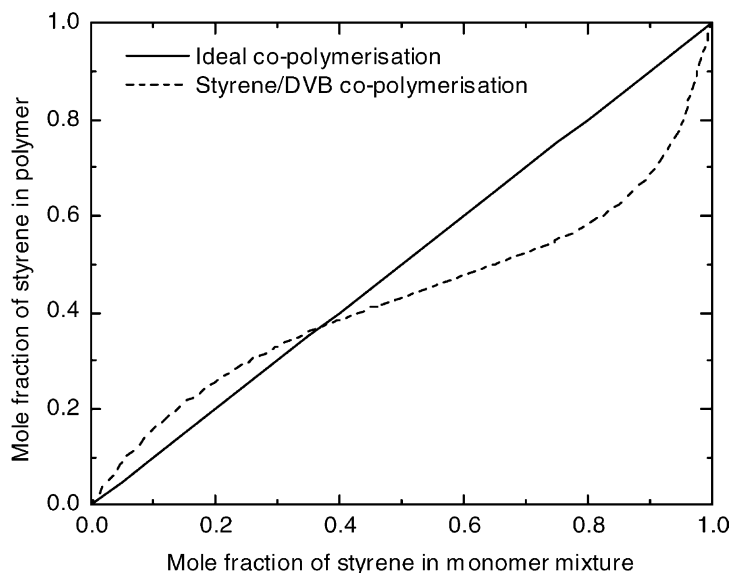

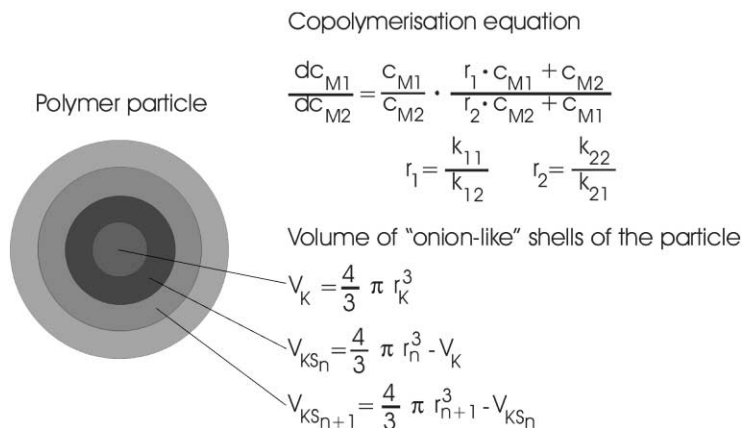Fig. 1. Co-polymerisation diagram of styrene and p-divinylbenzene.

Copolymerisation equation

Polymer particle

$$\frac{dc_{M1}}{dc_{M2}} = \frac{c_{M1}}{c_{M2}} \cdot \frac{r_1 \cdot c_{M1} + c_{M2}}{r_2 \cdot c_{M2} + c_{M1}}$$

$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

Volume of "onion-like" shells of the particle

$$V_K = \frac{4}{3} \pi r_K^3$$

$$V_{KS_n} = \frac{4}{3} \pi r_n^3 - V_K$$

$$V_{KS_{n+1}} = \frac{4}{3} \pi r_{n+1}^3 - V_{KS_n}$$

Fig. 2. Model for particle growth during precipitation polymerisation.

solvent. Monomers reach the surface of the first particles by diffusion and convection. According to their reactivity they are built into the growing polymer chains at the surface of the already existing particles. Because of the large amount of solvent, the polymer particles include no solvent.

This leads to the model, that the polymer particles in precipitation polymerisation grow in an onion shell like manner. At the beginning of the particle growth there is a large amount of divinylbenzene in the reaction mixture, so it is built into the polymer particles according to its high reactivity at a higher rate than styrene. Consequently, a highly cross-linked core and a less cross-linked shell of the polymer particles is obtained.

For the calculation of divinylbenzene concentration profiles inside the polymer particles the co-polymerisation equation was combined with a shell like growth. In a first step the formation of the particle layers was calculated by using the co-polymerisation equation for the starting mixture composition. Caused by the higher reactivity of DVB the polymer formed contains more DVB than styrene. The remaining monomer phase now has a new composition, with a lower concentration of DVB. Now for this mixture the concentration of the next formed polymer phase is calculated. This polymer forms a shell surrounding the first polymer particle. The particle formation was divided in many shells until all the monomers were consumed. The shells were assumed with spherical

shape. In Fig. 2 the model equations and a schematic drawing of a polymer particle is depicted.

Based on the aforementioned assumptions and the conditions mentioned in Section 2 the calculated *p*-divinylbenzene concentration profiles for different initial concentrations of DVB in the starting mixture are shown (Fig. 3). As expected the concentration of the cross-linker drops rapidly leading to a particle with low degree of cross-linking at the outer surface. This result is independent of the absolute size of the particle, so the calculated curves were normalised for better comparison. The typical diameter of the particles discussed here is in the micrometer range (compare Fig. 6).

The described model gives an explanation that the polymer particles formed during precipitation polymerisation are non-porous. In an onion shell like growth the solvent is not included inside the polymer particles. Polymer growth only happens at the surface of the particles at a well-defined interface and not all over the polymer phase as it is the case in suspension polymerisation. As well known for commercial resins, highly cross-linked resins swell less than low cross-linked ones. Consequently, the core of the particles formed in a precipitation polymerisation swells less than the shell. This leads to a high mechanical stability.

As shown in Fig. 3 the composition of the particles changes smoothly with the diameter. This amplifies the mechanical stability because we have a material
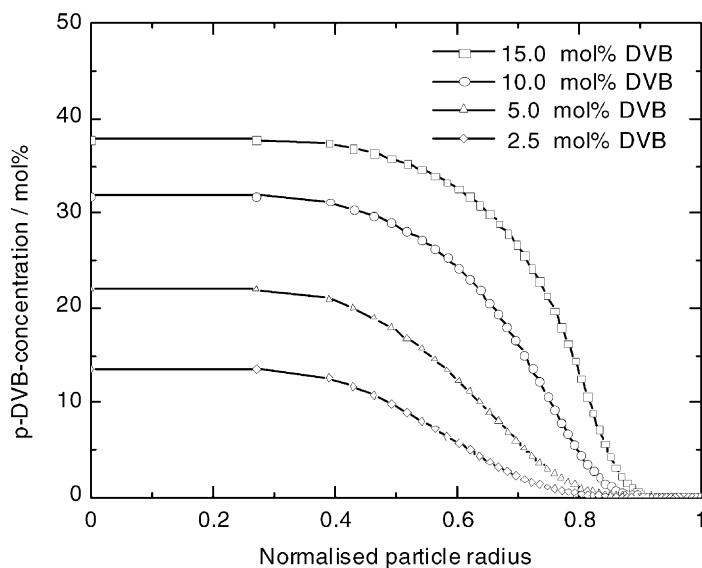
Fig. 3. Calculated cross-linker concentration profiles for particles of styrene/*p*-divinylbenzene formed during precipitation polymerisation.

which gradually changes its properties. The calculations presented here were performed for *p*-DVB. Similar results can be obtained for *m*-DVB. The only difference is, that the concentration drops more slowly.

4. Results and discussion

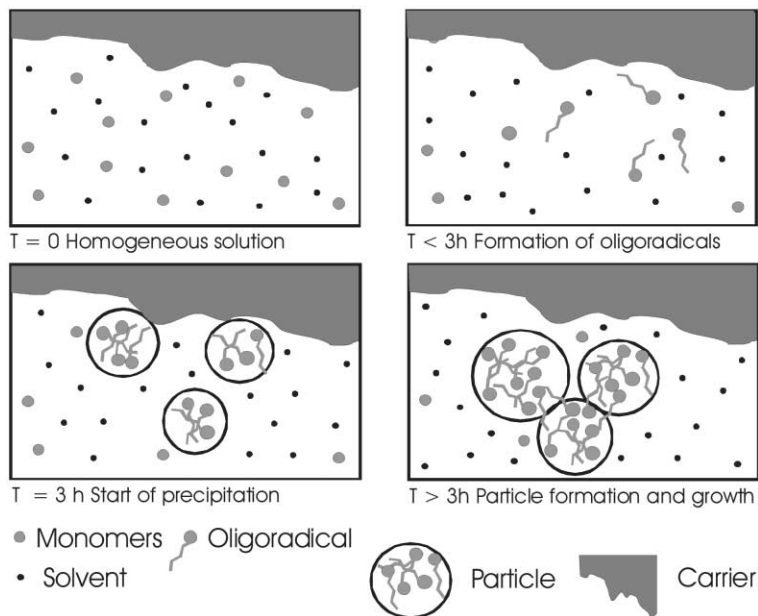The course of particle formation inside the pore volume of the carrier materials is depicted in Fig. 4.

Fig. 4. Course of precipitation polymerisation inside porous carrier materials.

In the beginning of the preparation process a homogeneous solution fills the pore volume. After initiating the polymer chains grow and at a certain molecular mass the polymer is no longer soluble in the chosen solvent. Small polymer particles are formed. At this moment there are still monomer molecules in the surrounding solution. They diffuse to the existing particles and cause further growth. In classical dispersion polymerisation processes detergents are used to keep the particles separated. For our application this is not desired, so detergents were omitted. Therefore, the particles are coming in contact and are connected by polymer bridges. At the end of the polymerisation process the polymer phase consists of small interconnected particles, filling a certain space of the carrier pore volume. The space occupied by the solvent remains as a pore volume between the particles. In Fig. 5 typical dimensions of the new materials are depicted.

The empty carrier contains pores ranging from 50 to $300\,\mu m$, the polymer particles themselves have a diameter of $1–2\,\mu m$, the pores between the polymer particles are in the range of $1–30\,\mu m$. This morphology was confirmed by scanning electron microscopy. An example is given in Fig. 6. This morphology is different compared with macroreticular resins obtained by suspension polymerisation. The pores in classical macroreticular resins are much smaller (several $10\,nm$), the resin particles are much bigger (mm range). A convective flow involving the whole polymer phase will hardly occur in conventional resin beads. Even with perfusion resins with much larger pores a convective flow through the particles happens with low efficiency, in a packed bed most of the solvent by-passes the particles.

4.1. Sulphur distribution of the polymer phase

The polymer phase within the carrier, poly(styrene-co-divinylbenzene), is modified with active sites. For most applications it is necessary that these active sites are distributed uniformly in the carrier to avoid zones of lower capacities. Problems can occur sulfonating monolithic rods of larger diameters and with higher polymer loads because the sulfonation solution has to reach the polymer phase completely. In the case of large diameters of the polymer/carrier components the sulfonation procedure has to be carried out carefully and has to be repeated once or twice to ensure that the polymer matrix is sulfonated completely.
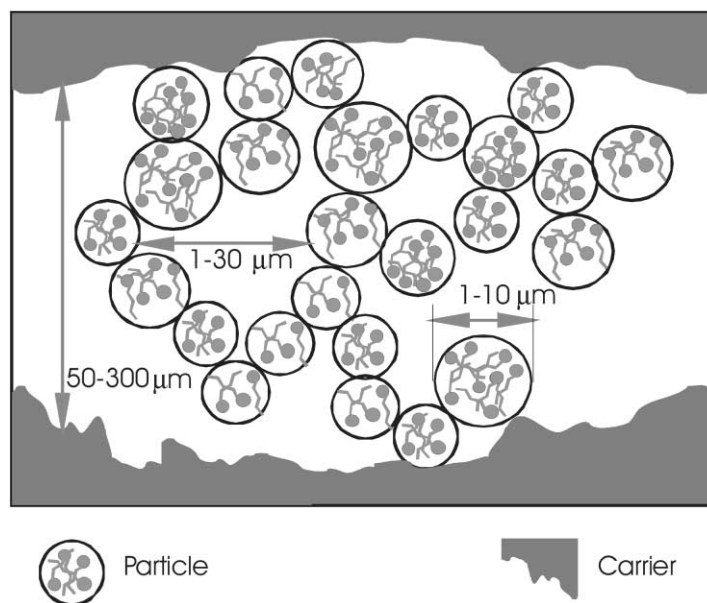

Fig. 5. Typical dimensions of polymer/carrier composites prepared by precipitation polymerisation.
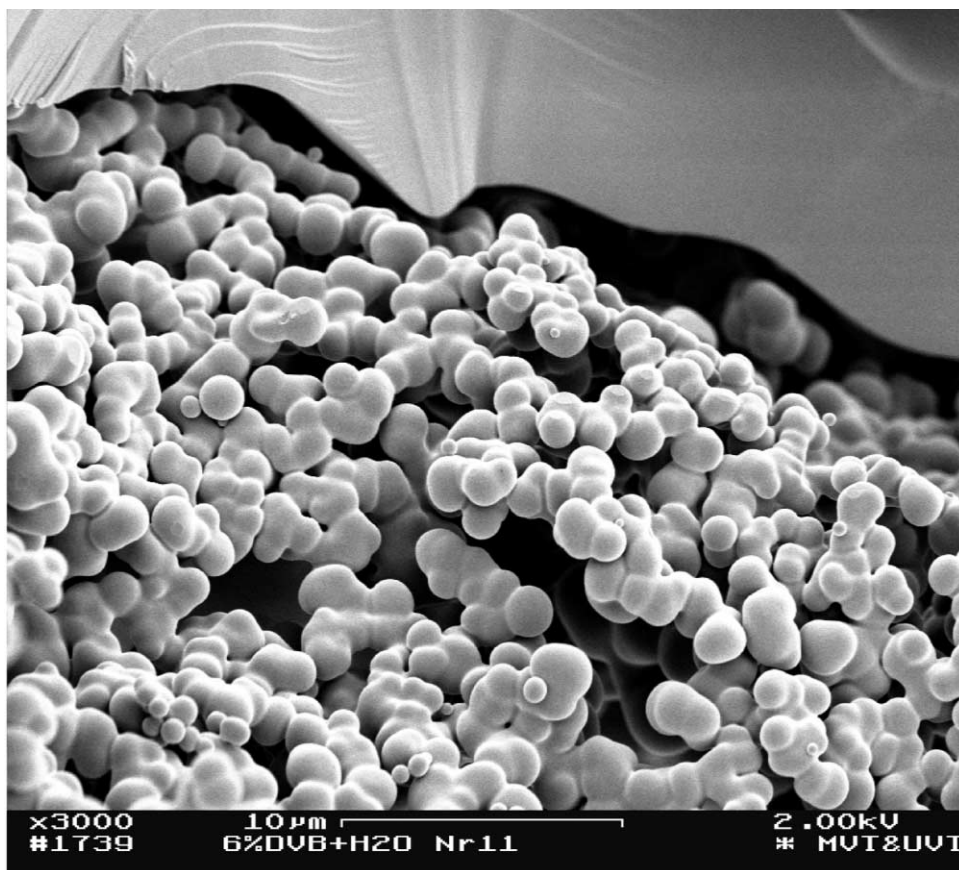
Fig. 6. Morphology of polymer/carrier composites by scanning electron microscopy.

The distribution of the active sites was determined via electron probe microanalysis (EPMA), measuring the sulphur atoms. The measurements were performed with an electron micro probe SX 100 of the Cameca company. A microscopy is depicted in Fig. 7. The brighter area represents the sulphur atoms, darker areas the glass matrix and the pore structure of the carrier. Monolithic rods of different sizes were analysed both in the core and in the shell of the rod by integrating the bright areas. As a result one obtains the sulphur content of the investigated sample. Results of all samples are given in Table 1. The values of the sulphur content in the core and in the shell of the rod are almost equal and meet the theoretical expectations. This implicates that the polymer matrix is sulfonated completely and offers a homogeneous exchange capacity. The polymer matrix itself seems

to be distributed homogeneously inside the pore system of the carrier. Both criteria are important for an enhanced mass transfer and an optimal accessibility of the active sites.

4.2. Sulphur distribution inside a single ion exchange resin particle

Diffusion path length inside the ion exchange resin should be as short as possible. This task is important for chromatographic purposes in order to have a good resolution and a symmetric peak. With regard to catalytic properties, short diffusion path length, activity and selectivity are required. For example esterification reactions are often homogeneously catalysed by inorganic acids. Heterogeneous catalysts like acidic ion exchange resins are not generally applicable, because
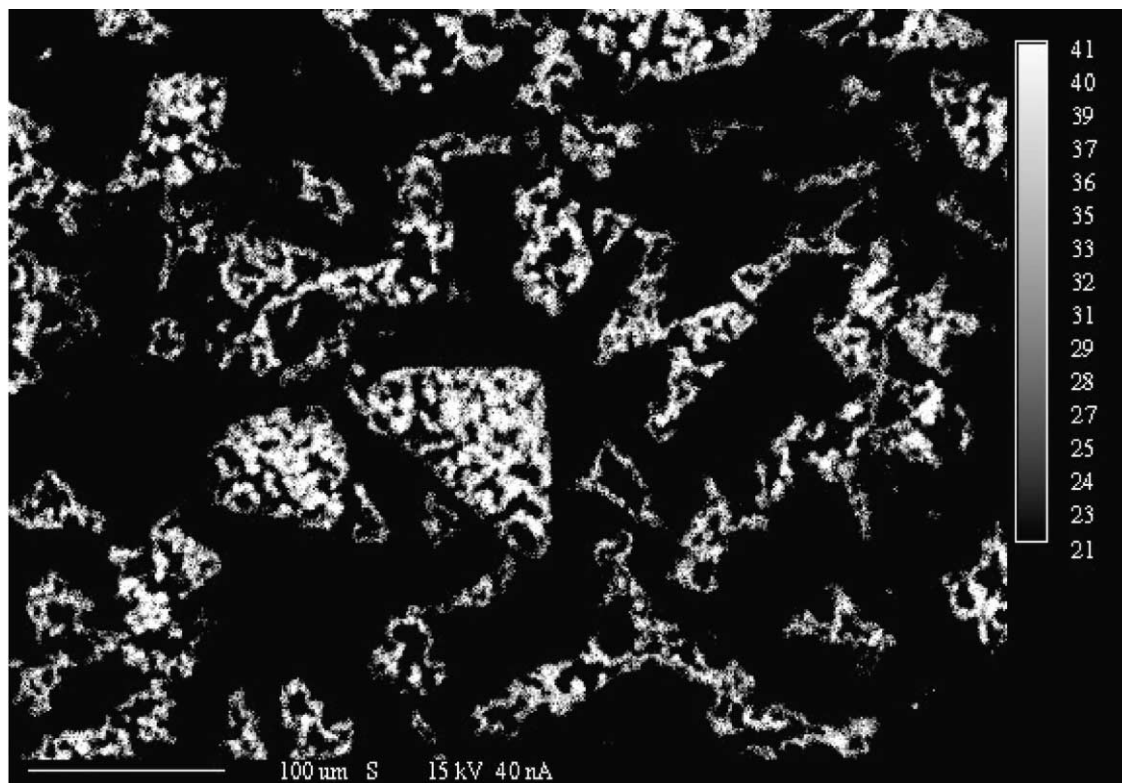
Fig. 7. Sulphur distribution of a poly(styrene-co-divinylbenzene) polymer phase.

the reactants might be separated inside the polymer phase due to different swelling behaviour and diffusion velocities. In this case side reactions take their course and diether or alkenes are formed.

Ways to shorten the diffusion path are the minimisation of the resin particle diameter and a partly sulfonation, so that just the outer surface of a resin particle is activated. This can improve the selectivity of resin catalysts.

The particle diameter is fixed by the described preparation method, so that the sulfur distribution inside a polymer particle is varied in the following. The sulfonation method was varied with regard to the two parameters time and chlorosulfonic acid concentration. Table 2 presents the influence of both parameters. By using a diluted acid combined with a short reaction time of 1 min it is possible to get polymer samples with low degree of sulfonation.

Table 1
Sulphur content in dependence on the carrier size and polymer loading in the core and in the shell of monolithic rods

	Monolith 1	Monolith 2	Monolith 3	Monolith 4	Monolith 5
Column length (mm)	110	110	110	150	150
Column diameter (mm)	5.3	5.3	5.3	12	12
Polymer load (mass%)	5.4	8.6	13.6	5.4	12.8
Core sulfur content (mass%)	6.0	8.5	14.0	6.1	11.6
Shell sulfur content (mass%)	5.7	8.5	13.5	6.2	12.4

Table 2
Specific capacity of the composite catalysts depending on the sulfonation conditions[a]

Time (min)	Capacity of composites (meq. g^{-1}), sulfonation with 10% chlorosulfonic acid	Capacity of composites (meq. g^{-1}), sulfonation with 1% chlorosulfonic acid
1	0.426	0.072
5	0.540	0.148
30	0.566	0.221
One day	0.630	0.618

[a] Solvent for chlorosulfonic acid was trichloromethane, experiments done at room temperature.

Assuming $q = 1/3q_{max}$ the depth of penetration amounts to 13% of the particle radius. Consequently it can be expected that the active sites are localised in the shell of the particle and the diffusion paths are reduced significantly.

To prove this, the sulphur distribution was measured by EPMA with a resolution of 0.1 μm. As described before a microprobe SX 100 of the Cameca company was used, measuring backscattered electrons. The results are presented in Fig. 8. It is obvious that the distribution is nearly homogeneous for $q = q_{max}$ where q is the exchange capacity of the sample and q_{max} is the exchange capacity when the whole polymer particle is sulfonated (corresponds to a value of 4.5 meq. g^{-1}). If the degree of sulfonation is reduced to one-third, the distribution is changed completely and most active sites are situated in the shell of the particle. The great difference between the absolute values in Fig. 8 refers to the fact, that the EPMA was not calibrated with respect to the sulphur density inside polymer resins. These measurements indicate that it was possible to apply selective sulfonation even in the complicated morphology of our new monolithic composite materials.

The experimental test of the new prepared surface activated ion exchange resin with regard to selectivity and chromatographic aspects is a task of the future. Preliminary results indicate, that a surface sulfonated polymer phase leads to an improved selectivity in the esterification of high molecular mass alcohols with long chain acids.

4.3. Monolithic column as reactor for chemical reaction with simultaneous separation

With regard to Agar and Ruppel [20], Westerterp [21], Mazotti et al. [22] there is an increasing interest in the combination of a chemical reaction and a separation in a multifunctional reactor unit during the last years. Especially for reversible reactions or reactions with product inhibition a higher conversion and a better selectivity is expected. The simultaneous product separation is a big advantage in processes where a high product purity is demanded, e.g. in the pharmaceutical industry. Recently the concept of a chromatographic reactor was developed. In this reactor unit simultaneously with the chemical reaction a separation process based on different adsorption strength of the reactants occurs. In many cases ion exchange reactions like esterification and etherification are carried out in these chromatographic reactors. The ion exchange resin has to be capable both to catalyse the reaction and to separate the species of the reaction system. Now a days commercially available ion exchange resins are used.

A catalytic monolithic composite column based on poly(styrene-co-divinylbenzene) activated with
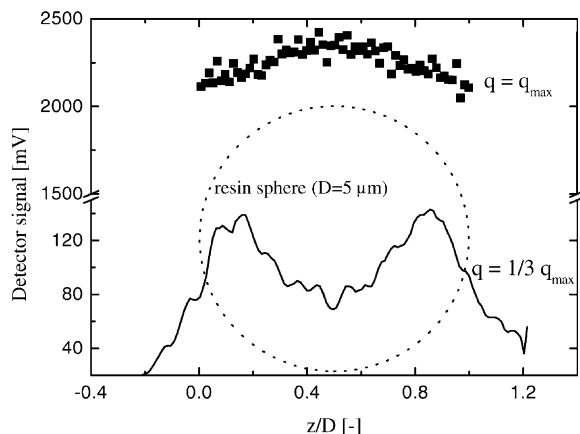

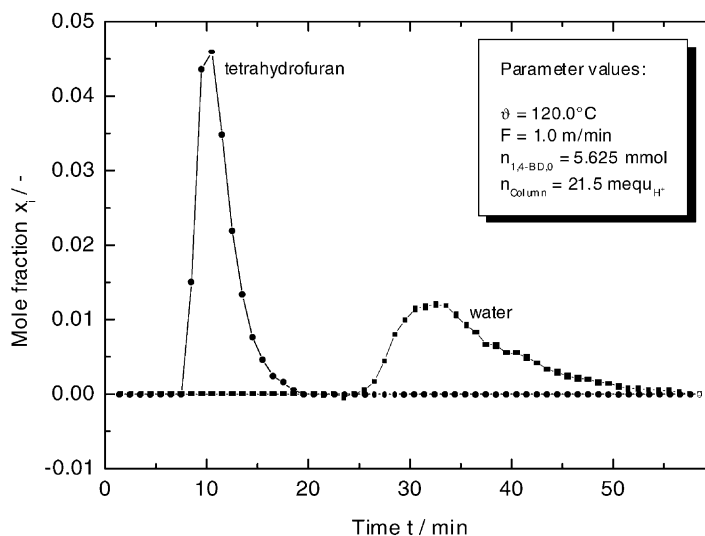Fig. 8. Sulphur distribution across the diameter of a single resin particle.

Fig. 9. Conversion of 1,4-butanediol with simultaneous separation of the products tetrahydrofuran and water on a monolithic column; column length: 180 mm; column ∅: 12 mm.

sulfonic acidic sites as described in Section 2 should also be capable for such a process. Experiments were carried out characterising the monolithic column as a medium for an acid ion exchange catalysed reaction with an integrated separation. As a model reaction the etherification of 1, 4-butanediol $\rightleftarrows$ tetrahydrofuran + water diluted in 1,4-dioxane was chosen. Investigations by Limbeck et al. [23] on the reaction mechanism and the reaction rate have shown that this reaction is inhibited by the by-product water:

$$r = \left(\frac{k}{1 + K_{H_2O}\sqrt{a_{H_2O}}} \right) \left(\frac{K_{BD}a_{BD}}{1 + K_{BD}a_{BD}} \right)$$

where r is the specific rate ($mol\,s^{-1}\,eq.^{-1}$), a_i the activity of component i, k the rate constant ($mol\,s^{-1}\,eq.^{-1}$), and K_i is the sorption constant of component i.

So, the reaction rate is decreasing continuously with an increasing amount of water in the reaction mixture.

For a first evaluation of the new composite materials monolithic rods were equipped with a pressure resistant casing. Standard HPLC connectors were attached. As a solvent dioxan was pumped through the monolithic column at a volumetric flow rate of $1\,ml\,min^{-1}$. As shown in Fig. 9, the reaction products can be separated in the monolithic chromatographic

reactor after a pulse injection of the reactant 1,4-butanediol. A mathematical model describing the chemical reaction with the integrated separation based on the above-mentioned kinetics, the different sorption strength of the species and considering special effects of the monolithic column was prepared by Altwicker [24].

5. Conclusions and outlook

Based on a precipitation polymerisation process inside the pore volume of megaporous carrier materials monolithic polymer/carrier components are available. The stability against swelling forces of the polymer particles is high because the precipitation polymerisation leads to particles with a gradual change of the cross-linker concentration across the particle diameter. This is supported by model calculations. The accessibility of the active sites is high due to the small particle size of the polymer phase and the forced convective flow through the monolith. The pressure drop of composite rods in flow-through applications is one order of magnitude lower than for commercial resins due to large pores between the interconnected polymer particles. These materials in the shape of the

newly developed monolithic column has a high commercial potential for a lot of applications. Provided by the opportunity of tailor-made polymeric resins, the enhanced mass transfer, short and uniform diffusion path length inside the polymeric particles and a low pressure drop this leads to monolithic columns for processes where these criteria are essential for a high and selective conversion, e.g. in reaction systems, in separation techniques or in a combination of both. The use of monolithic rods in the field of polymer assisted solution synthesis with the aim to prepare potential pharmaceuticals is a field of our current activities.

Acknowledgements

References

[1] H. Spes, German Patent 1 285 170, (1969).
[2] H. Spes, German Patent 1 300 233, (1970).
[3] H. Spes, Chemiker Zeitung 90 (1966) 443–446.
[4] D.N. Chaplits, V.P. Kazakov, E.G. Lazariants, V.F. Chebotaev, M.I. Balashov, L.A. Serafimov, US Patent 3 965 039, (1976).
[5] T. Yoshioka, Bull. Chem. Soc. Jpn. 56 (1983) 3726–3729.
[6] T. Yoshioka, Bull. Chem. Soc. Jpn. 58 (1985) 2618–2625.
[7] L.A. Smith, European Patent 0 466 954 A1, (1992).
[8] L.A. Smith, US Patent 4 250 052, (1981).
[9] K. Rock, L. Smith, J. Chen, AIChE Spring Meeting, New Orleans, LA, USA, 1992.
[10] J.P. Stringaro, European Patent 0 631 813 A1, (1993).
[11] D. Hearn, Int. Patent WO 94/00235, (1993).
[12] U. Kunz, U. Hoffmann, H. Bruderreck, K. Gottlieb, H.K. Schädlich, S. Becker, Int. Patent WO 94/08713, (1993).
[13] U. Kunz, Entwicklung neuartiger Polymer/Träger-Ionentauscher als Katalysatoren für chemische Reaktionen in Füllkörperkolonnen, Cutec-Schriftenreihe, Clausthal-Zellerfeld, 1998.
[14] U. Kunz, H. Künne, U. Hoffmann, Erdöl-Erdgas-Kohle 113 (1997) 35–37.
[15] N.B. Afeyan, N.F. Gordon, I. Mazsaroff, L. Varaday, S.P. Fulton, Y.B. Yang, F.E. Regnier, J. Chromatogr. 519 (1990) 1–29.
[16] D. Hudson, J. Combinatorial Chem.: Part I 1 (5) (1999) 333–360.
[17] D. Hudson, J. Combinatorial Chem.: Part II 1 (6) (1999) 403–457.
[18] J.F. Pfeiffer, J.C. Chen, J.T. Hsu, AIChE J. 42 (1996) 932–939.
[19] G. Schwachula, D. Lukas, J. Chromatogr. 102 (1974) 123–130.
[20] D.W. Agar, W. Ruppel, Chem.-Ing. Tech. 60 (1998) 731–741.
[21] K.R. Westerterp, Chem. Eng. Sci. 47 (1992) 2195–2206.
[22] M. Mazotti, B. Neri, D. Gelosa, A. Kruglov, M. Morbidelli, Ind. Chem. Res. 36 (1997) 3163–3172.
[23] U. Limbeck, C. Altwicker, U. Kunz, U. Hoffmann, Chem. Eng. Sci. 56 (2001) 2171–2178.
[24] C. Altwicker, Ph.D. thesis, Technische Universität Clausthal, Institut für Chemische Verfahrenstechnik, 2001.