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A novel strategy for heterogenisation of homogeneous and colloidal chiral catalysts and their application in enantioselective reactions

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Dedicated to Prof. Dr. B. Lücke on the occasion of his 65th birthday.

Abstract

For the heterogenisation of chiral catalysts, a novel method has been developed and applied to different enantioselective reactions. The new heterogenisation method is based on the three-dimensional entrapment of catalysts by electrostatic attraction between a polyelectrolyte and an oppositely charged catalyst. An easy preparation procedure, a simple separation and a good retention of the active metal in the polymeric material and a high long-term stability of the entrapped catalyst are the significant features of this new heterogenisation method. Applying these entrapped catalysts in the hydroformylation of vinyl acetate, an enantiomeric excess (ee) of 39% could be obtained with a rhodium diphosphine complex. The activities and selectivities in the hydrogenation of dimethyl itaconate have been found to be competitive with homogeneous catalysts. A change in the direction of enantioselectivity has been observed by using entrapped Ru catalysts in different solvents. For the entrapment of chirally stabilised Pt-colloids used in the enantioselective hydrogenation of ethyl pyruvate, different polyanions have been found to be suitable. A constant enantioselectivity and a good activity during 25 hydrogenation cycles were obtained employing alginate-entrapped Pt-colloids. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chiral catalysts; Diphosphines; Entrapment; Heterogenisation; Polyelectrolytes

1. Introduction

In the last 20 years, the production of enantiomerically pure compounds became more and more important in the field of pharmaceuticals, flavours, fragrances and agrochemical agents and several industrial processes using asymmetric stochiometric or catalytic reactions have been developed [1]. Most transition metal complexes with chiral ligands are employed in homogeneous catalysis [2]. The disadvantages of such homogeneous processes are the difficult separation and recycling of the expensive catalysts. Therefore, numerous methods have been introduced for the development of heterogeneous or heterogenised chiral catalysts [3–5]. For example, metals can be supported on chiral polymers [6–8]. Metals or metal oxides have been modified with chiral agents like tartaric acid or cinchona alkaloids [9–12]. Metal–ligand complexes can be immobilised by covalent [13–15] or coordinative linkage [16–18] or electrostatic attraction

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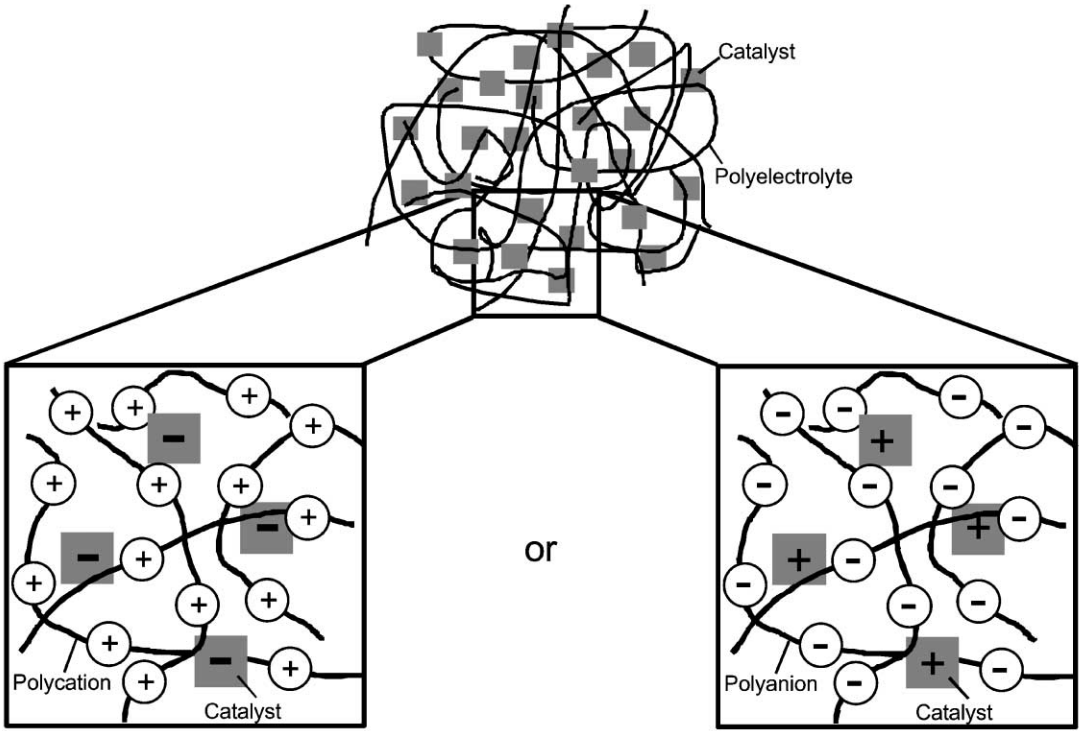

Fig. 1. Scheme of polyelectrolyte catalysts (left: negatively charged catalyst entrapped in a polycation network; right: positively charged catalyst entrapped in a polyanion network).

(e.g. on ion-exchange material) [19,20] via functionalised ligands or by adsorption on porous supports [21] to combine the good activities and selectivities of the homogeneous catalysts and the simplicity of recycling and recovery of the heterogeneous ones. Another method of heterogenisation is the inclusion of the metal complex in the pores of molecular sieves or sol–gel matrices [22–26]. Many of these heterogenised chiral catalysts suffer from the decrease or the complete disappearance of enantioselectivity. Other problems are the leaching of the active metal into the solvent and the insufficient stability of the catalyst.

To avoid these disadvantages, we developed a novel heterogenisation method for chiral catalysts. This new heterogenisation method is based on electrostatic attraction between a polyelectrolyte and an opposed charged catalyst, either a homogeneous catalyst with an ionic-functionalised ligand or a colloidal metal. The charged catalyst is entrapped in a three-dimensional matrix of a polyelectrolyte and held back in this polymer by electrostatic interactions (Fig. 1). The network of the polyelectrolyte and the catalyst is formed according to the ionotropic gelation of alginate by calcium ions [27,28]. An easy preparation procedure, a high long-term stability, a simple separation and a good retention of the active metal in the polymeric material are regarded as the advantages of the new polyelectrolyte catalysts used in different catalytic reactions.

2. Experimental

2.1. General heterogenisation procedure

A significant feature of the new heterogenisation method for chiral catalysts is the simple preparation procedure. For entrapment, a solution of the homogeneous or colloidal catalyst is mixed with an aqueous solution of a polyelectrolyte while stirring (Fig. 2). Using a syringe equipped with a capillary (approximately 1 mm in diameter), the resulting mixture is

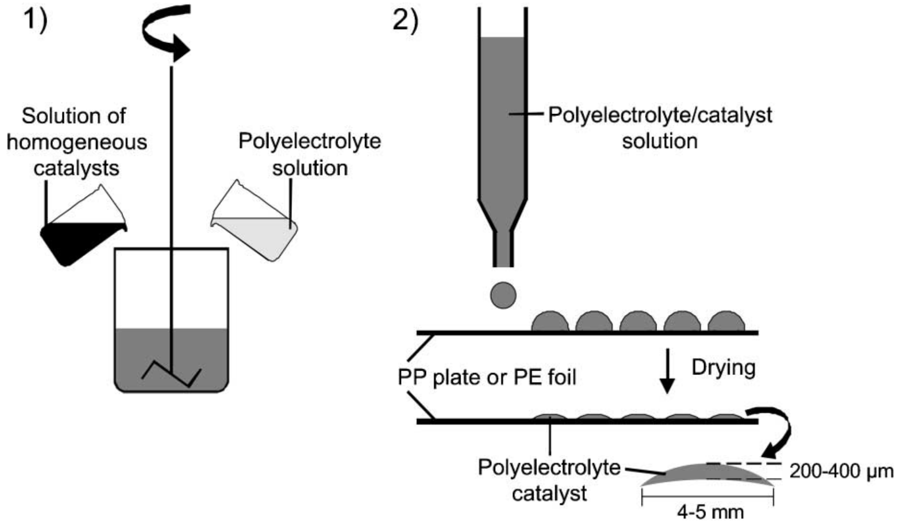

Fig. 2. Scheme of the novel heterogenisation procedure for homogeneous chiral catalysts, e.g. transition metal complexes or colloids: (1) mixing the solutions; (2) dropping the mixed solutions on a suitable surface.

dropped onto a suitable surface, e.g. a polypropylene (PP) plate or a polyethylene (PE) foil. Afterwards the droplets have to be dried by exposing the plate resp. foil to air or an argon atmosphere for at least 24 h. Very plain lens-shaped particles of about 4–5 mm in diameter were obtained. The catalyst is dispersed homogeneously inside the polyelectrolyte matrix. After complete drying the entrapped catalyst particles can easily be removed from the surface and be used in catalytic processes in organic solvents.

2.1.1. Heterogenisation of chiral homogeneous catalysts

All preparative and catalytic operations concerning diphosphine complexes were carried out using Schlenk techniques with argon as inert gas. The preparation of (*R*)-(+)-2,2′-bis(diphenylphosphino)-4,4′-bisphosphono-1,1′-binaphthyl (**1**) has been described elsewhere [29]. The compounds $[RuCl_2(p\text{-cymene})]_2$, PDADMAC I and II, P(ASA)DADMAC and PMVPB (Fig. 3) were used as purchased (Aldrich, Polysciences).

The compound $[Rh(OMe)(cod)]_2$ was prepared according to a literature procedure [30]. The polyelectrolyte catalysts containing rhodium and ruthenium diphosphine complexes were prepared as follows (Table 1).

2.1.1.1. Hydroformylation catalysts. The compound **1** (0.18 mmol) was dissolved in 2 ml EtOH and $[Rh(OMe)(cod)]_2$ (0.03 mmol) was dissolved in 4 ml EtOH. Thereafter, the solutions were merged

Table 1
Composition of the polyelectrolyte catalysts

Catalyst	Metal precursor	Compound **1**:metal	Spacer	Polymer
2	$[Rh(OMe)(cod)]_2$	3:1	Octyl-phosphonic acid, sodium salt	PDADMAC I
3	$[Rh(OMe)(cod)]_2$	3:1	Decyl-phosphonic acid, sodium salt	P(ASA)DADMAC
4	$[RuCl_2(p\text{-cymene})]_2$	1:1	Decyl-phosphonic acid, sodium salt	PDADMAC I
5	$[RuCl_2(p\text{-cymene})]_2$	1:1	Decyl-phosphonic acid, sodium salt	PDADMAC II
6	$[RuCl_2(p\text{-cymene})]_2$	1:1	Decyl-phosphonic acid, sodium salt	P(ASA)DADMAC
7	$[RuCl_2(p\text{-cymene})]_2$	1:1	Decyl-phosphonic acid, sodium salt	PMVPB

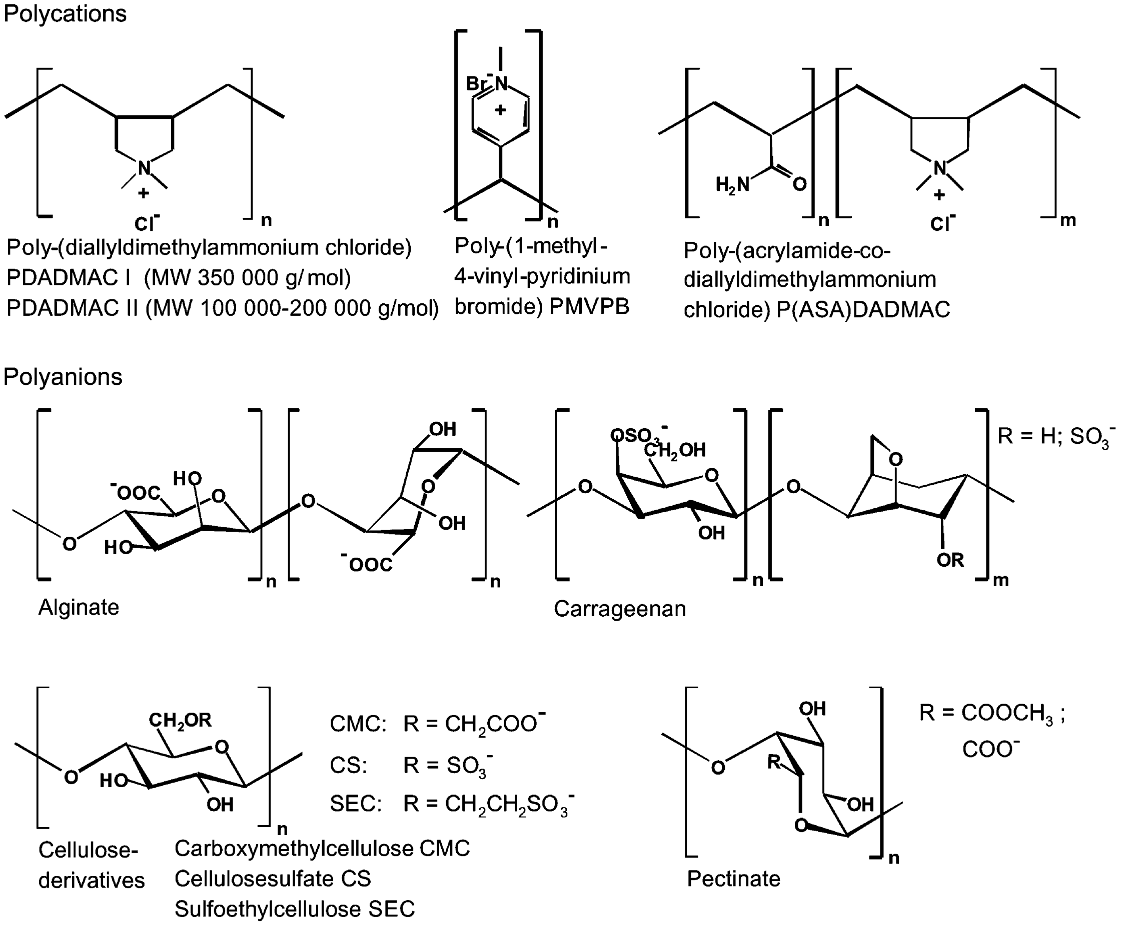

Fig. 3. Different polycations and polyanions used for the entrapment of chiral transition metal complexes and colloids.

and stirred for 1 h. Octyl-phosphonic acid or decyl-phosphonic acid (1.64 mmol) in 3 ml H_2O was added to 2 ml 2N NaOH (4 mmol). This solution was added to the solution of the rhodium complex. Then, the purchased aqueous solution of the polyelectrolyte (4 mmol) (PDADMAC I was dissolved in 2 ml H_2O) was added and the resulting mixture was stirred for one additional hour. Subsequently, the viscous solution was filled in into a syringe equipped with a 1/16 in. capillary made of stainless steel. Droplets with a diameter about 4–5 mm were formed by dropping the mixture on a PP plate. These droplets were dried in the argon atmosphere of a glove box for 24 h to form plain lens-shaped catalyst particles which can be used in the catalytic reaction (Fig. 4).

2.1.1.2. Hydrogenation catalysts. The entrapped catalysts were prepared similarly to the above mentioned procedure, using the following molar amounts of the components: **1** (0.12 mmol); $[RuCl_2(p\text{-cymene})]_2$ (0.06 mmol); decyl-phosphonic acid (1.26 mmol); 2N NaOH (3 mmol); polyelectrolyte (4 mmol).

2.1.2. Heterogenisation of chirally stabilised Pt-colloids

By reduction of an aqueous solution of $PtCl_4$ with formic acid in the presence of protonated 10,11-dihydrocinchonidine (DHCIN) chirally stabilised Pt-colloids can be prepared [31]. The positively charged alkaloid stabilises not only the Pt-particles in

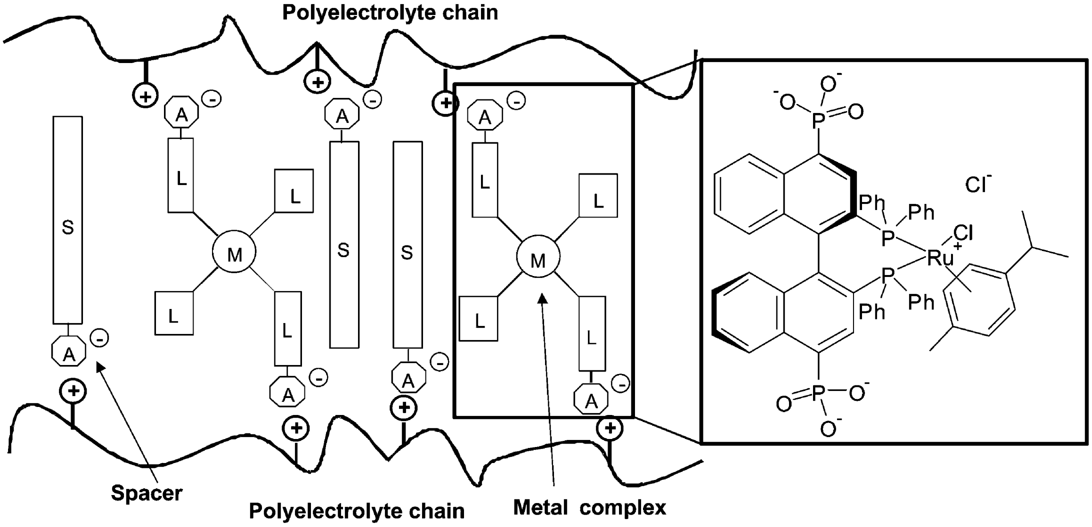

Fig. 4. Scheme of a polyelectrolyte-entrapped ruthenium complex.

solution, it also has an enantiodifferentiating effect in the hydrogenation of ethyl pyruvate [31]. For entrapment, 100 ml of an aqueous solution of the Pt-colloid (containing 125 mg Pt), prepared according to [31], were mixed with 42 ml of a 3 wt.% aqueous solution of sodium alginate (PROTANAL LF 20/60, Pronova Biopolymer, Norway) and dropped onto a PE foil by a syringe equipped with a 1 mm capillary. After drying for at least 24 h in air, very plain lens-shaped particles of 4–5 mm in diameter with a homogeneous distribution of the Pt-colloid inside the alginate matrix were obtained (Fig. 5). These particles can be used in

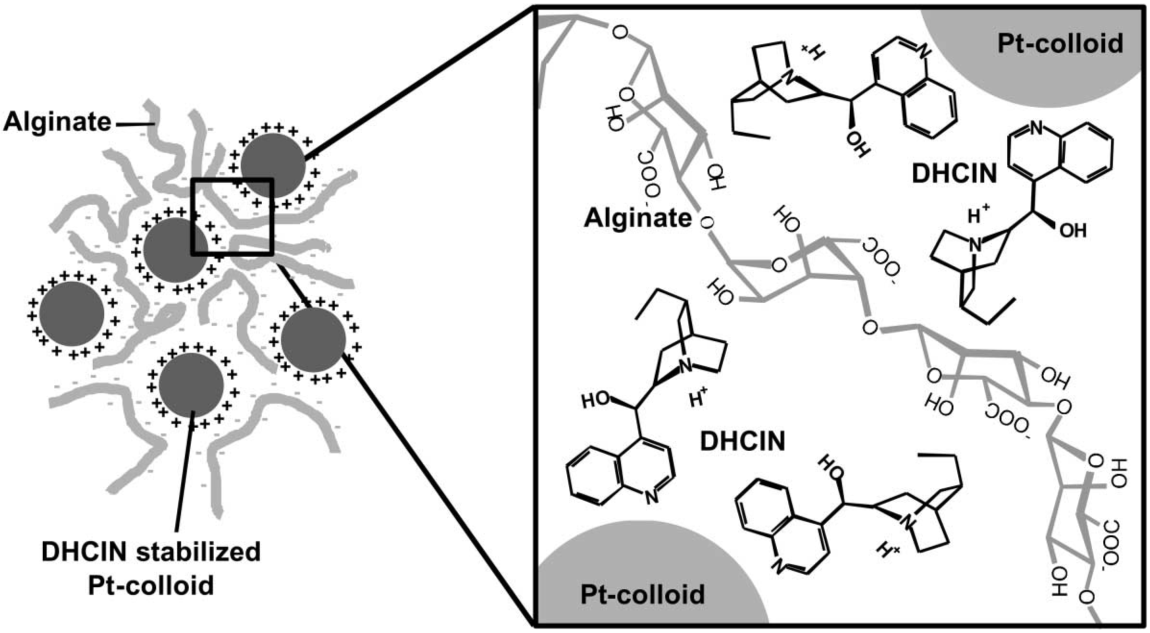

Fig. 5. Scheme of the alginate-entrapped Pt-colloid stabilised by DHCIN.

enantioselective hydrogenation of ethyl pyruvate in non-polar solvents like cyclohexene.

In addition to alginate other polyanions, such as pectinate (Pectin Classic AF 707, Herbstreith and Fox, Germany), carboxymethylcellulose (Blanose 7MXF, Hercules, Germany), carrageenan (GENUGEL X-0828, Copenhagen Pectin Factory, Denmark), cellulosesulphate (Kelco SCS-LV, Kelco, Norway), and sulphoethylcellulose (Wolff Walsrode, Germany) were used for the entrapment of the chirally stabilised Pt-colloid (Fig. 3). For this purpose, the amount of the Pt-colloid was kept constant. The amount of 3 wt.% aqueous solution of the polyelectrolyte was varied so that the molar ratio of Pt to DHCIN to one monosaccharide unit of the polyelectrolyte was always 1:2:10.

2.2. Catalytic and analytical procedures

2.2.1. Hydroformylation of styrene, vinyl acetate and hydrogenation of dimethyl itaconate

Synthesis gas ($CO:H_2 = 1:1$, 99.98%) and hydrogen (99.999%) were purchased from Messer Griesheim. Tetrahydrofuran, toluene and styrene were distilled in an argon stream before use. Vinyl acetate, dimethyl itaconate, ethanol, dichloromethane and water were deoxygenated by repeated evacuation and argon purging.

Using Schlenk techniques, a 100 ml stainless steel autoclave (Parr Instruments, Illinois) equipped with a magnetic stirrer was filled with the solid polyelectrolyte catalyst and the dissolved substrate. Then the autoclave was purged with synthesis gas or with hydrogen for three times and heated up to the desired temperature. Synthesis gas or hydrogen was added to adjust the reaction pressure. Samples were taken to follow the reaction using GC analysis (HP 5890, FID, helium as carrier gas). A $30\,\text{m} \times 0.25\,\text{mm} \times 0.25\,\mu\text{m}$ capillary with a β-cyclodextrine/DV-101 phase (BGB 174, Seitz) was used for the separation and quantitative analysis of the products. The autoclave was depressurised and opened cautiously after the end of the catalytic reaction. For the repeated use of the catalyst, the solvent with the product was carefully decanted from the catalyst that was located at the bottom of the autoclave. The catalyst was washed twice with 5 ml of the solvent and the autoclave was refilled with the substrate dissolved in 20 ml of the solvent. The next run of the catalytic reaction was carried out (Table 2).

2.2.2. Hydrogenation of ethyl pyruvate

Enantioselective hydrogenation of ethyl pyruvate was carried out in a 300 ml stirred laboratory autoclave (Parr Instruments, Illinois) at 20 °C and 60 bar H_2 pressure which was kept constant by a high pressure burette. In all cases, the entrapped Pt-colloid was filled in a catalyst basket and used in the hydrogenation of 10 ml ethyl pyruvate (Fluka, used as received) dissolved in 150 ml cyclohexene (Fluka, p.a. grade). The conversion of ethyl pyruvate was monitored by the pressure drop in the high pressure burette. Conversion and enantiomeric excess (ee) were determined by quantitative analysis without derivatisation by gas chromatography. The optical yield was expressed as the ee of (*R*)-ethyl lactate determined as

$$\text{ee}\,(\%) = 100 \times \frac{[\text{R}] - [\text{S}]}{[\text{R}] + [\text{S}]}$$

The detailed experimental procedure and the complete analytical conditions have been published previously [32].

For repeated use of the entrapped catalyst, the enantioselective hydrogenation of ethyl pyruvate was stopped after complete conversion and the H_2 pressure was released. Afterwards, a sample was taken to determine the conversion and the ee, and the reaction solution was discarded. The autoclave was

Table 2
Results of the hydroformylation of styrene and vinyl acetate

Catalyst	Substrate	Substrate: metal	Solvent	Time (h)	Temperature (°C)	Conversion (%)	$S_{\text{aldehydes}}$ (%)	*Iso*:*n*	ee (%)
2	Vinyl acetate	560:1	Toluene	16	60	1.4	87	5.7	39
3	Vinyl acetate	570:1	THF	48	60	5.3	94	0.12	19
2	Styrene	450:1	Toluene	20	70	3.2	100	4.9	1
3	Styrene	460:1	Toluene	48	60	6.2	95	3.9	2

refilled with 150 ml cyclohexene and 10 ml ethyl pyruvate. The next hydrogenation was started under identical reaction conditions. No fresh modifier was added to the reaction solution at any time. During the hole procedure no special care was taken that the catalyst was not exposed to air between the hydrogenations cycles.

3. Results and discussion

In contrast to immobilisation on ion-exchangers, the new entrapment concept is based on creating three-dimensional polymeric networks around the catalysts. This entrapment can be easily achieved by mixing solutions of the dissolved polymer and of the transition metal complex or the colloid, respectively. Accordingly, the polymeric network is formed in the presence of the catalytically active precursor compound in solution allowing an ideal wrapping of the polymeric matrix around the active catalyst and a homogeneous distribution of the catalyst inside the polymeric network. Owing to the flexible structure of partially swollen polyelectrolyte networks, conformational changes of the catalyst are assumed to be less restricted than on inorganic or organic polymeric supports, such as modified silica materials and hydrotalcites [33–35] or cationic or anionic ion-exchange resins [36–39] which have rigid pre-formed structures. After drying the retention of the catalyst in the three-dimensional matrix of the polyelectrolyte by electrostatic attraction is so strong that nearly no metal leaching is observed (in general less than 1%). A further advantage of the new catalysts is seen in the possibility to adjust the catalyst properties, such as a hydrophobic/hydrophilic balance, by addition of an excess of the ligand or a catalytically ineffective compound functionalised with ionic groups. Furthermore, these additives can serve as spacers to improve the mass transport inside the polymeric matrix. The metal–ligand complexes or spacers with more than one ionic group can be used to cross-link the polyelectrolyte chains.

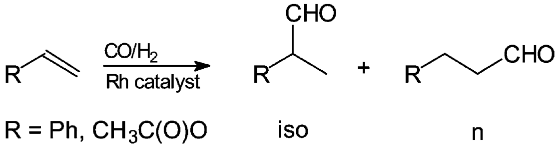

Fig. 6. Hydroformylation of styrene and vinyl acetate.

3.1. Heterogenisation of transition metal complexes

Rhodium and ruthenium complexes of the phosphorylated BINAP ligand **1** [40] were used as chiral model transition metal complexes. These were entrapped in polyelectrolytes and tested in the asymmetric hydroformylation of vinyl acetate and styrene and in the asymmetric hydrogenation of dimethyl itaconate (Figs. 6 and 7).

In the hydroformylation, high aldehyde selectivities have been found but the conversions were low, probably due to the slow mass transfer inside in the polymeric matrix. A remarkably high ee of 39% was observed in the hydroformylation of vinyl acetate using toluene as the solvent. Thus, the enantioselectivity of the entrapped chiral Rh catalyst exhibited the same enantioselectivity as observed in aqueous biphasic hydroformylation [40] and is in the same order as obtained with homogeneous Rh-BINAP catalysts (45–60% ee) [41]. As far as we know, this is the highest ee-value observed in enantioselective hydroformylation using immobilised rhodium diphosphine catalysts [5]. Compared to vinyl acetate, the enantioselectivity in the hydroformylation of styrene was rather low. As established in our recent investigations, the different behaviour of both substrates can be explained with their different polarities. A dipolar substrate like vinyl acetate is able to interact with both the polar phosphonate group and the polar polyelectrolyte leading to the preference of one of the diastereomeric transition

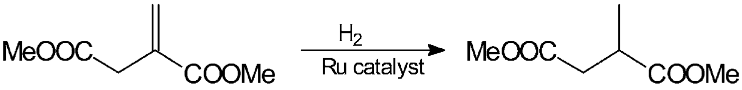

Fig. 7. Hydrogenation of dimethyl itaconate.

states. However, similar interactions are not likely for the non-polar styrene which would explain the low enantioselectivity.

Recently, a polyelectrolyte-based hydroformylation catalyst was reported by Mecking [42]. The immobilisation of Rh–NaTPPTS complexes succeeded on the surface of pre-formed polyelectrolyte-coated latex particles. These charged particles have a rigid lattice structure similar to ion-exchangers. The catalysts showed in the hydroformylation of methyl acrylate a steady activity of ca. 30 turnovers/h and could be removed from the reaction mixture by ultracentrifugation.

The hydrogenation of dimethyl itaconate was carried out with catalysts made of different polyelectrolytes and in solvents of different polarity. Ethanol has been found to be the most suitable solvent to obtain high activities and selectivities (Table 3, entry 1, 2, 4). It has been shown that alcohols are favourable solvents in many hydrogenations but less polar solvents like acetone are also suitable [43]. Comparing the polyelectrolytes, we obtained the highest values in conversion and selectivities after 2 h with PDADMAC I (Table 3, entry 1, 5, 9, 13; Fig. 8).

The best enantioselectivities of different polyelectrolyte catalysts ranged from ee-values of 80–89% (Fig. 9) are only slightly lower than the 91% ee obtained with a homogeneous Ru-BINAP catalyst. One reason for these good selectivities may be that the polyelectrolyte catalyst was partially dissolved (**4**) or swollen up strongly (**6**, **7**) in ethanol. In the first case, the solid catalyst was recycled completely after the reaction by precipitating with acetone.

A strong influence of the solvent and a low influence of the polyelectrolyte on the enantioselectivity was observed (Fig. 9). Surprisingly, the change from a non-polar solvent like toluene to a polar solvent like ethanol resulted in the reversal direction of the configuration. While with **4** in ethanol, the *S* enantiomer could be obtained in 89% ee in toluene the *R* enantiomer was formed in 19% ee with the polyelectrolyte catalyst **5**. Catalysts **4** and **5** only differ in the chain length of the ionic polymer. Obviously, the changes of the solvent causes the reversal of the absolute product configuration for identical or slightly differing polyelectrolyte catalysts which contained the same chiral Ru complex in all cases. Normally, to induce an opposite configuration, the other enantiomer of the chiral ligand or of an auxilliary has to be employed. To the best of our knowledge, reports on such dramatic changes of enantioselectivity caused by changes in the achiral environment have been published very scarcely. A significant effect of the solvent polarity or of the support on the enantioselectivity has

Table 3
Results of the hydrogenation of dimethyl itaconate[a]

Entry	Catalyst	$n_{\text{substrate}}/n_{\text{metal}}$	Solvent	Conversion (%)	$S_{\text{2-methyl-succinate}}$ (%)	ee (%)	TON
1	**4**	48[b]	Ethanol	100	86	89 (*S*)	48
2	**5**	144	Ethanol	93	33	11 (*S*)	133
3	**6**	166	Ethanol	88	97	52 (*S*)	147
4	**7**	150	Ethanol	100	98	83 (*S*)	150
5	**4**	126	CH_2Cl_2	52	92	50 (*S*)	65
6	**5**	145	CH_2Cl_2	98[c]	84	2 (*R*)	142
7	**6**	167	CH_2Cl_2	19	70	11 (*S*)	31
8	**7**	151	CH_2Cl_2	68	99	2 (*R*)	103
9	**4**	126	THF	71	91	54 (*S*)	90
10	**5**	144	THF	45	70	4 (*R*)	65
11	**6**	166	THF	31	14	26 (*S*)	52
12	**7**	150	THF	47	98	6 (*S*)	71
13	**4**	128	Toluene	14	74	41 (*S*)	19
14	**5**	144	Toluene	84	77	19 (*R*)	121
15	**6**	166	Toluene	30	87	8 (*S*)	50
16	**7**	151	Toluene	39	60	3 (*R*)	59

[a] 200 mg polyelectrolyte catalyst; 10 ml solvent; 20 bar; 60 °C; 2 h.

[b] 310 mg polyelectrolyte catalyst.

[c] Sampling after 6 h.

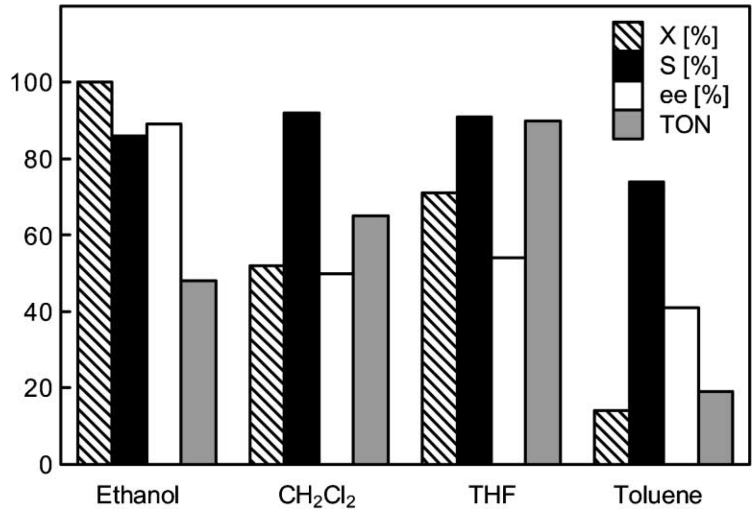

Fig. 8. Conversion, selectivity, ee and TON of the hydrogenation of dimethyl itaconate with **4** in different solvents.

been found for enzyme-catalysed reactions [44–46]. Cossu et al. [47] induced a complete change in the stereoselectivity of the products when they used either sodium or lithium bases in the desymmetrisation reaction of bis(phenylsulphonyl)alkenes. Iggo and co-workers [48] described a change in enantioselectivity when they used different solvents and supports in the Pd-catalysed hydrogenation of ethyl pyruvate.

Several investigations were carried out concerning the recycling and reuse of the polyelectrolyte catalysts

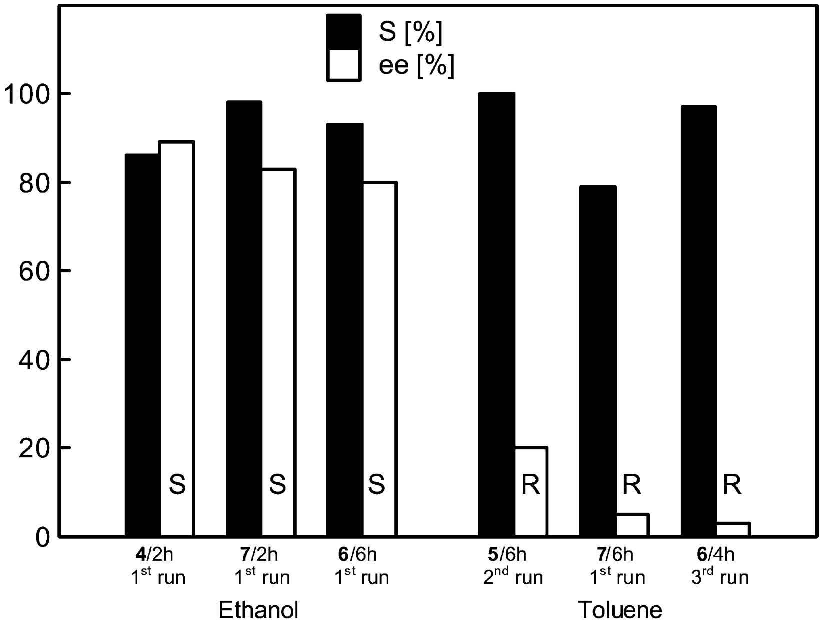

Fig. 9. Highest ee of (*S*)- and (*R*)-dimethyl 2-methylsuccinate of different polyelectrolyte catalysts used in ethanol and toluene.

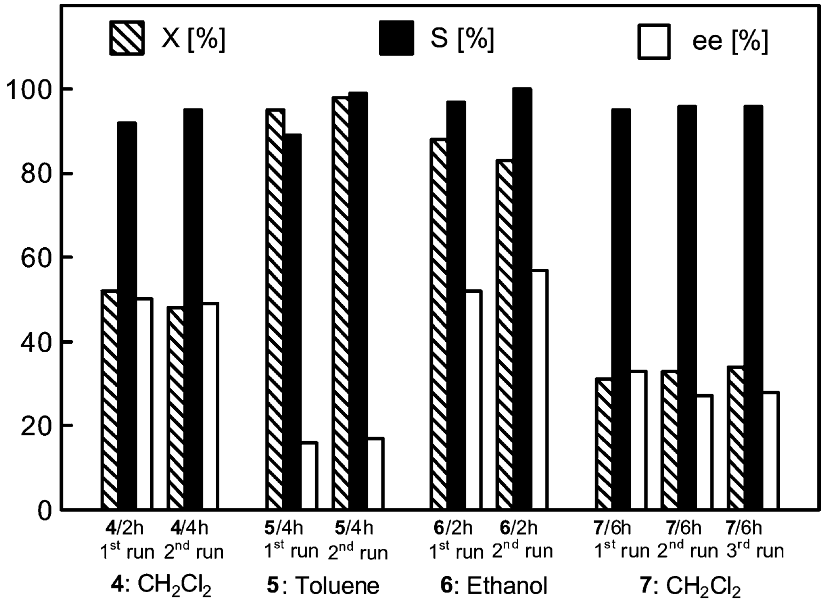

Fig. 10. Conversion, selectivity and ee of different polyelectrolyte catalysts used repeatedly in the hydrogenation of dimethyl itaconate in different solvents.

(Fig. 10). After two or three repetitions of the hydrogenation, no or only a negligible decrease in chemo- and enantioselectivity was observed.

The metal leaching of the catalysts during the reactions was very low and in many cases below the detection level of the AAS method (Ru and Pt: 0.001 mg/l; Rh: 0.005 mg/l).

Recently, the asymmetric hydrogenation of dimethyl itaconate using different types of heterogenised Ru-BINAP catalysts has been reported by other groups. Tas et al. [49] immobilised sulphonated Ru–BINAP complexes in layered double hydroxides by anion exchange and obtained moderate ee of 48 and 11% and TOFs of 27 and 25 h^{-1}, respectively. Lemaire and co-workers [50] integrated the BINAP ligand into a polymeric chain by condensing the bis-aminomethylated derivative with 2,6-diisocyanatotoluene. The Ru complex formed by addition of a Ru precursor to this polymeric ligand reduced dimethyl itaconate to 2-methyl succinate in 94% ee and 100% conversion.

3.2. Heterogenisation of colloids

The novel heterogenisation method of catalysts in polyelectrolyte complexes via electrostatic interaction was also applied to chirally stabilised colloids. Therefore, the platinum sol stabilised by the alkaloid DHCIN [31] was used as chiral model colloid in the enantioselective hydrogenation of ethyl pyruvate (Fig. 11).

Primarily, different polyanions functionalised by carboxy-groups or sulphate-groups, respectively (Fig. 3), were tested if they would be suitable for

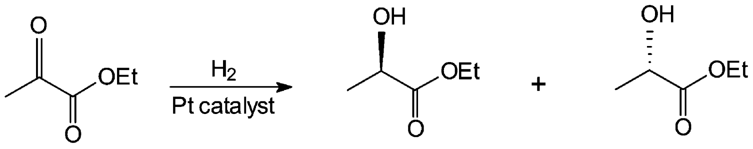

Fig. 11. Enantioselective hydrogenation of ethyl pyruvate.

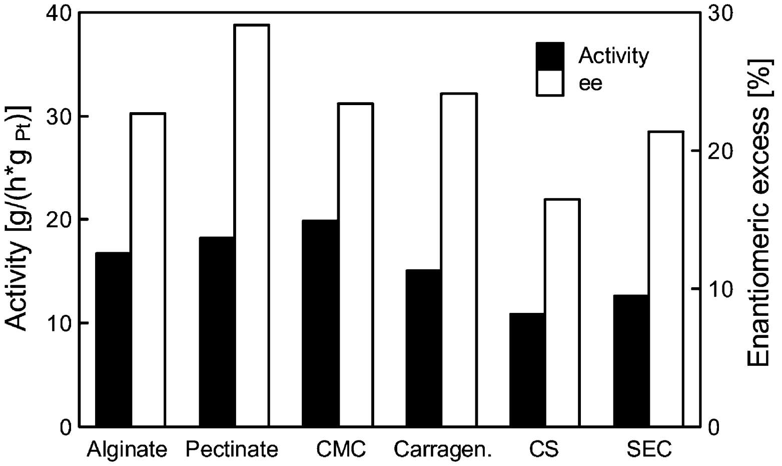

Fig. 12. Activity and ee of the chirally stabilised Pt-colloid entrapped in different polyanions used in the enantioselective hydrogenation of ethyl pyruvate in cyclohexene.

entrapment of chirally stabilised colloids. Each of these polyanions could be used to form the polyelectrolyte catalysts. The entrapped catalysts were still active in the hydrogenation of ethyl pyruvate using cyclohexene as solvent. The type of polyanion used for the entrapped has no significant influence on the enantioselectivity (Fig. 12). The pectinate-entrapped Pt-colloid has reached the best enantioselectivity. The catalysts entrapped in polyanions functionalised by carboxy-groups have been found to be slightly more active than the sulphate-functionalised ones. After complete drying, no Pt-colloid could be found in the reaction solution if the catalyst is used in non-polar solvents like cyclohexene or toluene. In ethanol and acetic acid, the polyelectrolyte catalyst was resolved and a low Pt-leaching was observed.

For technical application, a high long-term stability of the catalyst is essential. However, reuse of the chirally modified platinum catalyst used in the enantioselective hydrogenation of ethyl pyruvate is up to now only possible by addition of fresh modifier at the beginning of each new hydrogenation cycle [51,52] or by feeding cinchonidine permanently in continuous use [53] to maintain the enantioselectivity of the catalyst. The loss in enantioselectivity is caused by the partial hydrogenation of the quinoline ring system of cinchonidine [32] and the washing out of the modifier from the Pt surface by the flowing fluid in continuous use, respectively. Using the chiral modifier as stabiliser of the Pt-colloid, the washing out of the modifer from the Pt surface is prevented [31]. However, the retention of the quasi-homogeneous catalyst has remained problematic. By entrapment in polyelectrolytes, the Pt-colloid is held back in the polymeric material and therefore is easy to separate from the reaction solution. The alginate-entrapped Pt-colloid stabilised by DHCIN was used repeatedly for the enantioselective hydrogenation of ethyl pyruvate in cyclohexene. Even without adding fresh modifier at the beginning of each new hydrogenation cycle, the entrapped catalyst shows a very high long-term stability (Fig. 13). During the first 13 runs, the activity of the catalyst increases, then it remains nearly constant at 60–70 g/(h g_{Pt}). The increase in activity is probably due to the activation of the Pt-particles since the colloid was exposed to air during the heterogenisation procedure. It has been shown previously that pretreatment of conventional Pt-Al_2O_3 catalysts with hydrogen at 400 °C improves the performance of the catalysts [54]. However, a thermal activation before using the catalyst in the enantioselectivie hydrogenation of ethyl pyruvate was not possible in the case of the entrapped catalyst system. The ee remains constant during more than 25 runs even though contact to air during each hydrogenation cycle could not be excluded. Probably, the polymeric matrix prevents an oxidation of the entrapped platinum particles. Only after the first hydrogenation cycle, a small amount of Pt-colloid was found in the reaction solution

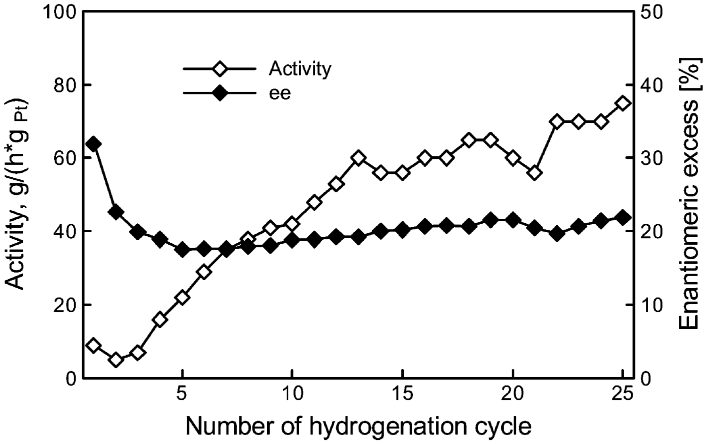

Fig. 13. Activity and ee of the alginate-entrapped Pt-colloid stabilised by DHCIN used repeatedly in the enantioselective hydrogenation of ethyl pyruvate in cyclohexene.

probably because of incomplete drying. In all further runs, no leaching of the active metal was observed.

4. Conclusions

A novel concept of heterogenisation of chiral catalysts has been developed and applied to different enantioselective reactions. This new heterogenisation method is based on the entrapment of the catalysts in a three-dimensional network of a polyelectrolyte by electrostatic attraction between the polyelectrolyte and the oppositely charged catalyst. The significant features of this new immobilisation method are the easy preparation procedure, the simple separation and good retention of the active metal in the polymeric material and the high long-term stability of the polyelectrolyte catalyst. These entrapped catalysts have been applied in enantioselective reactions. In the hydroformylation of vinyl acetate an ee of 39% could be obtained with a heterogenised rhodium diphosphine catalyst. The activities and selectivities of some of these new polyelectrolyte catalysts in the hydrogenation of dimethyl itaconate have been found to be competitive with homogeneous catalysts. A strong influence of the solvent leading to a change in the direction of enantioselectivity has been observed with entrapped Ru catalysts. The new heterogenisation concept was also applied to chirally stabilised colloidal catalysts used in the enantioselective hydrogenation of ethyl pyruvate. Different polyanions have been found to be suitable for immobilisation. By entrapment of the Pt-colloid in alginate, a constant enantioselectivity and a good activity during 25 hydrogenation cycles were obtained.

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References

[1] R.A. Sheldon, Chirotechnology, Marcel Dekker, New York, 1993.
[2] M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, Wiley, New York, 1998.
[3] A. Baiker, Curr. Opin. Solid State Mater. Sci. 3 (1998) 86.
[4] H.U. Blaser, Tetrahedron: Asymm. 2 (1991) 843.
[5] D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs (Eds.), Chiral Catalyst Immobilization and Recycling, Wiley, New York, 2000.
[6] S. Akabori, S. Sakurai, Y. Izumi, Y. Fuji, Nature 178 (1956) 233.
[7] K. Harada, T. Yoshida, Naturwiss 57 (1970) 131 306.
[8] C.F. McFadden, P.S. Cremer, A.J. Gellman, Langmuir 12 (1996) 2483.
[9] A. Tai, T. Harada, Tailored Metal Catalysts, Reidel, Dordrecht, 1986.

[10] T. Osawa, T. Harada, A. Tai, Catal. Today 37 (1997) 465.
[11] A. Baiker, J. Mol. Catal. A: Chem. 115 (1997) 473.
[12] H.U. Blaser, H.P. Jalett, M. Müller, M. Studer, Catal. Today 37 (1997) 441.
[13] C. Saluzzo, R. Ter Halle, F. Touchard, F. Fache, E. Schulz, M. Lemaire, J. Organomet. Chem. 603 (2000) 30.
[14] D. Brunel, Micropor. Mesopor. Mater. 27 (1999) 329.
[15] A. Heckel, D. Seebach, Angew. Chem. 112 (2000) 165.
[16] E.N. Prabhakaran, J.P. Nandy, S. Shukla, J. Iqbal, Tetrahedron Lett. 42 (2001) 333.
[17] T. Punniyamurthy, J. Iqbal, Tetrahedron Lett. 38 (1997) 4463.
[18] A. De, P. Basak, J. Iqbal, Tetrahedron Lett. 38 (1997) 8383.
[19] R. Selke, M. Capka, J. Mol. Catal A: Chem. 63 (1990) 319.
[20] D. Tas, D. Jeanmart, R.F. Parton, P.A. Jacobs, Stud. Surf. Sci. Catal. 108 (1997) 493.
[21] W. Van Brussels, M. Renard, D. Tas, R. Parton, P.A. Jacobs, V.H. Rane, US Patent 5,997,840 (7 December 1999).
[22] F. Gelman, D. Avnir, H. Schumann, J. Blum, J. Mol. Catal. A: Chem. 146 (1999) 123.
[23] H. Kosslick, H. Landmesser, E. Höft, R. Fricke, L. Frunza, J. Mol. Catal. A: Chem. 123 (1997) 179.
[24] A. Corma, M. Iglesias, C. del Pino, F. Sanchez, J. Chem. Soc., Chem. Commun. 1253 (1991).
[25] M.E. Davies, Acc. Chem. Res. 26 (1993) 111.
[26] C. Schuster, W.F. Hölderich, Catal. Today 60 (2000) 193.
[27] J. Klein, K.-D. Vorlop, in: M. Moo-Young (Ed.), Comprehensive Biotechnology, Vol. 2, Pergamon Press, Oxford, 1985, p. 203.
[28] V. Smidsrod, G. Skjåk-Bræk, Trends Biotechnol. 8 (1990) 71–78.
[29] M. Kant, S. Bischoff, R. Siefken, E. Gründemann, A. Köckritz, Eur. J. Org. Chem. 477 (2001) 477.
[30] R. Usòn, L.A. Oro, J. Cabeza, Inorg. Synth. 23 (1985) 126.
[31] H. Bönnemann, G.A. Braun, Angew. Chem. Int. Ed. Engl. 35 (1996) 1992.
[32] V. Morawsky, U. Prüße, L. Witte, K.-D. Vorlop, Catal. Commun. 1 (2000) 15.
[33] V. Rives, M.A. Ulibarri, Coord. Chem. Rev. 181 (1999) 61.
[34] E. Lindner, T. Schneller, F. Auer, H.A. Mayer, Angew. Chem. 111 (1999) 2289.
[35] A.J. Sandee, L.A. van der Veen, J.N.H. Reek, P.C.J. Kamer, M. Lutz, A.L. Spek, P.W.N.M. van Leeuwen, Angew. Chem. 111 (1999) 3428.
[36] A.J. Seen, K.J. Cavell, A.W.-H. Mau, A.M. Hodges, J. Membr. Sci. 87 (1994) 149.
[37] R.T. Smith, R.K. Ungar, L.J. Sanderson, M.C. Baird, Organometallics 2 (1983) 1138.
[38] A. Iwado, M. Mifune, R. Harada, H. Akizawa, N. Motohashi, Y. Saito, Inorg. Chim. Acta 283 (1998) 44.
[39] C. Palazzi, F. Pinna, G. Strukul, J. Mol. Catal. A: Chem. 151 (2000) 245.
[40] A. Köckritz, S. Bischoff, M. Kant, R. Siefken, J. Mol. Catal. A: Chem. 174 (2001) 119.
[41] D. Hoegaerts, P.A. Jacobs, Tetrahedron: Asymm. 10 (1999) 3039.
[42] S. Mecking, R. Thomann, Adv. Mater. 12 (2000) 953.
[43] J.A. Wiles, S.H. Bergens, Organometallics 17 (1998) 2228.
[44] G. Fernandez-Lorente, R. Fernandez-Lafuente, J.M. Palomo, C. Mateo, A. Bastida, J. Coca, T. Haramboure, O. Hernandez-Justiz, M. Terreni, J.M. Guisan, J. Mol. Catal. B: Enzym. 11 (2001) 649.
[45] B. Herradon, S. Valverde, Tetrahedron: Asymm. 5 (1994) 1479.
[46] F. Secundo, S. Riva, G. Carrea, Tetrahedron: Asymm. 3 (1992) 267.
[47] S. Cossu, O. De Lucchi, P. Peluso, R. Volpicelli, Tetrahedron Lett. 41 (2000) 7263.
[48] P.J. Collier, T.J. Hall, J.A. Iggo, P. Johnston, J.A. Slipszenko, P.B. Wells, R. Whyman, Chem. Commun. (1998) 1451.
[49] D. Tas, D. Jeanmart, R.F. Parton, P.A. Jacobs, Stud. Surf. Sci. Catal. 108 (1997) 493.
[50] R. ter Halle, E. Schulz, M. Spagnol, M. Lemaire, Tetrahedron Lett. 41 (2000) 3323.
[51] J.T. Wehrli, A. Baiker, D.M. Monti, H.U. Blaser, H.P. Jalett, J. Mol. Catal. 57 (1989) 245.
[52] U. Böhmer, F. Franke, K. Morgenschweis, T. Bieber, W. Reschetilowski, Catal. Today 167 (2000) 167.
[53] N. Künzle, R. Hess, T. Mallat, A. Baiker, J. Catal. 186 (1999) 239.
[54] H.U. Blaser, H.P. Jalett, D.M. Monti, J.T. Wehrli, Appl. Catal. 52 (1989) 19.