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Aspects of Immobilisation of Catalysts on Polymeric Supports

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Abstract: In this review the authors intend to make a tutorial review on catalyst immobilisation from the viewpoint of the catalyst designer, emphasizing the use of promising concepts in this area, rather than trying to be exhaustive. The following topics are covered:

Keywords: immobilisation; membranes; polymers; supported catalysts

1 Introduction

The traditional comparison between homogeneous and heterogeneous catalysis[1] attributes to each of the catalytic procedures typical advantages and disadvantages that are at the basis for the numerous literature attempts to immobilise homogeneous catalysts. Whereas homogeneous catalysts usually are well-defined at the molecular level, they often show a pronounced sensitivity in synthesis and handling, as is evident from the available literature procedures. On the other hand, heterogeneous catalysts often allow easy separation and recovery from the reaction medium, and show repeated recycling potential, good stability and easy handling. In contrast to homogeneous catalysts, they often lack good characterisation at the molecular level, show high complexity as far as preparation procedures are concerned and consequently are not always easy to reproduce. Moreover, the presence of the active site in a (micro)porous environment often causes diffusion control of the catalysed reaction and reduced activity as well as selectivity.

Immobilised heterogeneous catalysts should exhibit all mentioned advantages of both homogeneous and heterogeneous catalysts,[2] such as simple and efficient preparation, general applicability and generic character of the procedures, comparable performance to that of the free catalyst, and sufficient chemical and thermal stability of the support. When used in batch operation, leaching of catalyst elements into the reaction medium should be minimal, while its separation from the products should be possible with simple techniques such as filtration. Finally, reuse without activity and selectivity loss should be possible as well. In continuous flow operation with a fixed bed of immobilised catalyst, stability in time of both activity and selectivity is a prerequisite. Present-day require-

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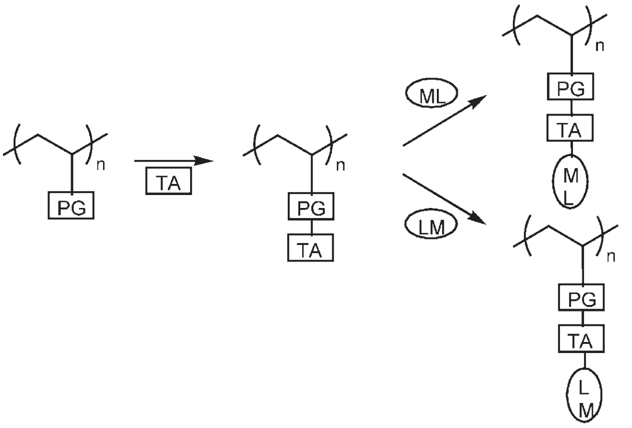
ments imply that such catalyst preparation and operation should be designed to cope with the concept of sustainability and in an industrial environment to show minimal energy consumption.[3]

The numerous attempts combining the best properties of homogeneous and heterogeneous catalysts are using either polymeric or porous inorganic solids as catalyst support, *viz.* (cross-linked)polystyrene and silica, respectively. Traditionally, both approaches originate from discrete research communities that always have felt the need to interact more closely.[4] Therefore, the present review aims at bridging further the gap between both communities, and at providing selected coverage on key advances and on specific topics in the field rather than presenting a fully comprehensive review. The style of the review is of a tutorial nature, the young scientist being encouraged to consult the specific sources for detailed information. Bridging the gap among the various disciplines concerned with catalyst preparation not only requires interaction among the research communities dealing typically with homogeneous and heterogeneous catalysis, but with bio-catalysis as well. Growing awareness in the literature exists not only on the potential of Nature’s catalysts that are hyperselective and show extremely high turnover numbers, but also on their limited range of operational conditions and the susceptibility of their cellular machinery to degradation, only regenerable *via* bio-synthetic paths.[5] For the catalysis research community it should therefore remain an irresistible challenge to do better than Nature and attempt the design of materials with the properties of “immortal” bio-catalysts that are applicable in a broad range of conditions, that do not deactivate and are recoverable with 100% efficiency.

The approach to the subject will be that of a catalyst designer and a catalytic chemist trying to present a concise picture of the intervening disciplines, rather than advancing viewpoints specifically for or from organic and/or polymer chemists.

2 Classic Ways of Immobilisation of Homogeneous Catalysts

A straightforward strategy to combine the best properties of homogeneous and heterogeneous catalysts, allowing efficient catalyst from product mixture separation, is to immobilise irreversibly the suitably ligated transition metal on a polymeric or siliceous support using a tethering agent (Scheme 1).[1,6,7]



Scheme 1. Immobilisation of a (ligated) metal ((L)M) *via* covalent binding of a tethering agent (TA) with the pending group (PG) of a polymer (adapted from ref.[1]).

The versatility of functional groups for reaction with tethering groups on siliceous materials (surface silanols) is distinctly lower than that on the polymeric supports. With the advent of hierarchically ordered silica materials, however, such supports show a wide variety in porosity.[8] Whereas the use of non-cross-linked polymers yields catalysts with good mass transfer properties, separation by (nano- or ultra-)filtration or precipitation is often not straightforward.[9] Next to the nature of the support, its degree of loading, and the nature of the solvent used, the length and flexibility of the spacer require fine tuning to reach optimal catalytic behaviour.[10]

Polystyrene cross-linked for a few percent with 1,4-divinylbenzene, although readily filtered, should be used in swellable solvents, the nature of which is determining diffusion behaviour. On the other hand, highly cross-linked polystyrene or polyacrylate as well as inorganic supports like silica, show permanent and fixed porosity and can be used in presence of a large variety of solvents.[9] Immobilisation of charged complexes *via* electrostatic interactions with a charged support often has been applied. As an example, cationic Rh-diphosphine cationic complexes are retained on anionic resins *via* ion-pair formation, yielding recyclable catalysts devoid of metal leaching.[11] Although all inorganic or organic supports with ion exchange properties can be used, such as anion and cation exchange resins, clays, and zeolites, the retention of such complexes is governed by mere ion-exchange equilibria between the complex and the support. Multivalent metal complexes show good retention, provided that the active form of the complex does not undergo reduction. Heterogenisation *via* complex entrapment is a typical method that occurs with zeolite supports. The term “ship-in-bottle” catalysis has been coined for this method. The strategy consists in the *in situ* synthesis of the transition metal complex in support cages, assuring retention for steric reasons.[12] Alternatively, functionalised ligands can be prepared that are soluble in the reaction medium but allow the catalyst complexes to be separated from the reaction medium by extraction, filtration or precipitation after temperature or pH change.[13–15] In a second approach, the functionalised complexes allow one to perform the reactions in two-phase conditions.[16] This development found industrial applications in the case of olefin hydroformylation.[17] In this biphase technique the homogeneous catalyst is dissolved in water, acting as the “mobile support”. Simple decantation allowing phase separation, results in the separation of the catalyst present in the aqueous phase from the organic phase containing the products. This approach yields an immobilised catalyst, which is not anchored chemically to any support.

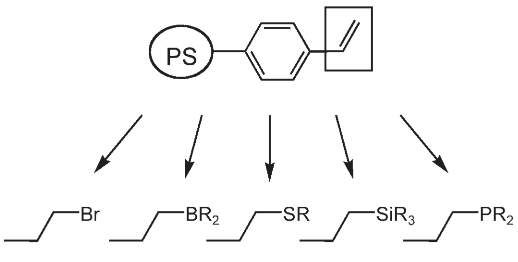
3 General Remarks on Catalyst Heterogenisation on Polymeric Supports

3.1 Polymeric Supports

Inspiration on the functionalisation of polymeric supports and tethering potential of linking agents to these supports can be found in the literature on polymer-supported reagents.[18] Functionalised polystyrenes present as linear or cross-linked polymers are very often used as catalyst or reactant support.[19] They are (commercially) available in different bead sizes (50–500 μm) and degrees of functionalisation and cross-linking. Suspension polymerisation with the organic phase consisting of monomer (and co-monomer), radical initiator, cross-linking agent dispersed in an aqueous phase, yields either microporous or macroporous polystyrene. Only sufficient amounts of cross-linker, *viz.* divinylbenzene, will yield insoluble supports.[20] At first sight issues here are the homogeneous distribution across the polymer bead and easy accessibility of the catalytic sites, mainly when they are located in domains with a high degree of cross-linking. Experimental evidence is present, however, indicating that a homogeneous distribution of the catalytic sites is mostly not a problem.[21]

Macroporous polystyrene beads with a typical degree of cross-linking between 20 and 25%, show permanent porosity, even in the dry state.[22,23] The actual pore structure during suspension polymerisation is generated with the help of a porogen agent, i.e., a low boiling solvent molecule which is removed after completion of the polymerisation reaction. Suitable monomers are styrene, vinylpyridine, acrylamide, and glycidyl methacrylate. In such beads highly cross-linked, non-porous regions responsible for the bead rigidity, separate porous domains with specific surface areas varying between 100 and $1000\,\mathrm{m^2\,g^{-1}}$. These supports have loading capacities ($2–4\,\mathrm{mmol\,g^{-1}}$) comparable to those of zeolites and of mesostructured silicas, are resistant towards osmotic shocks when added to reaction mixtures, but tend to be brittle.[24,25] These polystyrenes received renewed interest through post-grafting on residual vinyl functions.[18] As a result of the high contents of cross-linking agent used, residual vinyl groups can be used for further grafting (Scheme 2).

Microporous beads are obtained when the suspension polymerisation occurs in the absence of a porogen agent and in the presence of low amounts of cross-linking agent (e.g., 1 to 2% divinylbenzene in styrene), yielding a loading of typically $1.5\,\mathrm{mmol\,g^{-1}}$.[26] The so-called Merrifield resin is a typical example of such a chloromethylated polystyrene resin cross-linked with divinylbenzene.[27] Many functional groups have been introduced into the polymer by nucleophilic reactions at the benzylic position (Scheme 3).[28]

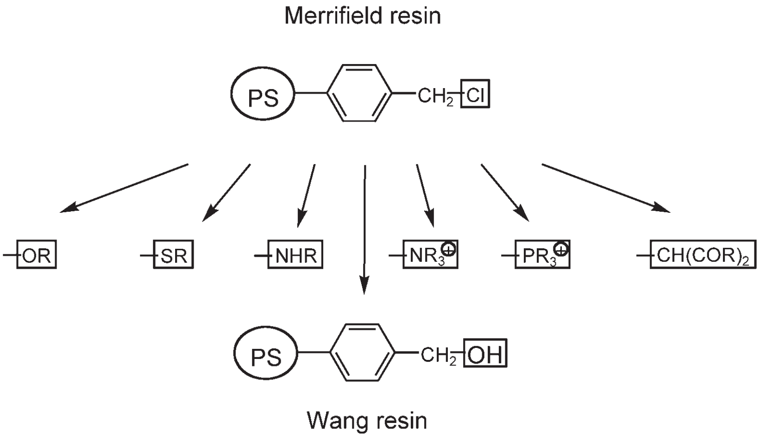


Scheme 2. Grafting of functional groups on residual vinyl groups of macroporous polystyrene (after ref.[18]).

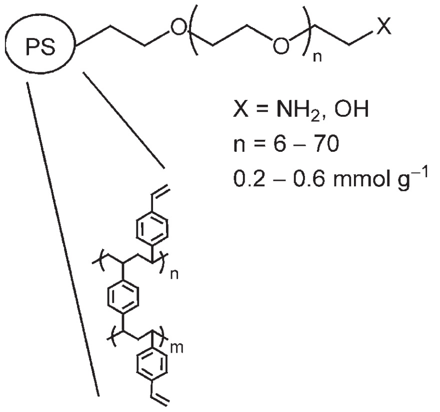
Microporous resins do not exhibit permanent porosity, and swell in the reaction medium. With a comparable number of active sites in the reactor, they often show superior behaviour compared to their macroporous analogues.[29] Microporous polystyrene resins only will swell in non-protic solvents like dioxane, dimethylformamide, toluene, tetrahydrofuran, dichloromethane, but not in apolar aprotic solvents like alkanes and polar protic solvents like alcohols and water.[30] The use of alternative cross-linkers can affect the swelling properties, flexibility and compatibility with various solvent classes. Among them are ethylene glycol dimethylmethacrylate, trimethylolpropane trimethylacrylate, 1,4-bis(vinylphenoxy)-butane and PEG.[31,32] The use of cross-linkers with highly functional groups such as dendrimers, will be treated later on.

Amphiphilic resins consisting of a polystyrene (PS) backbone, cross-linked with 1% divinylbenzene, containing 70 wt% of grafted poly(ethylene oxide) chains swell in solvents ranging from apolar aprotic to polar protic. These resins are obtained *via* *O*-alkylation of phenols or polyethylene glycols (PEG) with chloromethylated PS in basic medium. Such PS-PEG hybrid resins are commercially available as TentaGel® (Scheme 4), Argogel® and Nova gel®.[33,34] Due to the hygroscopic nature of PEG, such beads of hybrid resins may become difficult to separate from a polar reaction medium.

Soluble polystyrene-type supports evidently show some typical disadvantages of support immobilised catalysts such as low loading with active sites, lack of



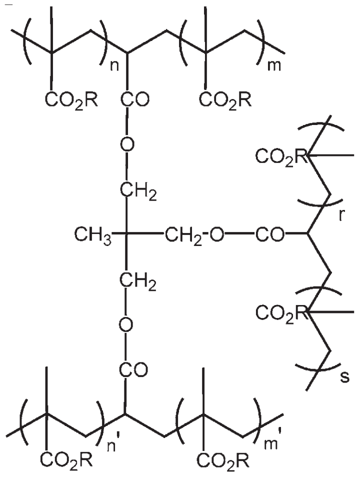
Scheme 3. Introduction of additional functional groups into chloromethylated polystyrene (after ref.[18]).



Scheme 4. Tentagel®: an insoluble PS-PEG hybrid resin for use in a wide variety of polar reaction media.

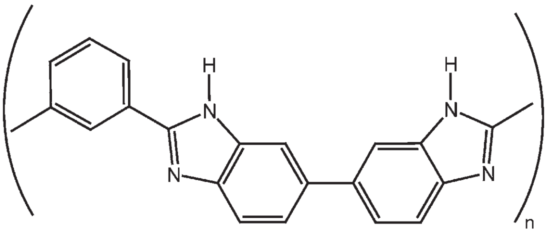
mechanical stability of the support beads, and reduced access to active sites. On the other hand, the use of soluble polymer supports requires specialised catalyst separation techniques after reaction. A common protocol for separation of soluble polymeric catalysts occurs *via* precipitation/filtration. It works well with crystalline polymers with glass transition temperatures above room temperature.[19,29] Alternatively, membrane separation techniques such as ultrafiltration, supercritical extraction, dialysis and nanofiltration are possible as well.[35,36]

Cross-linked polyacrylate resins (Scheme 5) show good swelling properties in a broad range of solvents, although the presence of the ester linkage restricts their use in acidic, basic and strongly reducing conditions.[37] Polyacrylates with pending halomethyl groups are the polyester analogues of chloromethyl polystyrene.[18] Polyacrylates with pending iodomethyl groups can be prepared in a one-step ring-opening reaction of the epoxide group in polyglycidyl methacrylate copolymers.



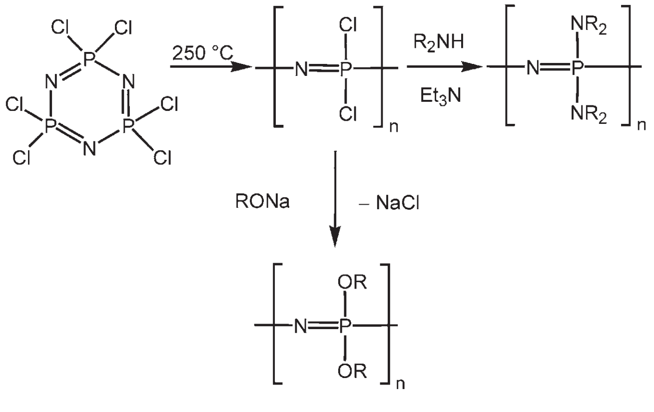
Scheme 5. Cross-linked polymethylmethacrylate (after ref.[37]).

DVB cross-linked polyvinylpyridine beads are now commercially available and are obtained from 4- or 2-vinylpyridine. They can be further functionalised in various ways, the polymers with the 4-isomer yielding the more active materials.[38] Polybenzimidazoles are homopolymers that are not cross-linked, but are thermally inert and resistant to oxidation. They are made from phthalic acid and tetraaminobiphenyls (Scheme 6). Limited ways of chemical modifications are available.[39,40]



Scheme 6. Polybenzylimidazole homopolymers.

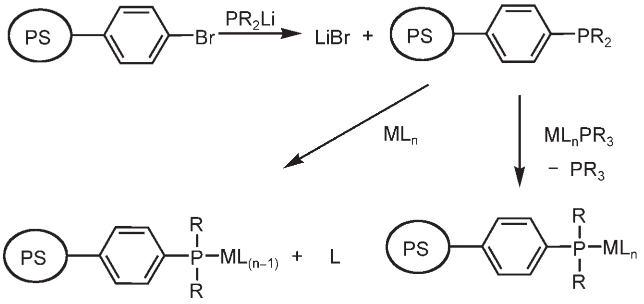
Unlike organic polymers, polyphosphazenes, $[N{=}YPR_2]_n$, show a backbone with alternating N and P atoms, with side-chains exclusively present on the P atoms. Most polyphosphazenes are derived from the poly(dichlorophosphazene), which is obtained by ring-opening polymerisation of cyclotri(dichlorophosphazene). This polymer contains very electrophilic chlorine atoms which react with a variety of nucleophiles such as amines, alcohols and phenols (Scheme 7).[41,42] Alternatively, cyclophosphazene ligands containing exocyclic donor groups can be readily adapted to the C-backbone of traditional polymers and subsequently metallated.



Scheme 7. Synthesis routes for polyphosphazene polymers.

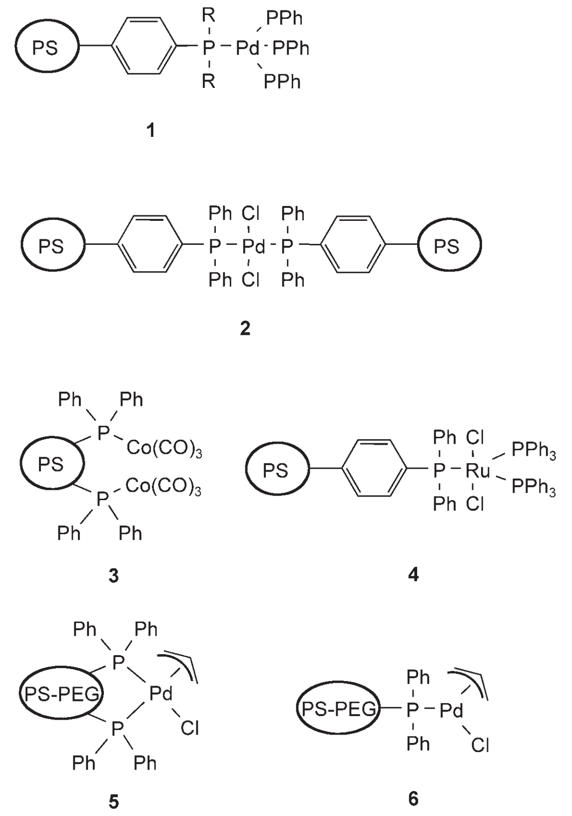
3.2 Polymer Supported Monodentate Phosphine Complexes

Polystyrene-supported triphenylphosphine ($PS\text{-}PPh_2$) is the supported analogue of triphenylphosphine.[19] A wide range of polymer supported phosphine ligands commonly used for monodentate phosphines arises *via* reaction of bromo- or chloromethylated resins with, e.g., $LiPR_2$. The main disadvantage of the procedure is the retention of the formed LiBr on the support. Metallation is possible *via* ligand exchange (Scheme 8). Incomplete metallation due to oxidation of the immobilised phosphine to the corresponding oxide is possible as well as metal release in solution (during reaction). A loading range between 0.2 and 1.5 $mmol\,g^{-1}$ of complex is possible.



Scheme 8. Metallation of phosphinated PS *via* ligand exchange after reaction of bromomethylated phosphine with PR_2Li (after ref.[9]).

Typical PS-type phosphinated supports after metallation are shown in Scheme 9. The immobilised Pd phosphine complex catalyst **1** was used for numerous catalytic applications with selectivity that often was different from that in the homogeneous phase.[9] Unfortunately, the complex after preparation and in working conditions was not always characterised sufficiently to allow rationalisation of this behaviour. Catalyst **2** although active in Suzuki reactions, was insufficiently characterised to validate the claim about catalyst structure.[43] Catalyst **3** has been used in the Phauson–Khand reaction. Catalyst **4** found use for the oxidation of alkanes and alcohols. Although in batch conditions it released the metal in solution, after reaction the metal was re-complexed by the support,[44] reminding one of the 'boomerang' effect observed for metathesis reactions.[45] Amphiphilic derivatives of PS-PEG yielded the mono- (catalyst **6**) or diphosphine complex (catalyst **5**), depending on the P/Pd stoichiometry used.[46]

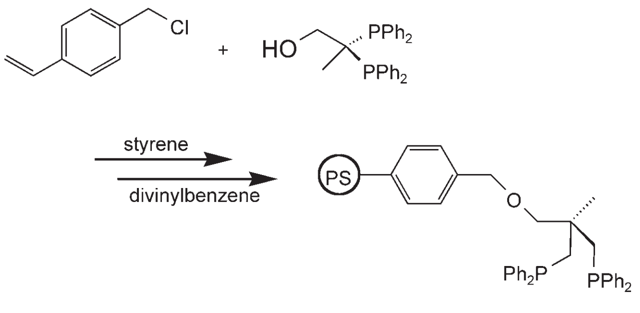


Scheme 9. Typical monophosphinated PS catalysts.

3.3 Polymer Supported Bidentate Phosphine Complexes

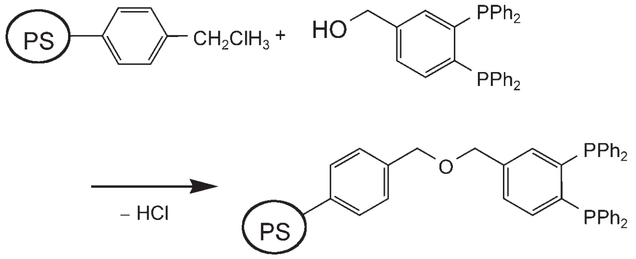
Much attention has been devoted to polymer supported bidentate phosphines as the latter show superior ligating properties.[44] Examples are known of their preparation *via* radical suspension copolymerisation of a ligand, cross-linker, a vinyl derivative of the bidentate ligand, a porogen and an initiator.[47] The macromolecular beads obtained showed a high degree of cross-linking with isolated ligand sites quantitatively retaining Pd. The ligand concentration amounted to 0.22 $mmol\,g^{-1}$. In a similar way a styrene-derived bidentate phosphine was prepared from the condensation of 2,2-bis(diphenylphosphinomethyl) propanol and 4-chloromethylstyrene, co-polymerised with styrene and divinylbenzene (Scheme 10).[48] In a similar way tridentate phosphines can be prepared as well.[49]

It appears that the co-polymerisation procedure in the presence of phosphines is superior to that of grafting them onto the preformed support, as the former procedure is simpler, at no stage is reduction of the formed phosphine oxide necessary, and no removal of entrapped salts (as in Scheme 8) is required.[44]

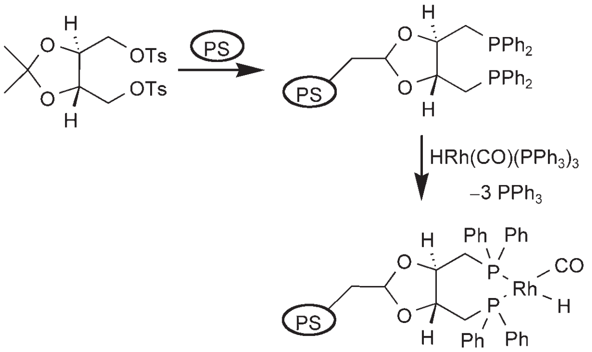


Scheme 10. Typical preparation of diphosphinated PS.

Worth mentioning in this context is the immobilisation of a hexa-ruthenium cluster as hydrogenation catalyst starting from an amine functionalised Argogel® treated subsequently with bidentate phosphine and a Ru$_6$-carbonyl cluster.[50] Phosphine and metal loadings were 0.68 and 0.12 mmol g^{-1}, respectively, pointing to an incomplete metallation (< 20 %). In an attempt to immobilise the Wilkinson hydrogenation catalyst, Merrifield's resin was linked with a bidentate phosphine *via* an ether linkage (Scheme 11).[51] The results from several characterisation techniques of the immobilised species (MAS NMR, UV-VIS, EXAFS) were consistent with the existence of an immobilised Wilkinson catalyst. It should also be noted that during this phosphination procedure no salts are formed. Upon metallation of this resin immobilised bidentate phosphine with PdCl$_2$(PPh$_3$)$_2$, several complexes are formed as evidenced by the formation of Pd–P, Pd–C, Pd–Cl, and Pd–Pd bonds. The rigidity of the polymer backbone and of the ligand can account for this.[44]



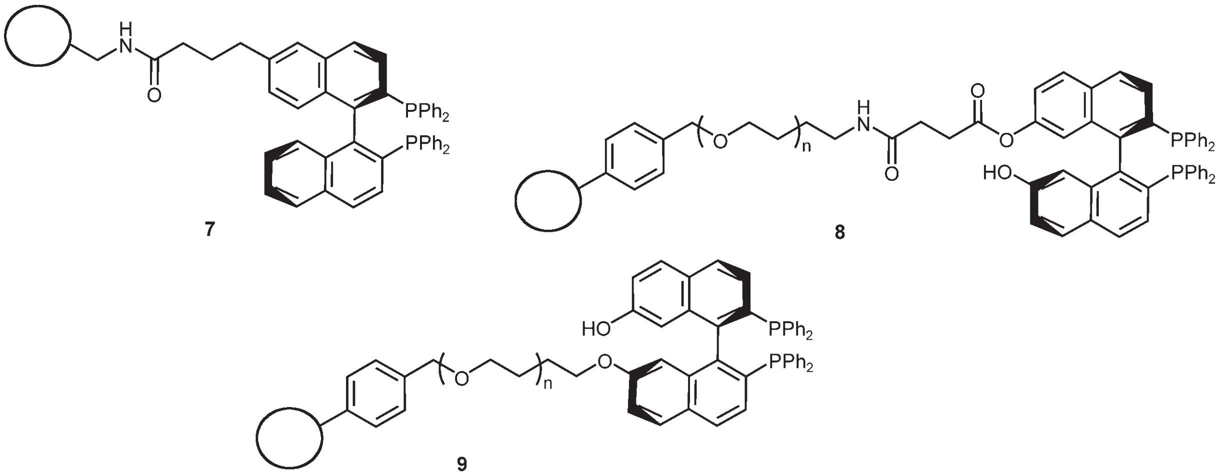
Scheme 11. Phosphination of Merrifield's resin with a bidentate phosphine (after ref.[51]).



Scheme 12. Immobilisation of Wilkinson's catalyst on PS-immobilised DIOP (from refs.[52,53]).

PS-supported DIOP [= 2,3-*O*-*iso*propylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] was the first immobilised asymmetric bidentate phosphine (Scheme 12).[52,53] Upon hydrogenation of prochiral substrates identical chemical and enantioselectivities was observed with the homogeneous and with the immobilised Rh-DIOP catalyst.

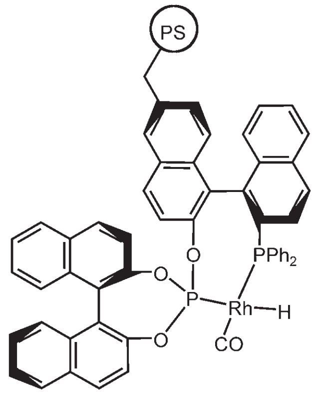
For polymer supported BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] ligands several rather complex and tedious routes have been proposed. The starting material for synthesis of the modified BINAP ligand was the enantiomerically pure (*R*)-BINOL that after protective methylation of the two hydroxy groups was acetylated with ethylsuccinyl chloride followed by hydrolysis of the two methyl ether functions. The OH groups of the latter molecule were then phosphinated with HPPh$_2$, and subsequently the ester function of the acylated BINAP was hydrolysed. The carboxyl function of this derivatised BINAP reacted with amino-PS, yielding the immobilised BINAP *via* an amide linkage, which is stable under the hydrogenation conditions in which the catalyst is being used ultimately (Scheme 13, catalyst **7**). From the 0.21 mmol g^{-1} amine functionalised PS, 0.18 mmol g^{-1} could be ligated.[54] *Via* an alternative procedure dihydroxy-functionalised BINAP was reacted with acid-derived Tentagel® (**8**). With Tentagel®-Br an ether linkage is formed with dihydroxy-functionalised BINAP (**9**).[55] The immobilised BINAP catalysts



Scheme 13. Polymer immobilised BINAP ligands.

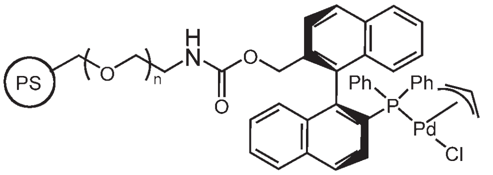
show chemo- and enantioselectivities comparable to those of the homogeneous catalyst and can be re-used in successive batch operations.

Attempts to immobilise the BINAPHOS ligand required a redesign of the ligand synthesis procedure, involving ultimately the preparation of a vinyl-derivatised ligand, which was co-polymerised with ethylstyrene and divinylbenzene (Scheme 14). When the Rh-BINAPHOS vinylated complex was used in the polymerisation reaction, a catalyst with superior chemo- and enantioselectivities in alkene hydroformylation was obtained.[56] It should be stressed that BINAPHOS is a unique ligand for use in chiral hydroformylation of alkenes.



Scheme 14. Immobilised chiral hydroformylation catalyst of the BINAPHOS type.

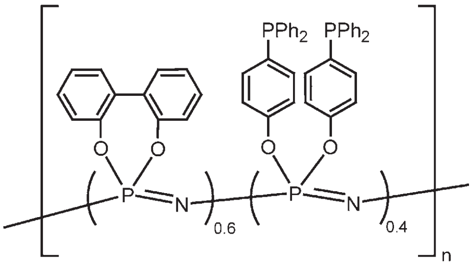
Supported MOF ligands (2-diarylphosphino-1,1′-binaphthyl) and their Pd complexes can be easily prepared using PS-PEG-MOF supports treated with $[PdCl(\eta^3-C_3H_5)]_2$ (Scheme 15), with a P/Pd ratio of 1.[57]



Scheme 15. Supported Pd-MOF type catalyst (after ref.[57]).

3.4 Phosphazene-Based Catalysts

Many linear polyphosphazenes carrying ligands as lateral groups can be used to fix transition metal complexes.[58,59] On a polyphosphazene random copolymer diphenylphosphane ligands (Scheme 16, **10**) and 2,2′-dioxy-1,1′-biphenyl (**10**) or the chiral (*R*)-2,2′-dioxy-6,6′-dibromo-1,1′-binaphthyl (**11**) groups were fixed. To the diphenylphosphane ligands a neutral $[RuCl_2(\eta^6\text{-}p\text{-cymene})]$ or cationic $[RuCl(\eta^6\text{-}p\text{-cymene})]^+$ complex was attached.[58] Both catalysts were active for transfer hydrogenation of acetophenone and in contrast to the homogeneous counterparts could be recycled in batch reaction without significant metal loss up to around 2500 TON. The activity of the achiral catalyst is similar to that of a commercially available Merrifield-PR_2-Ru catalyst.[60]



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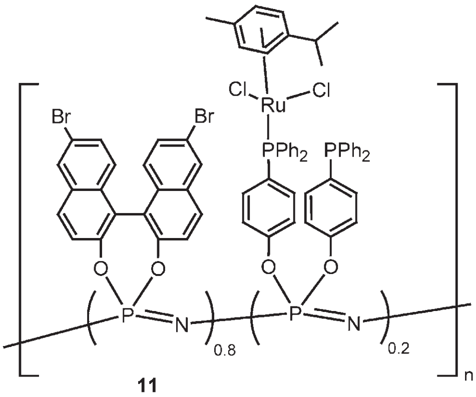


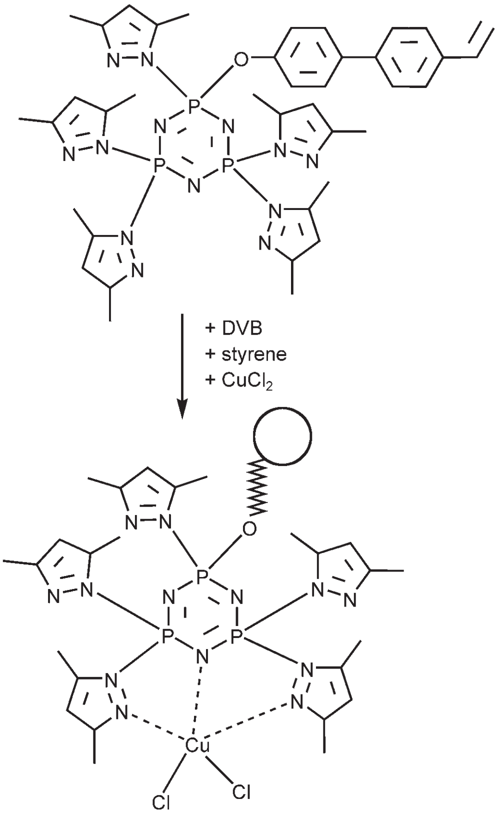
11

Scheme 16. Achiral (**10**) and chiral (**11**) polyphosphazene polymers carrying diphenylphosphane side-groups and $[RuCl_2(p\text{-cymene})]$ complexes (after ref.[58]).

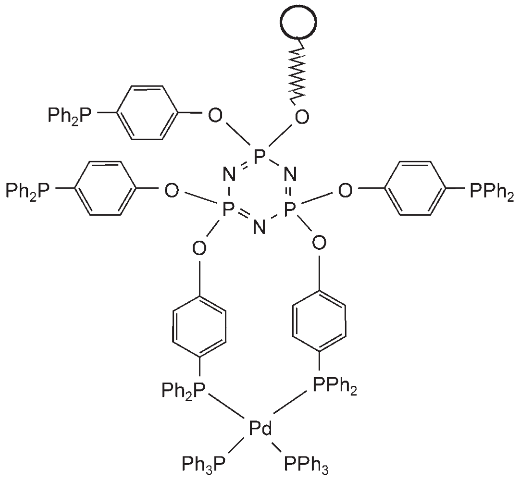
The sites in the chiral polymer **11** do not induce any enantioselective excess in the product from the hydrogen transfer reaction, possibly because the pockets are too wide for enantioselective induction and because chiral polymeric units within a secondary helical structure may not be suited for asymmetric induction.[58]

Alternatively, a pyrazolylcyclophosphane-containing hybrid polymer with an intact cyclophosphazene ring containing exocyclic donor groups (e.g., 3,5-dimethylpyrrazole) as pendant group attached to a regular polymer (Scheme 17) has been metallated with Cu salts. The extremely versatile multi-site coordination ligands are a potential family of new immobilised catalysts.[59] The former catalyst has been tested as a phosphoesterase mimic in the hydrolysis of several *p*-nitrophenyl phosphates. This robust catalyst can be recycled several times.[61]

Phosphinylcyclotriphosphazene-containing polymers (Scheme 18) can be made in a similar way and after metallation with palladium used as a Heck arylation catalyst.[61]



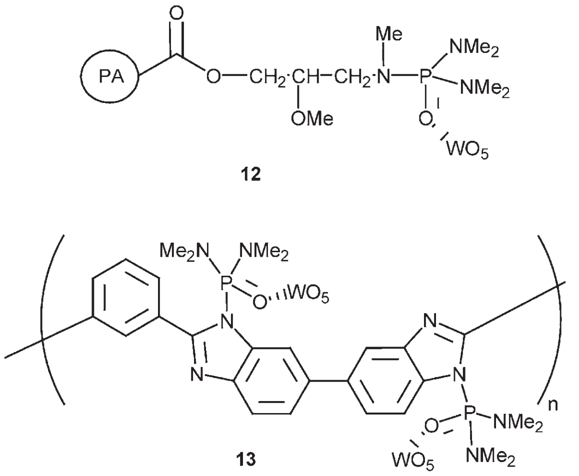
Scheme 17. Co-polymerisation of pyrazolylcyclophosphazene monomer with vinyl functional group with styrene and DVB and a Cu salt (after ref.[61]).



Scheme 18. Pd catalyst based on phosphinylcyclotriphosphazene cross-linked styrene polymer.

3.5 Various Polymer Tethered Ligands with O or/and N as Metal Chelating Atoms

Macroligands containing the phosphoryl unit belonging to the phosphine oxides, phosphonic, phosphinic, or phosphoric acid amide classes, $R_3P{=}O$, $R{-}P(O)(NRR)_2$, $RRPONR_2$, $PO(NR_2)_3$, respectively, grafted in hydrophobic polystyrene and hydrophilic polymethacrylate resins with gel and macroporous character were able to complex peroxotungstic species that allowed the epoxidation of alkenes with hydrogen peroxide.[62,63] Enhanced TONs compared to those found in the homogeneous phase, were correlated with the existence of lipophilic environments in some of the polymers in the vicinity of the catalytic site. Polymethacrylate-supported phosphotriamides (Scheme 19, **12**) yield a catalyst that is almost 20 times more active than the homogeneous catalyst. This unique behaviour was attributed to the existence of the right lipophilic-hydrophilic balance inside the polymer beads allowing optimal positioning of the polar H_2O_2 and the apolar alkene.[62,63] The same complex could be immobilised by simple grafting on a polybenzimidazole heat- and oxygen-resistant polymer (**13**), yielding active catalysts that could be reused and showed leaking of W below a level of 2 ppm.



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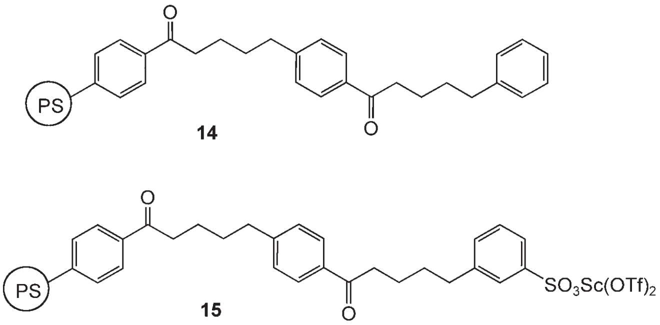
Scheme 19. Peroxytungstate species immobilised on polymethacrylate supported phosphortriamides (**12**) and polybenzimidazole-grafted phosphinamide (**13**).

Polyamides from low temperature interfacial condensation of 2,5- and 2,6-pyridinedicarboxylic chlorides and aliphatic diamines, $H_2N(CH_2)_nNH_2$, with n equal to 2 and 6, were used for Rh^I immobilisation in the hydrosilylation of alkenes, alkynes and dienes.[64] The catalyst could be reused (10 times) with some loss of activity. It was proven spectroscopically that the three potential Rh coordination sites (N_{amide}, $N_{pyridine}$ and $OC{=}O$) were at the origin of this stability. The use of the 2,5-pyridinecarboxylic acid instead of the 2,6-moiety, changed the traditional *cis*- into *trans*-selectivity in the hydrosilylation of phenylacetylene. Moreover, the polyamides concerned were semi-crystalline polymers, the increasing length of the aliphatic spacer, $(CH_2)_n$, yielding less crystalline materials with pore sizes increasing from 1.0 to 2.0 nm.

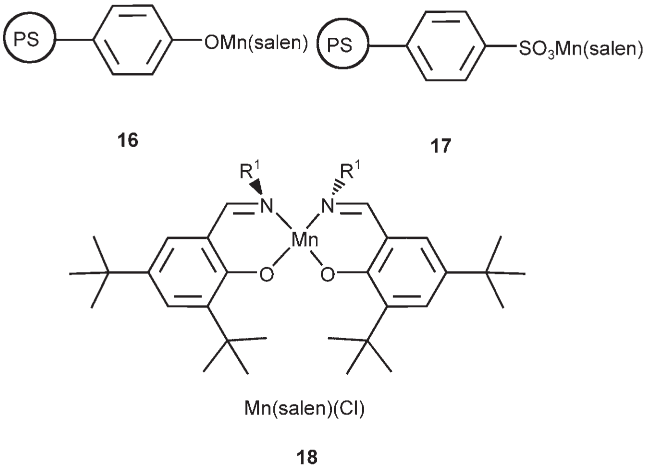
$Rh_2(CO)_4Cl_2$ immobilised on poly(4-vinylpyridine) was reported to be very stable and active as a low temperature water gas shift catalyst (in liquid water) and in the reduction of nitrobenzene to azoxybenzene.[65] Reaction kinetics as well as spectroscopic results, however, indicated the presence of non-paramagnetic mononuclear and polynuclear Rh carbonyl immobilised species. Also in poly(4-vinylpyridine) cross-linked with DVB it was shown that Mo(VI) of a $MoO_2(acac)_2$ complex was attached on the pyridine N.[66] The most active catalyst in the epoxidation of alkenes with *tert*-butyl hydroperoxide was obtained at an intermediate degree (4%) of cross-linking. Cross-linked poly(4-vinylpyridine) as such could retain mononuclear Cu species and catalysed in basic medium the low temperature water gas shift reaction as well as the hydrodechlorination of chlorobenzene into benzene and biphenyl.[67]

Treatment of phenyl pendant groups in polystyrene cross-linked with DVB (1%) successively with 5-phenylvaleryl chloride yielded a double spacer resin (Scheme 20, **14**), after sulphonation and treatment with scandium chloride and trifluoromethanesulphonic acid (OTf). This polymer-supported scandium Lewis acid (**15**) shows high activity in water and in contrast to earlier systems does not form a dispersed colloidal system in water, resulting in easy catalyst recovery and reuse.[69] The polymer chains and spacers help to form hydrophobic sites in water, useful in C–C bond forming reactions in water in the absence of organic co-solvents.



Scheme 20. PS resin with double spacer resin (**14**) transformed into a sulphonated resin for scandium-Lewis acids (**15**).

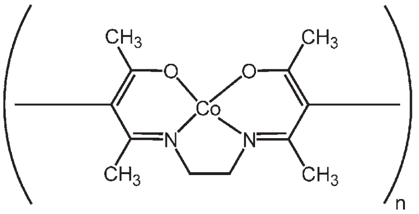
Grafting of chiral Mn(salen) complexes (Scheme 21, **18**) on highly cross-linked insoluble PS resin with phenoxy or phenylsulphonic pendant groups *via* the metal (**16** and **17**), is an unusual way of catalyst immobilisation.[69] These axially immobilised Mn(salen) catalysts were easy to handle, showed epoxidation activity comparable to that of the respective homogeneous catalysts, with strongly enhanced enantioselectivity and changed *cis/trans* ratios in the epoxides. The *ee* values for the epoxide of *cis*-β-methylstyrene typically increased from 25 to 70%, while the *cis/trans* ratio was increased from 0.5 to 1.0, for the homogeneous and heterogeneous systems, respectively. It is thought that this is caused by steric effects of the support *via* a big rigid ligand axially coordinated to the metal. The stability of the catalyst in biphasic conditions (aqueous NaClO as oxidant and alkenes as substrate) is the result of its positioning at the interphase, avoiding self-oxidation of the complex.



Scheme 21. Axially anchored Mn(salen) (**18**) to the phenoxy (**16**) and phenylsulphonic (**17**) pendant groups of cross-linked PS.

Traditional immobilisation of (Mn)salen catalysts occurs *via* grafting from the salen ligand itself *via* a long flexible alkane-type linkage, thus yielding chemo- and enantioselectivities comparable to those of the homogeneous catalyst.[70] When immobilised on a soluble polymer, such as PEG-OMe, Mn(salen) can be precipitated with a suitable solvent at the end of the reaction.[71,72] Complexes of salen perfluorinated alkyl side chains can be recycled by phase separation,[73] while functionalised salen complexes can be co-polymerised[74] or self-polymerised[75] to form cross-linked insoluble polymers. In the latter two cases, always strongly reduced *ee* values are obtained compared to the homogeneous case, possibly due to unsuited steric restriction by the polymer microenvironment.

A PS resin with heterogenised Schiff base was obtained *via* suspension copolymerisation of styrene, DVB, and allyl chloride in the presence of *N,N'*-bis-(acetylacetone)ethylenediamineCo(II) [Co(acen)] (Scheme 22). The amount of cross-linking agent was found to determine the degree of swelling, the porosity, and the pore size of the support as well as the Co ion loading of the complex.[76] Detailed characterisation of the complex and the polymer showed that in homogeneous and heterogeneous conditions the Co-(acen) complex was square planar, with the electronic



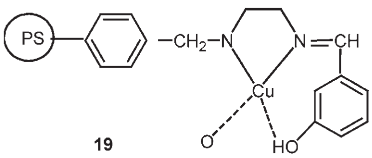
Scheme 22. Immobilisation of Co(acen) complex on cross-linked PS *via* suspension co-polymerisation.

properties of Co(II) determined by the degree of cross-linking. On such catalysts the decomposition rate of hydrogen peroxide increased not only by the presence of the polymer but also by its degree of cross-linking.

An alkoxytitanate, [Ti(O-*i*-Pr)$_4$], was grafted on to the phenol pendant groups of poly(*p*-hydroxystyrene) resins with different degrees of cross-linking prepared *via* suspension polymerisation.[77] The specific surface area increased with the DVB level and consequently a number of 5 nm pores were formed. The materials became more active in the transesterification of methyl methacrylate with 2-ethylhexanol when the level of cross-linking of the support increased, with deposition of polymeric products causing catalyst deactivation. In the epoxidation of cyclohexene with *tert*-butyl hydroperoxide, the activity of the heterogeneous catalysts always surpasses that of the homogeneous complex, and increased in parallel with the degree of cross-linking of the polymer. PS macroporous resins obtained *via* copolymerisation of styrene, DVB, and *N*-(*p*-hydroxyphenyl)maleimide with Ti(O-*i*Pr)$_4$ grafted on the pendant hydroxyphenyl units initially showed good activity/selectivity in the same transesterification and epoxidation reactions, though inevitably showed significant Ti leaching.[78]

An insoluble polymer supported cobalt-ethylenediaminetetraacetic acid Co(EDTA) complex was prepared *via* copolymerisation of methacrylic acid and acrylonitrile. It was compared with the homogeneous complex and with the same complex ion exchanged onto an ion exchange resin.[79] The catalytic effect of the complex in the autoxidation of benzaldehyde was most significant with the co-polymerised support, pointing to the active participation of the macroligand to this radical reaction.

Cu(II)L Schiff-base complexes were immobilised on a DVB cross-linked PS using vinylbenzyl chloride that has undergone an aminolysis reaction with ethylenediamine (**19**) or urotropine (**20**) and a subsequent modification with salicylaldehyde (**19**) or picolinaldehyde (**20**). Cu(II)L$_2$ complexes could only be obtained with an excess of ligand.[80] The solid was active in the oxidation with *tert*-butyl hydroperoxide of 2,6-di *tert*-butylphenol into diphenoquinone. In a similar way Fe(III)L$_2$ complexes were immobilised on PS with chlorotolyl as pendant groups (Scheme 23, **21**).[81] An epoxidation catalyst for alkenes with *tert*-butyl hydroperoxide was obtained. The lacking coordination site in the square planar geometry was filled with an oxygen atom from the oxidant. Unfortunately, the solid gradually degraded. From a family of diamine-supported ligands on polymethacrylate-based resins, ethylenediamine was shown to be the most prominent one for Pt(II) retention.[82] Whereas gel-type support morphologies were found to be totally unsuitable for the hydrosilylation of 1-octene, possibly because of a lack of disposable surface area, macroporous PS-base resins show excellent activity and stability and show probably optimum design morphology.



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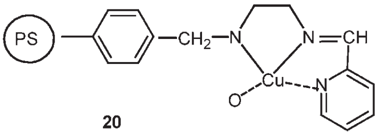

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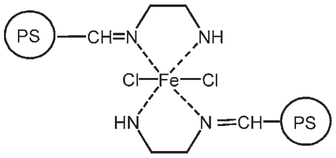

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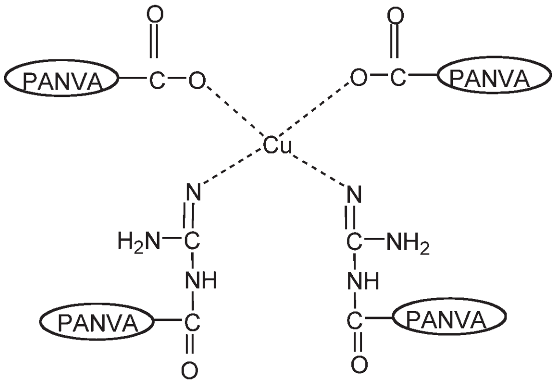
Scheme 23. Schiff base Cu(II)L and Fe(III)L$_2$ complexes immobilised on PS *via* co-polymerisation and grafting (after ref.[83]).

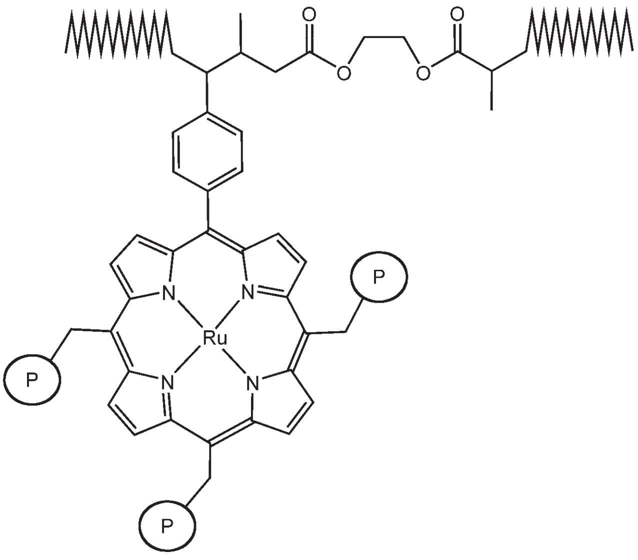
A terpolymer from acrylonitrile (AN), vinyl acetate (VA), and DVB in which the nitrile groups are modified with aminoguanidine carbonate was shown to be able to coordinate Cu *via* square planar geometry, using acetate oxygen and guanidine nitrogen atoms (Scheme 24).[83] In this more polar environment hydrogen peroxide could be used as an efficient oxidant in the oxygenation of hydroquinone into *p*-benzoquinone.

Imidazole groups linked to the chlorotoluyl pendant groups in a PS resin lightly cross-linked with DVB allowed the immobilisation of Mo(CO)$_6$ as Mo(CO)$_5$ species.[84] High alkene epoxidation activity with *tert*-butyl hydroperoxide was obtained with these reusable catalysts. Vinyl-substituted *meso*-tetraarylprophyrin Ru was co-polymerised with ethylene glycol dimethylacrylate in the presence of CHCl$_3$/THF as porogen



Scheme 24. Copper complexed by acetate O and guanidine N in a terpolymer of AN, VA and DVB (after ref.[83]).

(Scheme 25), yielding a site-isolated catalyst in a rigid matrix with strongly reduced auto-oxidation of the catalyst and the support. With this catalyst being superior to its homogeneous version, alkenes, secondary alcohols and even alkanes could be oxidised effectively in the presence of HBr.[85]



Scheme 25. Isolated porphyrin catalysts on polymeric support.

In general, polymerisable transition metal complexes containing a vinylated ligand, can be co-polymerised with suitable vinyl group-containing monomers. Numerous candidates for both partners are present and have been evaluated in a wide spectrum of catalysed reactions.[86] Among them are the hydrogenations of alkenes, functionalised and prochiral alkenes, the oxidation of many substrates such as alkenes, sulphides, alcohols and aldehydes, as well as the stereoselective epoxidation of hindered alkenes, Heck-type reactions, allylic alkylation and Michael additions. Whereas in many cases activity and selectivity of the same order of magnitude as the homogeneous complex are obtained, values often surpassing them are achievable. Chemical homogeneity of the active centre and potential tailoring of the support properties are the strong points of the co-polymerisation concept of metal-containing polymers.

Worth mentioning are a few examples in which catalysts are immobilised *via* ion exchange on ion exchange resins, with retention *via* electrostatic interactions. The extremely poisonous but exceptional osmium tetroxide catalyst, exchanged on a short PEGylated ionic polymer, could be used and recycled in the (asymmetric) dihydroxylation of alkenes.[87] Specific ionic polymers were designed to achieve high affinity of the polymer for osmium. Quaternisation of poly(4-vinylpyridine-styrene) with tri(ethylene glycol) allowed the use of polar solvents, while finally the mesylate ionic derived polymers were exchanged with $[BF_4]^-$. Immobilisation of osmate on such supports became possible *via* electrostatic forces. *cis*-Glycolysation of styrene (derivatives) was possible with high enantioselectivity. The latter requires the supplementary addition of a chiral ligand that is complexed with the immobilised osmate.

Immobilised osmate *via* a bisdiolate complex has been reported on an ion exchange resin[88] as well as on inorganic supports.[89,90] While Os leaking is inhibited, the operation in a chiral cycle becomes less evident. Immobilisation of Os-chiral ligand complexes both on soluble and insoluble polymers as well as on silica yielded invariably immobilised ligands with an affinity for Os that is too low to assure its quantitative retention.[91,92]

In a recent approach to catalyse hydrogen transfer reactions from formate to functionalised alkenes, imines, nitroarenes, and 1,2-diketones, both the Pd catalyst (from palladium acetate) and the H-source (from formate) were ion exchanged on an Amberlyst® ion exchange resin.[93]

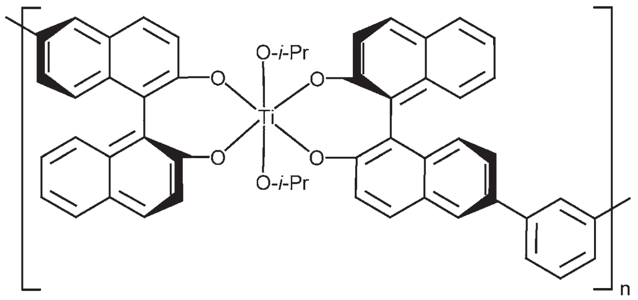
4 Recent Advances in Immobilisation of Chiral Catalysts

As in many other catalytic reactions, the immobilisation of homogeneous chiral catalysts could decrease the difficulty of reuse and increase the efficiency of the catalysis compared to the homogeneous counterparts. Moreover, the expensive nature and large amounts of catalyst required, usually between 5 and 10 mol%, and the required high enantioselectivity in the products make this problem even more stringent.

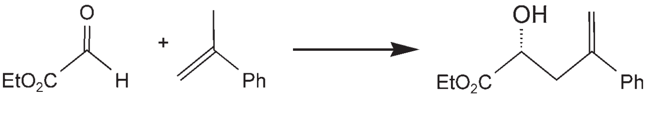
Immobilised chiral catalysts on support *via* covalent linking in the best case show performances equal to the homogeneous case.[94] The incorporation of chiral ligands on the main chain of polymers like polyester and polyamide chains *via* a specific linker has been successfully done in the case of the BINAP.[95–99] All catalysts showed high enantioselectivity and negligible leaching of metal, usually below 16 ppb.[96]

Incorporation of chiral complexes into the polymeric matrix, may result in significant catalytic changes, pointing to an active role of the polymeric backbone. Pseudo-dilution effects precluding aggregate formation often favour the activity of supported species, while the presence of the hydrophobic matrix may increase the stability of water-sensitive active sites.[100] Efforts done with polymer immobilised chiral auxiliaries such as supported amino alcohols, bisoxazolines, chiral polyamides and amines, supported TADDOLs, all show polymer backbone effects that are often difficult to rationalise at this stage. Co-polymerisation in the presence of a chiral auxiliary in conditions that yield rigid resins seem to favour the generation of appropriately ordered chiral sites. With less rigid resins obtained with lower degrees of cross-linking, this effect is lacking. On the other hand, oxygen donor atoms in the polymer backbone may compete for coordination with the catalytic site, thus introducing a large achiral fragment, resulting in a decreased enantioselectivity. The immobilisation of chiral auxiliaries in monolithic polymers is promising in this respect.

So-called metal-ligand polymers have been developed with high enantioselectivity and efficiency. A classical chiral ligand with a single coordination site is modified into one with two (or more) coordination sites, thus assuring self-assembly and formation of a metal ligand polymer.[101–103] These metal organic materials usually show low solubility in reaction media, thus behaving like heterogeneous catalysts. Whereas metal-organic self-assembled frameworks (MOFs)[104] are robust chiral frameworks with a high density of catalytic units, they initially showed low enantioselectivity. Recently, the potential of such an approach has been discovered, yielding chiral porous hybrid solids exhibiting high enantioselectivity for the hydrogenation of prochiral ketones.[105,106] As an example, Ru-BINAP with the ligand functionalised with phosphonic acid groups was reacted with zirconium *tert*-butoxide, yielding highly porous hybrid solids with total BET surface areas between 300 and 500 $m^2 g^{-1}$, micropore volumes between 60 and 160 $m^2 g^{-1}$ and pore volumes between 0.5 and 1.0 $cm^{-3} g^{-1}$. Alternatively, rigid BINOL-type ligands (BINOL = 1,1′,2,2′-binaphthol) containing two linked BINOL units can assemble with metal ions to form insoluble metal-organic coordination polymers. In the previous case, the metal (ruthenium) was present as pendant group on the Zr-linked backbone. Now the active metal is located on the polymer backbone (Scheme 26).[107,108] This offers the possibility of immobilising multi-component enantioselective catalysts devoid of any support. Such an asymmetric catalyst with high enantioselectivity is used in a Michael-type addition, and in the carbonyl-ene reaction yielding α-hydroxy esters (Scheme 27).[109] It is noteworthy that the nature and position of the spacer between the two BINOL units significantly influence the enantioselectivity of the catalyst, probably by altering the self-assembly process and the structure of the catalyst.[109]



Scheme 26. Tri-bridged polymer made by self-assembly of BINOL containing ligands with Ti (after refs.[107,108]).



Scheme 27. The carbonyl-ene reaction.

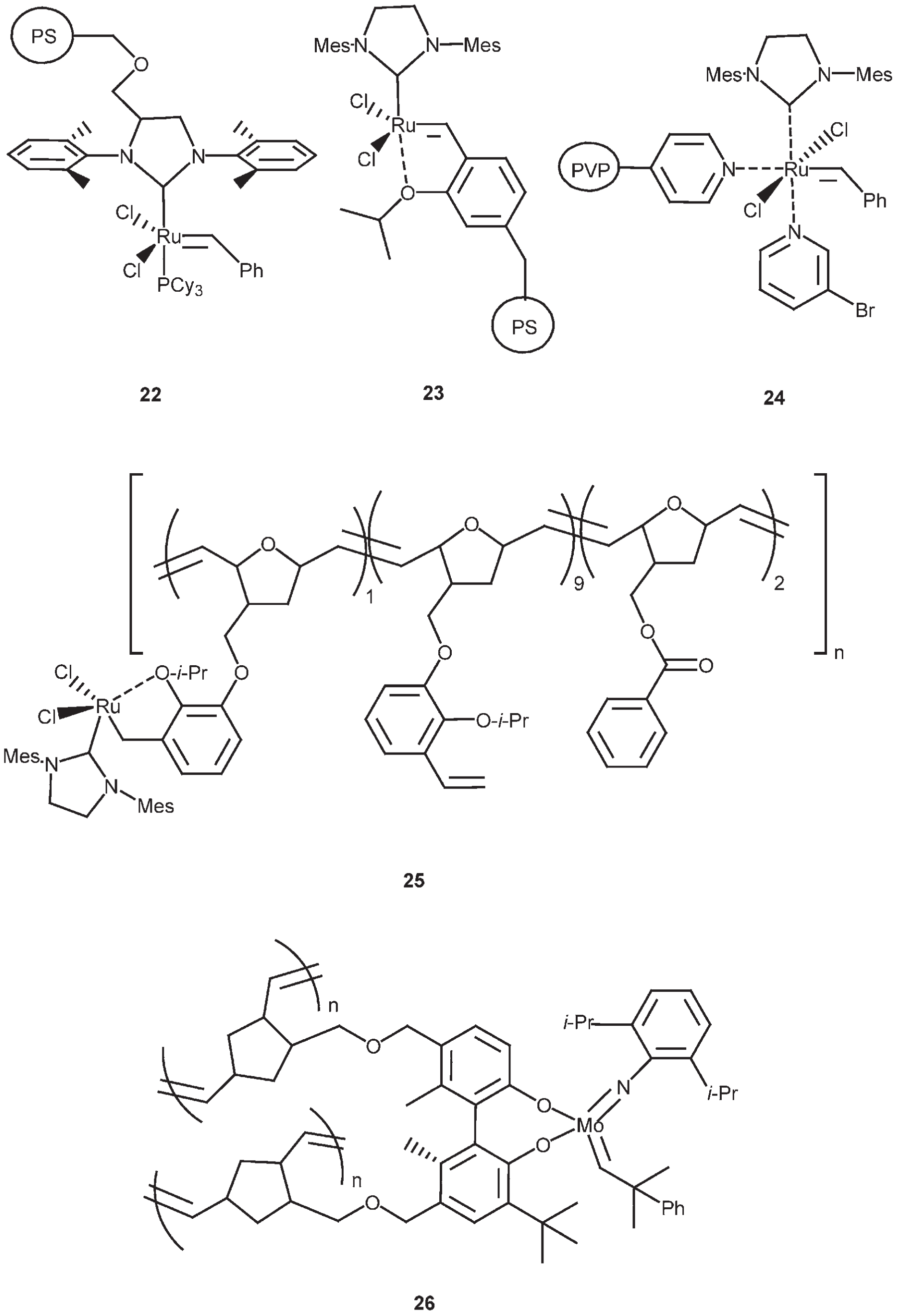
For the enantioselective addition of phenylacetylene to benzaldehyde yielding the corresponding propargylic alcohol, an immobilised chiral catalyst with the same activity and selectivity as the homogeneous one was obtained as follows: grafting of chiral amino alcohols with styrene as co-monomer was done on polyethylene fibres, pre-activated by electron beam pre-irradiation.[110]

In comparison, worth mentioning is the immobilisation of chiral catalysts on inorganic support by mere electrostatic interactions between chelated metal and support. A heteropoly acid, *viz.*, phosphotungstic acid, impregnated on γ-alumina, is very suitable for the irreversible retention of achiral complexes, *viz.*, $[Rh(COD)_2BF_4]$ and $[Rh(COD)Cl]_2$, modified with a chiral auxiliary, *viz.*, (*R,R*)-MeDuPHOS. The resulting solid is a stable, active and selective catalyst for the hydrogenation of prochiral alkenes.[111,112] The precise interactions of the different catalyst parts among each other remain obscure, however. The external surface of zeolite BETA, retains both Ru and Rh BINAP as well as MeDuPHOS complexes, possibly *via* electrostatic and van der Waals-type interactions. The solids are active and selective hydrogenation catalysts for prochiral alkenes. The unique behaviour of BETA zeolite in this respect is remarkable.[113,114]

5 Immobilised Metathesis Catalysts

N-heterocyclic carbenes (NHC) act as excellent donors to generate stable metal-carbon bonds and have turned out to be efficient ligands in transition metal complexes in numerous transformations, *viz.*, C–C coupling and metathesis reactions.[115] Such ligands can serve as a linker for the immobilisation of complexes, *viz.*, Ru-NHC. Immobilised very active NHC ruthenium benzylidene metathesis complexes linking *via* an ether linkage the NHC part of the complex to a Merrifield polymer with 1% DVB cross-linking were obtained (Scheme 28, **22**).[116]

This Ru-complex, known as Grubbs-type I catalyst, can also be tethered to a (polymeric) support *via* the alkylidene moiety,[117,118] *via* the phosphine ligand[119]



Scheme 28. Polymer metathesis Grubbs catalyst immobilised *via* NHC carbene (**22**), *via* 2-alkoxybenzylidene ligand (**23**), *via* ligand exchange (**24**) and *via* ROMP of a norbornene derivative in the presence of the catalytic complex (**25**) or of the Schrock chiral catalyst (**26**). Mes = mesitylene (2,4,6-trimethylbenzene).

or *via* chlorine ligand exchange.[120,121] Various Hoveyda–Grubbs carbenes were preferentially attached to different resins *via* the 2-alkoxy-benzylidene fragment (**23**).[122,123] A straightforward procedure for immobilisation of Grubbs III occurs *via* a coordinative binding using not a grafting but a polymerisation strategy involving polyvinylpyridine cross-linked with DVB as part of a monolithic highly porous polymer/glass composite (**24**).[124] Whereas the stability of the latter catalyst can still stand further improvement, the immobilised metathesis catalysts show remarkable regenerability.[115]

A new Grubbs–Hoveyda-type metathesis catalyst and its immobilised version on the usual polymers were prepared by substitution of one or two chlorine ligands of the complex with trifluoroacetate and trifluoromethanesulphonate. The resulting catalysts are monomeric and exhibit surprising activity in ring-closure metathesis, ring-opening cross-metathesis and enyne metathesis. The fixation of strongly electron-withdrawing ligands accelerates Grubbs–Hoveyda-type catalyst activity remarkably in contrast to prior work on alternatively immobilised complexes.[125]

The Grubbs I catalyst was also immobilised *via* ring-opening metathesis polymerisation (ROMP) of a norbornene derivative in presence of the complex (**25**).[116] In contrast, the same catalyst could easily be prepared *via* sol-gel polymerisation of an organosilica monomer and a Grubbs I complex, with a dimethylchlorosilyl group attached to the phenyl part of the 2-alkoxybenzylidene fragment. The products of the reaction were found to be ruthenium-free during a significant number of successive batch reactions. Heterogeneous NHC-based metathesis initiators, can be achieved *via* a “grafting from” as well as a “grafting to” approach.[126] In the first case precursors were grafted on a noborn-2-ene-based monolithic support prepared *via* ROMP. In the second case oligomeric NHC precursors were synthesised with the chain end functionalised with tri(ethoxy)silane groups. Such species were grafted on silica *via* standard silane chemistry. All heterogenised NHC precursors were successfully converted into Grubbs II-type catalysts, being active in ROMP, ring closure and cross-metathesis.

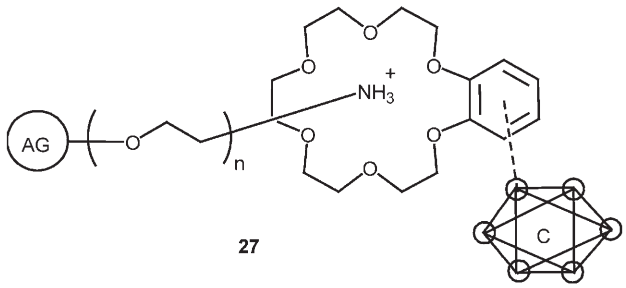
A polymer-supported, chiral Schrock molybdenum-containing catalyst for enantioselective ring-closing metathesis was also obtained *via* a ROMP metathesis reaction.[127] The Mo catalyst is incorporated in the backbone of a polymer *via* ruthenium-catalysed ROMP of a norborn-2-ene substituted chiral biphenyl-based phenoxide, (*R*)-5,5′-bis(norborn-5-ene-2-methyleneoxymethyl)-3,3′-di-*tert*-butyl-6,6′-dimethylbiphen-2,2′-diol) (**26**). The catalyst allows the transformation of prochiral alkene substrates into complex molecules with acceptable enantioselectivity.

ROMP is an immobilisation strategy that was also used for other than metathesis catalysts. Cross-over macrocyclisation of norbornenyl-tagged diaminomaleonitrile with dipropylmaleonitile gave an immobilised diaminohexapropylporpharizine, which after conversion into the Zn-form, was active in singlet-oxygen consuming reactions.[128]

6 Immobilised Clusters and Nanoparticles

Amphiphilic polystyrene-based resins containing polyethylene glycol (PEG) grafts show interesting properties to support ruthenium clusters of the type $[Ru_6C(CO)_{17}]$. The PEG enables swelling in a large number of solvents, and provides the flexibility needed to avoid steric congestion near the active site.[129] These clusters can be coordinated to the aromatic part of benzo-18-crown-6, while the crown can interact strongly with the ammonium part of a functionalised chain. In this way, site-directed deposition of the cluster was possible on ArgoGel amine resin (Scheme 29, **27**)[129] as well as in hierarchically structured mesoporous silica.[130] Although especially high turnover frequencies ($TOF = 6500\ h^{-1}$) were reported in the hydrogenation of alkenes, a site coverage of only 10%, was obtained. The immobilisation strategy further aimed at enhancing the cluster loading and binding on the bead, *via* a bidentate phosphine ligand (**28**).

Gel-type resins of approximately 200 to 400 μm in size, devoid of permanent macroporosity, consisting of $-[-CH_2-CHZ-]_n-$ cross-linked with DVB (~4%) either with one or two types of pendant groups form the basis for multi-functional resins. The respective pendant groups like methacrylic acid and *N,N*-dimethylacrylamide attribute, to microenvironments in the



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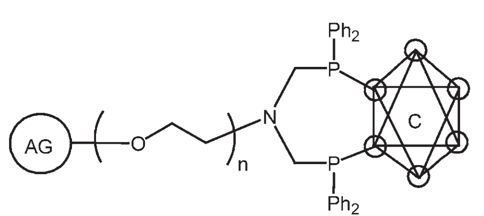

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Scheme 29. Immobilisation strategies of $Ru_6C(CO)_{17}$ cluster on ArgoGel amine resin.

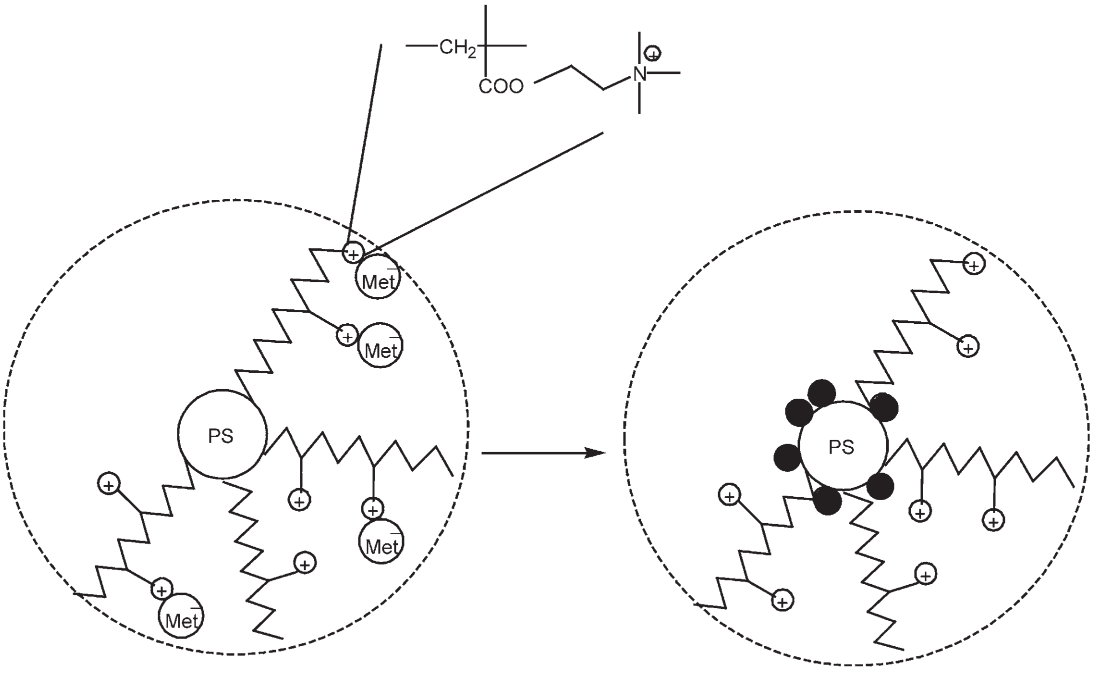
polymer, acidic and basic promoters to metal nanoclusters that are separated and do not neutralise each other, the acid sites usually being transformed into Lewis acid sites with Fe(II), Co(II) or Zn(II). Various resin-supported platinum catalysts, prepared *via* impregnation with solvated Pt atoms prepared *via* metal vapour synthesis, show regularly shaped 2–3 nm spherical nanoclusters.[131] Such dual-function supported platinum cluster catalyst shows not only activity enhancement in the complex hydrogenation chemistry of citral (3,7-dimethyl-2,6-octadienal) into α,β-unsaturated alcohols like geraniol and nerol, *viz.*, *trans*- and *cis*-3,7-dimethyl-2,6-octadienol, respectively, but also hydrogenate the aldehyde carbonyl preferentially over the double bonds.

Platinum and gold nanoparticles can also be immobilised on spherical polyelectrolyte brushes, preventing aggregation during the reaction to be catalysed.[132,133] The spherical polyelectrolyte brushes consist of a solid core of polystyrene with grafted long chains of poly(2-methylpropenoyloxyethyl)trimethylammonium chloride. These positively charged chains form a dense layer of polyelectrolyte chains on the surface of the core particles. The high grafting density assures that the average distance between two chains is much smaller than the contour length of the brush, thus keeping the surface layer of polyelectrolyte chains within the brush limit. $[PtCl_6]^{2-}$ anions immobilised in the brush layer upon reduction lead to nanosized platinum nanoclusters of approximately 2 nm (Scheme 30). This system of composite particles of a colloidal carrier with metal nanoparticles whose location is confined to the brush layer, not only shows a clean metal surface since strong binding agents like thiols are absent, but also good colloidal stability of the whole system for extended periods of time. It shows the absence of flocculation at elevated temperatures as well.

The formation of micro-heterogeneous catalysts for hydrogenation was reported using acetonylacetonate complexes of palladium with phosphine ligands. Polynuclear palladium complexes with phosphide and phosphinidene ligands that are stable in a hydrogen atmosphere are at the basis of the activity of such catalysts.[134] However, the corresponding amide complexes yielded highly dispersed palladium black.

7 Molecularly Imprinted Polymeric Materials for Enzyme-Like Catalysis

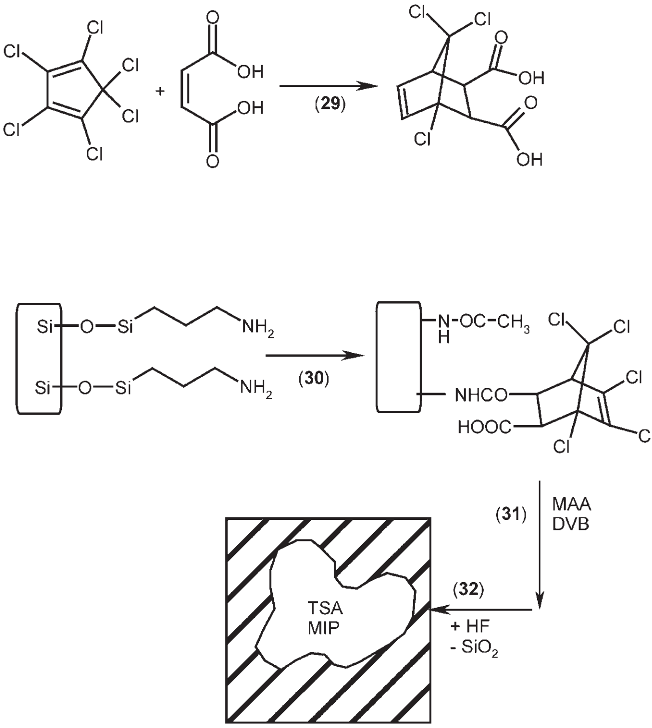
By tuning the enzyme active site through prior molecular imprinting of the support with the homogeneous complex or preferably with its reaction transition state, the catalytic counterparts can be synthesised that do not exhibit the generally accepted disadvantages of enzyme catalysis, *viz.*, the low TOF due to the presence of solvents, and perturbation of the solution by temperature and pH.[135] Generally, molecularly imprinted polymers (MIPs) can be synthesised from functional monomers using radical polymeri-



Scheme 30. Schematic representation of a spherical polyelectrolyte brush, consisting of a core-shell system that retains anionic Pt complexes before and platinum nanoparticles after reduction.

sation or polycondensation. Molecular imprinting allows one to produce a cavity with a memory of the transition state of a (catalytic) reaction by polymerisation and subsequent removal of the template used. Thus, a shape-selective reaction space is generated for a molecule similar to that of the catalytic transition state.[136]

A product-related transition state analogue of the Diels–Alder condensation of maleic acid with hexachlorocyclopentadiene (Scheme 31, **29**) was designed in this way.[137] An analogue of the transition state was prepared by covalently linking the mono-amide form of the condensation product on propylamino-silica (**30**), while neutralising residual amino groups. A polymerisation was done in presence of methacrylic acid and DVB (**31**) to obtain a silica-polymer composite, followed by removal of the silica with HF (**32**).



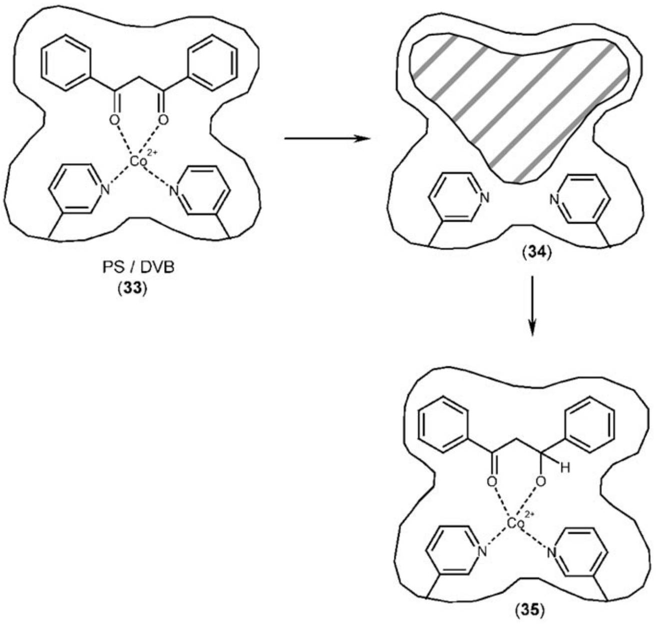
Scheme 31. MIP for Diels–Alder condensation of perchlorocyclopentadiene and maleic acid (**29**); propylaminated silica reaction with the mono-amide form of the reaction product (**30**); synthesis of a silica/polymer composite with methacrylic acid and cross-linker (**31**); silica removal from the composite and generation of the MIP (**32**).

Examples of imprinted catalysts without a metal encompass hydrolysis, condensation, transesterification reactions using imprinted transition state analogues on acrylate polymer, silica and silica-alumina gels.[138] Reported molecularly imprinted metal-complexes are concerned with aldol condensations, transfer hydrogenations, cross-coupling reactions and hydrogenation of alkenes. They deal mainly with bulk imprinting, surface imprinting and copolymerisation on/in organic substrates.[138] In order to design them successfully, the following sequence of events should be respected: i) attaching the metal complex to a (polymeric) solid support; ii) surrounding the complex by a polymer matrix; iii) forming an active structure in the matrix resembling the reaction transition state; iv) producing the shape-selective space near the metal of the complex.[138] Typical examples of imprinted transition metal complexes are the described in the following paragraphs.[138,139]

Theoretically, molecular imprinting of metal complexes in bulk polymers should closely mimic the transition state of the rate-determining event. The imprinting often occurs *via* polymerisation of organic monomers such as ethylene glycol dimethacrylate, styrene and DVB to locate the complex in the bulk of the polymer matrix. The presence of a large amount of cross-linker and of an inert solvent acting as a porogen, furnishes macroporous polymers with a permanent rigid pore structure and high internal surface area. On the other hand, fast equilibrium between uptake into and release from the cavity of the template, requires the preservation of a certain degree of flexibility, contradictory to the first requirement. Carefully balancing between these two requirements combines often good accessibility and surface areas (100–600 $m^2 g^{-1}$) with high thermal and mechanical stability.[139]

A well-know example consists in the design of an aldolase MIP containing a cobalt complex coordinated with dibenzoylmethane. This complex is a reactive intermediate analogue in the aldol condensation of benzaldehyde and acetophenone.[140] The Co ions of this complex were ligated with two pyridine ligands, anchored in the polymer during the co-polymerisation of styrene, DVB and vinylpyridine. Subsequently, the dibenzoyl ligand was removed, creating/emptying the shape-selective molecular reactor (Scheme 32). The molecular recognition of the site topography must have been excellent as the aldol condensation with the reactants mentioned results in an almost 10-fold increase in activity compared to the homogeneous case.[136,140]

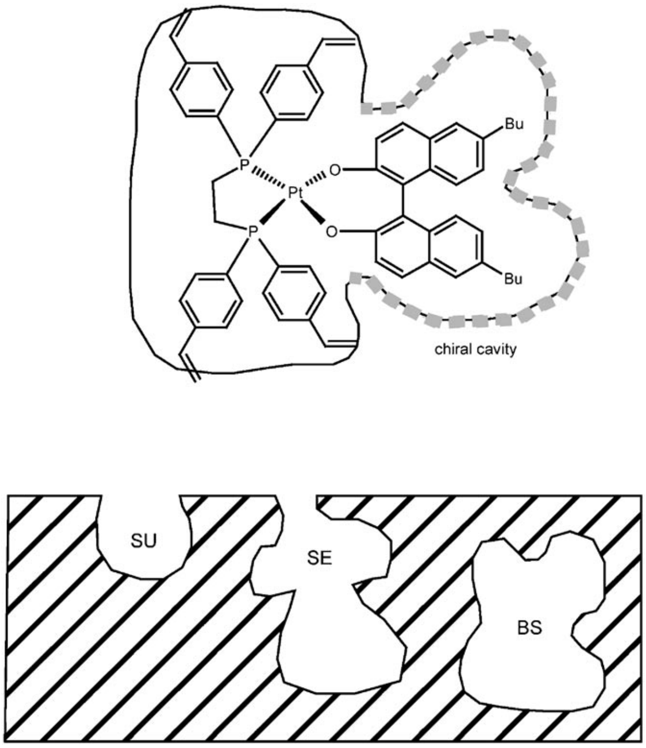
Another example is concerned with the enantioselective hydride transfer reduction of ketones.[141] This system showed substrate and regioselective hydrogen transfer. The half sandwich complexes of (η^6-arene)Ru coordinated either with mono- and bisubstituted amine-based ligands during polymerisation with ethylene glycol dimethacrylate monomer and a phosphinato ligand yielded mono- and bigrafted material, the phosphinato ligand forming the shape-selective cage (Scheme 33). The latter catalyst showed reduced flexibility related to the higher number of grafting points. The recognition of different ketones by the free cage shape is strongly related to the shape of the



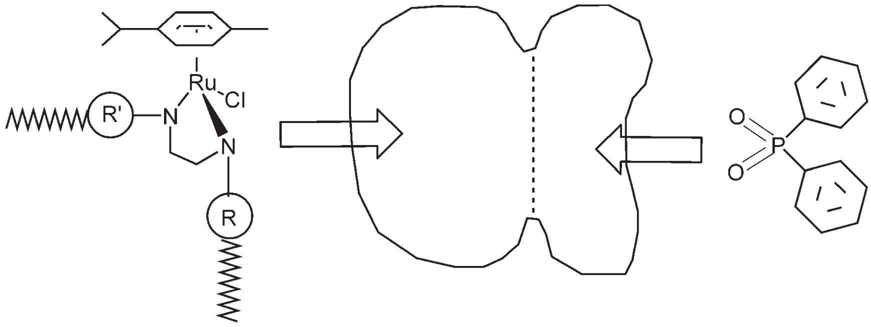
Scheme 32. Synthesis strategy for an imprinted PS bulk polymer for aldol condensation of benzaldehyde with acetophenone (**33**); co-polymerisation of styrene, DVB and vinylstyrene with dibenzoyl-ligated Co^{2+} (**34**); removal of dibenzoyl methane ligand and creation of the empty shape-selective space (**35**) transition state of the aldol condensation.

template molecule. Indeed, the conversion ratios on the bi- to monografted materials for benzophenone, acetophenone, methyl nonyl ketone decrease as follows: 7 > 4 > 2.

In a specific application of the MIP procedure polymerisable metal complexes were used that contain also a non-polymerisable ligand, thus controlling the outer-space environment of the complex.[142] By co-polymerisation of the complexes into rigid polymers and subsequent removal of the non-polymerisable ligand, a cavity (the imprint) is formed and vacated with the shape and/or functionality of the removable ligand. For such an imprint it could be shown that a chiral cavity effect existed. In this experiment, square planar Pt was linked to an achiral polymerisable bidentate phosphine ligand, dppe (1,2-bis-di-4-vinylphenylphosphinoethane), and a chiral imprinting ligand, (*R*)-Bu$_2$BINOL (1,1′-binaphthyl-2,2′-diol), during its co-polymerisation with ethylene dimethylacrylate and a porogen, forming a highly cross-linked and porous polymer (Scheme 34). The chiral cavity could be emptied with HCl, ArOH, and BINOL, showing recovery of (*R*)-Bu$_2$BINOL for 83, 67 and 27%, respectively.[142] This points to the existence of a distribution of sites (cages), bulkier molecules accessing the smaller number. After determination of the rebinding capaci-



Scheme 34. The preparation of a chiral cavity in MIP with buried (BS), selective (SE) and surface sites (SU).



Scheme 33. Schematic presentation of the occlusion of the Ru half-sandwich complex fixed in the polymer bulk by a dual tethering (*left*) and the removable phosphinato ligand mimicking the shape-selective cage for transfer reduction of ketones (*right*).

ties of MIPs opened with the three reactants, it was concluded that with *rac*-Br_2BINOL the BINOL rebinding selectivity of the sites ranged form 2/1 to 97/3 in favour of the imprinted isomer with 85:15 enantiomer selectivity. In terms of an (*R*)-Bu_2BINOL determined cavity, it seems that selective surface sites exist with high activity but devoid of enantioselectivity. At the other end of the distribution, completely buried, inaccessible sites exist. Alternatively, it is always possible that the MIP was freezing the flexible dppe ligand into chirally skewed conformations. It could be experimentally demonstrated that the observed BINOL rebinding data result exclusively from the effect of chiral cavities in the outer sphere of the metal complexes.[142]

Cavity functionalisation as a means of influencing the second coordination sphere of the palladium catalyst, was done by addition of a crown ether[142] since the latter is known to show synergetic effects in asymmetric catalysis.[143] The gain in activity of a palladium complex-crown ether assembly in a Suzuki reaction increased in line with the binding strength of 18-crown-6 with the added cation, *viz.*, $K^+ > Rb^+ > Cs^+ > Na^+$. Upon replacement of this counterion/crown ether ion-pair binding effect by more directional non-covalent bonds, more adequate solutions to the active site homogeneity would become available. Replacing one chloro substituent on each of the phenyl groups of the dppe ligand of the platinum complex with polymerisable dendritic arms was found to provide an interface to the polymer for each complex, resulting in more homogeneous cages.[142]

The well-known homogeneity of shape-selective cages in zeolites, triggered work trying to transfer chirality of chiral organic structure directing agents (SDAs) to inorganic porous crystalline frameworks.[144] The inability to achieve this was attributed precisely to the mobility of the SDA in synthesis conditions, the result of the absence of sufficient non-covalent interactions between SDA and the crystallising inorganic gel. The synthesis of a zeolite BETA with a fractional enrichment of the chiral polymorph A with helical pores, yielded low but significant enantioselectivity values.[145] It is not clear, however, whether in a homogeneous set of zeolitic chiral pores, the repeat distance of the chiral pore in the direction of the pore length, is not far too long to allow transfer of chirality of the pore wall to chemical molecules that still can enter such pores, but usually will be too short to feel the chirality of the pore wall.

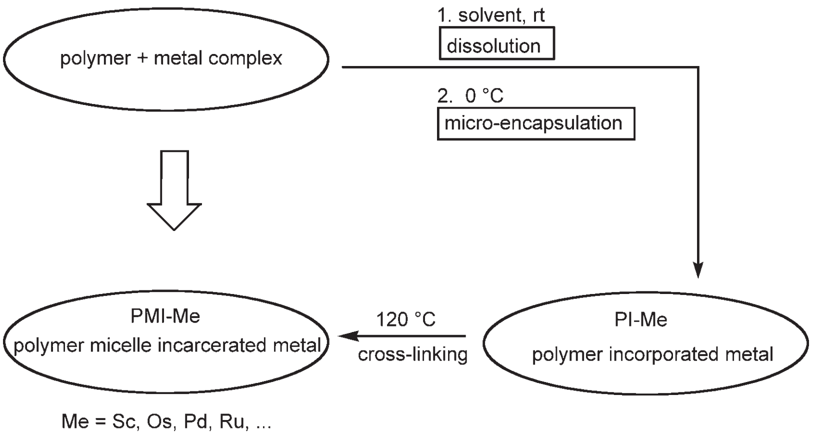
Although recognition of non-functional alkenes is difficult, and that of prochiral alkenes is impossible, several examples exist of successfully silica-imprinted rhodium catalysts for shape-selective hydrogenation of alkenes.[136] In this way, one side of the templated cavity determining the formation of the shape-selective space is still determined by the metal and its organic ligands, while the other side is now entirely siliceous. It was reported that the TOF in the hydrogenation of 3-methylpent-2-ene on a bi-nuclear rhodium complex was promoted 35 times with respect to the same supported catalyst. Shape-selective discrimination of alkenes with different sizes and shapes seems possible as well.[136] It remains, however, doubtful whether a continued effort along such lines will ever be able to beat the well-known results in terms of geometric discrimination and resulting shape selectivity effects obtained with zeolites.[146]

Although the preparation of chiral footprints on an entirely inorganic silica *via* sol-gel techniques received much attention,[147] the examples that show enantioselective discrimination surpassing values of 90% *ee* are limited.[148] An impressive result demonstrated that a silica-imprinted material catalysed hydrolysis of the D-enantiomer of an arginine derivative 35 times faster than the L-enantiomer.[149,150] In this type of footprint catalysis, surface imprinting of a sol-gel silica occurred using a surfactant-derivative of the imprint molecule as template, incorporated in a water-in-oil microemulsion, with added non-ionic surfactant. Added tetraethyl orthosilicate and carboxylate-functionalised silane started the base-catalysed surface imprinting and particle formation in the reversed micelle particles surrounded by the imprint molecules, the head being directed towards the micelle surface. In this way the imprint sites after polymerisation and template removal were created at the surface of the silica particle.

8 Microencapsulated Polymer-Based Catalysts

Catalysts such as $Sc(OTf)_3$ Lewis acid, OsO_4, $Pd(PPh_3)_4$, and $RuCl_2PR_3$, could be microencapsulated in PS-based polymer support.[15] The polymer is physically enveloping the encapsulated catalyst through interaction of π-electrons of the PS benzene rings and the vacant orbitals of the catalyst. Typically, the polymer and the concerned metal complex are dissolved in an appropriate solvent, *viz.*, tetrahydrofuran and cyclohexane, followed by cooling to ensure micro-encapsulation, occurring upon hexane addition. The procedure is shown in Scheme 35. Superior catalysts invariably were obtained compared to homogeneous or supported ones, prepared according to more traditional methods such as grafting.

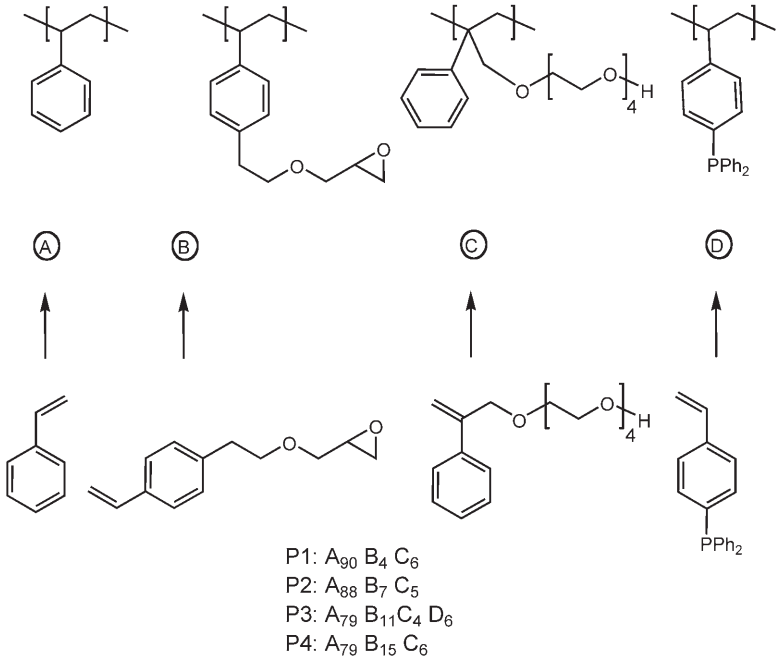
PS microencapsulated Lewis acids with capsule size in the nanometer scale, such as $Sc(OTf)_3$ [PS-MC $Sc(OTf)_3$] were found to be active and selective in a pleiade of reactions, such as C−C bond formation, aza Diels–Alder addition, cyanation, Mannich-type reactions, allylations, Strecker reactions, Michael additions, and Friedel–Craft acylations.[151]



Scheme 35. Catalyst immobilisation *via* incarceration in polymer microcapsules (coaservates) (after ref.[151]).

Microencapsulated OsO_4 either in PS [PS-MC OsO_4], poly(acrylonitrile-*co*-butadiene-*co*-styrene) [ABS-MC OsO_4], or poly(4-phenoxyethoxymethylstyrene-*co*-styrene) [PEM-MC OsO_4], with NMO as preferred oxidant yielded *cis*-glycolated products in good yields starting from many alkenes, including di- and trisubstituted ones.[15] Asymmetric dihydroxylation with high *ee* was possible with ABS-MS OsO_4 in an equimolar solution of water, acetone, acetonitrile, and added $(DHQD)_2PHAL$, as well as by using the Sharpless procedure, *viz.*, two-phase conditions and addition of $K_3Fe(CN)_6$ as co-oxidant. The catalysts could stand repeated batch use without Os loss.

PS polymer incarcerated (PI) Pd was prepared using microencapsulated $Pd(PPh_3)$ followed by cross-linking. The catalyst precursor $Pd(PPh_3)_4$ complex, was dissolved completely in the solvent, although three P ligands per Pd were not included in the microcapsules. The PI $Pd(PPh_3)$ catalyst was used successfully in allylic substitution reactions of allylic carbonates with various nucleophiles.[151] When the PS polymer was replaced with a variant slightly cross-linked with vinyl monomers with polar pendant groups, *viz.*, styrene epoxide and tetraethylene glycol monomer (Scheme 36, P1), a *P1I Pd* catalyst was obtained containing phosphine-free palladium, which was very active in many low temperature hydrogenation reactions at atmospheric pressure.[153,153] Using a compositionally slightly different polymer support (P2), the *P2I Pd* catalyst allowed hydrogenation



Scheme 36. Compositions of random co-polymers used in the PI and PMI methods of catalyst immobilisation (after refs.[152,153]).

under harsh conditions of temperature and pressure. *In casu*, successive benzothiophene batches could be hydrogenated with the same catalysts at 140 °C and 10 MPa of hydrogen. Moreover, this catalyst was completely resistant to sulphur poisoning. When phosphinated polymers were used as support for palladium (P3), the obtained catalyst *P3I Pd* showed excellent activity in Suzuki–Miyaura C–C coupling reactions.[154] Phosphine oxides formed on the copolymer during catalyst preparation could be completely reduced with $HSiCl_3$. Preliminary characterisation of such catalysts revealed that small Pd clusters are present with size below TEM detection limit (*ca.* 1 nm).

All such catalysts, as proven by the case of NMO oxidation with ruthenium of a wide range of alcohols and aldehydes, can, in principle, be used in a continuous flow reactor.[155] The catalyst prepared from the random co-polymer P1 and the complex $[RuCl_2(PPh_3)_3]$, dissolved in THF, formed superior catalysts. Although the catalyst operation is not understood at the molecular level, it is certain that all phosphine ligands were removed, though the two chloride ligands were retained. For comparative purposes, it is clear the latter catalysts are superior to polymer supported perrhuthenate.[156]

When, during the PI method, attention is drawn to micelle-forming conditions, *viz.*, the use of a suitable solvent composition, a random co-polymer with polar groups (like P1) and a $[RuCl_2(PPh_3)_3]$ complex in THF, pore wall hardening is observed in hexane and subsequent cross-linking at 120 °C (Scheme 35). Whereas for preparation of *PI MC Ru* in a THF-hexane system, the hydrophobic domains of the polymer chains are expected to be oriented towards the exterior, 90 % of available ruthenium was supported. In a CH_2Cl_2-CH_3OH medium the orientation of the polymers should be towards the exterior, resulting in a reduced ruthenium loading of 69 %.[157] The same was true with Sc.[158] The microencapsulation method has already led to a microencapsulated metathesis catalyst,[159] polyurea-encapsulated palladium catalysts[160] and $VO(acac)_2$ that allow smooth room temperature epoxidations with *tert*-butyl hydroperoxide.[161]

Dirhodium tetracarboxylate complexes could be readily immobilised on a highly cross-linked PS of an ArGo-Wang-type resin with pyridine attachment by simple agitation of the two components in a solvent.[162] This very systematic approach revealed that polymer backbone (PS), linker (Argopore-type), the terminal group (pyridine) and the catalyst structure, all were parameters contributing to the efficiency of immobilisation of the dirhodium tetracarboxylate complex. The solid catalyst in asymmetric cyclopropanation reactions was active, enantioselective, stable, recoverable and reusable. It was clearly proven that the catalyst was microencapsulated in the polymer and that a release-and-capture mechanism could be excluded. The study amounted to the discovery of a universal support for all standard dirhodium catalysts.

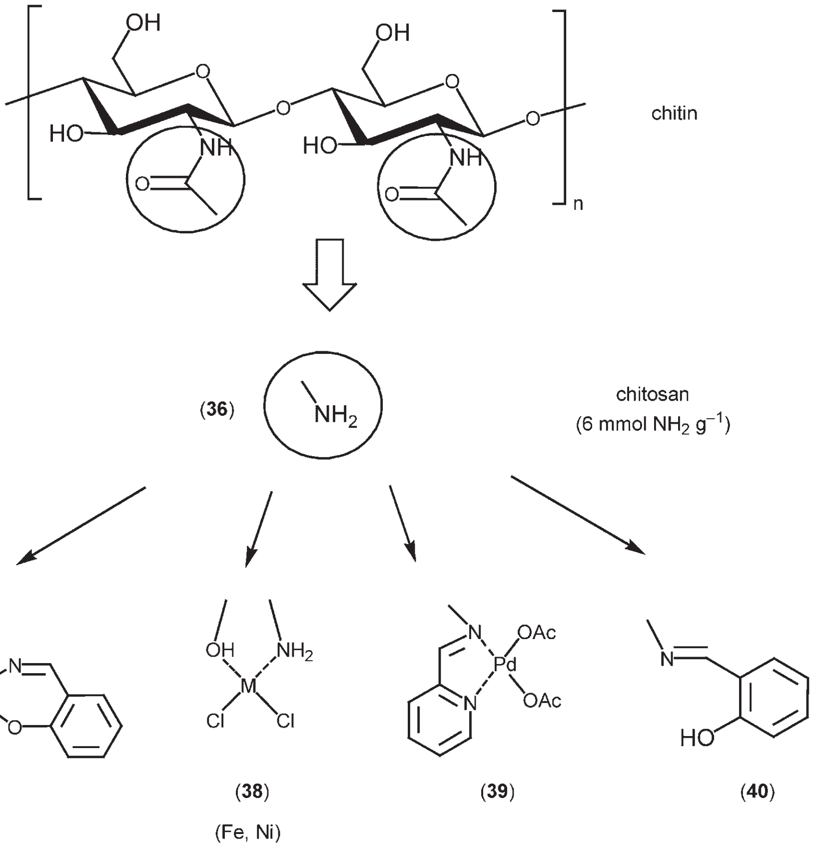
9 Catalyst Immobilisation on the Bio-Polymer Chitosan

Chitin, a natural polysaccharide analogue of cellulose together with its deacetylated form, chitosan (Scheme 37), show unique properties as bio-support for catalysts (and for many other applications such as bio-degradebility, hydrophilicity, lack of toxicity and presence of a chiral polymer backbone). This makes the polymers attractive as supports, also in aqueous medium. Recent review coverage of this topic is available.[163,164] Natural chitosan, *viz.*, from crab-shell, squid pen, shrimp shell, is at this stage difficult to use as a support in catalysis mainly for its strong interaction with metal ions.[165] Therefore in many studies, synthetic chitosan has been used as alternative to this bio-polymer support.

It should be stressed that although theoretically chitin and chitosan consist of acetylated glucosamine and glucosamine units, respectively, the deacetylation reaction is not always quantitative and controls many properties of the type of chitosan obtained.[163] The acid-base properties, *viz.* its dissolution in acid conditions and hydrophilic character, its affinity for metals amounting to approximately 6 $mmol\,g^{-1}$, are directly determined by the degree of deacetylation. It is worth mentioning that the potential site density proportional to the amine group concentration covers the range of the cation ion exchange capacity of zeolites.

The rheological properties of chitosan such as chain stiffness and chain coiling, degree of crystallinity, will determine the porosity and site accessibility and its use as colloidal catalyst support.[163] The low porosity of chitosan flakes, determined by the biopolymer conditioning, *viz.*, during gel formation, imposes a serious limitation to its use as a catalyst support. Gel bead conditions and use of low crystallinity material, limitation of the degree of cross-linking of the chains (*via* the hydroxy groups), use of small particles will allow expansion of the polymer network and increase of the porosity.

Polymer conditioning for catalytic uses[163] either encompasses flaking, or gel bead processing, fibre, hollow fibre and membrane formation, deposition on inorganic supports for composite materials. Chitosan polymer stability is dependant on its degree of cross-linking and allows its use in neutral and slightly alkaline conditions. Gel beads can be prepared by dissolution in acetic acid, followed by alkaline coagulation or co-precipitation. The viscous solution of dissolved polymer can also be extruded followed by one of the



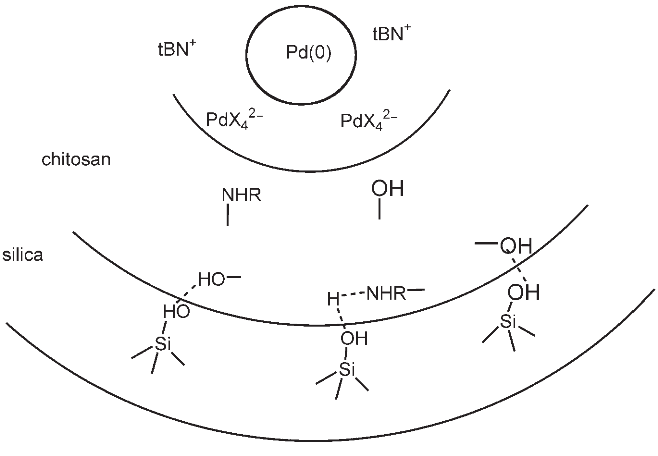
Scheme 37. Structure of chitin and derived chitosan, with some of its derived catalytic structures.

mentioned neutralisation techniques. Casting of acidic solutions in the presence of a porogen, *viz.*, silica, followed by neutralisation, yields chitosan membranes with good porosity. Chitosan can also be immobilised on non-porous and porous supports to form composite materials. It is important to note that all these treatments can be applied with pure or catalyst-loaded chitosan.

To attribute catalytic power to chitosan, the bio-polymer in principle can be subjected to all chemical treatments described earlier, taking into account the presence of amino and/or hydroxy functionalities to do so. In Scheme 37 typical examples are shown for the functionalisation of chitosan. A Me-salen complex (**37**) can be attached directly by coordination of the amine group to one of its apical positions.[165] A site dissolution effect is invoked to explain the inhibited formation of dimers and peroxo-bridged dimers, thereby promoting the formation of active superoxo Co complexes.[166] The Co and Pd versions were active in the autoxidation of cyclohexane.[167] Examples of chelated metal ions by chitosan are numerous (**38**). $ZnCl_2$ modified chitosan can be used for the fixation of carbon dioxide and its transformation into cyclic carbonate.[168] Chitosan-immobilised $NiCl_2$-$PdCl_2$ was used in the carbonylation of Naproxen esters, *viz.*, 6-methoxy-2-vinylnaphthalene. It seems that synergetic effects between the Pd-Ni bimetallic species protected by the polymer are at the basis of the high selectivity. In the hydroesterification of various substrates, nanoparticles seem to be formed ligated directly to the bio-polymer. Pd-iminopyridyl complexes supported on chitosan (**39**), making use of the full load of amine functional groups, *viz.*, 6 $mmol\,g^{-1}$, showed excellent activity in Suzuki and Heck reactions.[169] Pd nanoparticles on chitosan are very efficient catalysts for Heck reactions in ionic liquids.[170] Cross-linked chitosan condensed with salicylaldehyde (**40**) was a good scavenger for Pd ions. Subsequent use was possible as a Heck catalyst, an easily separable and reusable solid. Functionalisation of the primary amine groups in chitosan *via* stable bonds was also possible *via* reductive amination yielding *secondary* amines, amide formation yielding attached phthalimido derivatives, alkylation and Michael addition.[164] Numerous examples have been reported of chitosan supported catalysts for oxidation and hydrogenation reactions, allylic substitutions of the Trost–Tsuji-type, Suzuki and Heck reactions, cyclopropanations, asymmetric dihydroxylation of olefins, carbonylation reactions and synthesis of monoglycerides.[163]

Given the chiral character of the chitosan support, it seems worthwhile to address the effect of the underlying chiral support upon the enantioselectivity of asymmetric reactions. Silica-chitosan hybrids containing Pd,[171] Fe and/or Ni ions[172] were used in asymmetric hydrogenations, yielding average to excellent enantioselectivities. As the attached groups were not chiral, the chiral induction should stem from the close proximity of the underlying chiral backbone of the chitosan polymer. It should be noted that also in these papers *ee* determination occurred solely by optical yield determination. Earlier reported high *ee* values determined in the same way, have been questioned[164,173] as small amounts of dissolved polymer with high α_D values could easily significantly overestimate the optical density of the products with much lower α_D values.

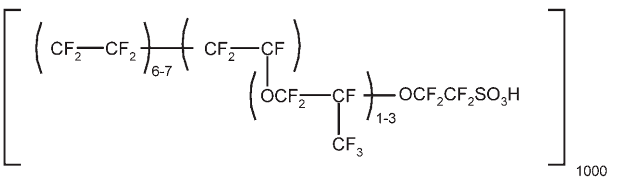
Chitosan-stabilised Pd nanoparticles (3–4 nm) (Scheme 38) can be obtained *via* stabilisation with a diffuse double layer consisting of tetrabutylammonium ions associated with palladium halide, the double layer interacting with the chitosan polymer backbone *via* hydrogen bonding. Thin layers of the polymer can then interact with the surface of an inorganic carrier like silica, either at the external surface of a non-porous material or in the macropore-mesopore system.[165,170] A binary composite with a film of a low loading of copper-chitosan supported on macroporous silica shows a substantially higher activity in the oxidation of hydroquinone than a film of co-polymer of acrylic acid and ethyleneimine on the same inorganic carrier.[165]



Scheme 38. Representation of Pd nanoclusters *via* diffuse double on chitosan polymer, making in its turn a hybrid composite with silica.

10 Nafion® as Support for Metal-Complex Catalysts

The perfluorinated ion-exchange polymer Nafion® (Scheme 39, **41**) based on styrene-sulphonic acids, being structurally and functionally related to Amberlyst® and Dowex® ion-exchange resins, shows excellent acid strength due to the presence of prefluorinated alkanesulphonic groups.[174] Nafion® is unaffected by strong bases, strong oxidising and reducing acids, chlorine, hydrogen, hydrogen peroxide up to 125 °C, while it is thermally stable up to 170 °C or to 200–280 °C upon replacement of the protons by metal ions.[174] Models explain the structure of Nafion® as a group of hydrophilic ionic clusters of around 4–5 nm separated by channels within a hydrophobic perfluorocarbon matrix, with dimensions of the clusters varying according to solvent, temperature and nature of counterions (Scheme 39, **42**). The permeability of the material in non-swollen conditions or in the gas phase is very low. In order to increase the (acid) site accessibility of Nafion®(-H), a silica-based nanocomposite was developed, with nanometer sized Nafion®(-H) resin particles entrapped within a highly porous silica network. Changes of the Nafion®(-H)/silica microstructure in turn affect the catalytic activity. For type I and II catalysts, silicon alkoxides and sodium silicate are used as silica precursors, respectively. For type I catalysts, the Nafion domains are 10–30 nm in size and distributed homogeneously throughout the silica network. Such spheres have a surface area of 100 $m^2 g^{-1}$, about 5,000 times higher than of the non-



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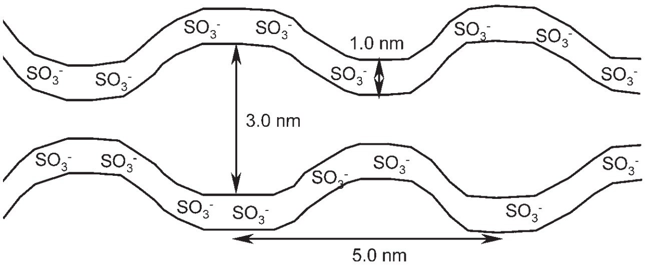

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Scheme 39. Nafion®: chemical composition (41), structure and porosity in hydrated conditions (after ref.[174]).

swollen polymer.[175] Most of the acid-catalysed reactions were performed with type II catalysts.

A more aggregated Nafion® resin, with particle cluster domains of 0.1 μm, shows more resin-like behaviour. Solvents that do not swell Nafion, like THF and chlorobenzene, are not suitable reaction media. Protic solvents and weakly coordinating anions like sulphonate, are important in catalysis with supported cationic palladium.[174] Whereas residual proton acidity seems to be detrimental to the stability of Pd complexes with N donor ligands, this does not occur with Na^+-Nafion. When ion exchange resins are compared for supported bis(oxazoline)Cu complexes, Nafion/silica is the preferred support for asymmetric cyclopropanations. For complexes covalently linked to resin-type supports, the catalytic behaviour is comparable in optimised conditions.[176] Recently, Nafion®(-H) was reported to be able to catalyse the oxidations of organics with hydrogen peroxide.[177]

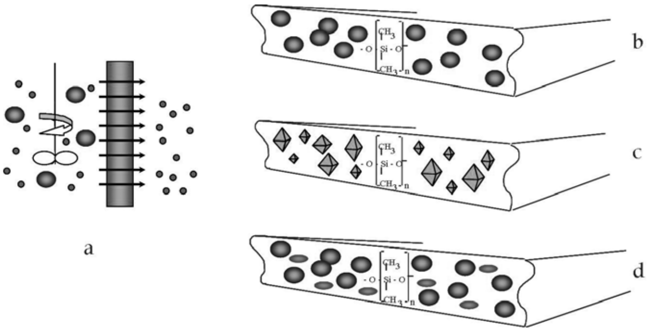
11 Catalysts Combined with Polymeric Membranes

Shaped as a membrane, polymers can offer specific advantages to catalytic processes as they intensify processes by combining reaction and separation. Polymer-based catalytic membrane applications can be divided in two major classes.

'Catalytically active' membranes have the catalyst incorporated in the polymer or deposited on it. They can be subdivided in membrane encapsulated catalysts and heterogeneous or homogeneous catalysts embedded in a polymeric matrix. A well chosen polymeric environment can regulate beneficially the selective sorption of reagents and products. The catalyst activity should remain guaranteed over the whole membrane preparation process. Moreover, a stable suspension (in the case of a heterogeneous catalyst) or good dissolution (in the case of a soluble catalyst) should exist. Additives can be co-incorporated to promote reaction yields. When embedding a homogeneous catalyst in a polymeric membrane, catalyst heterogenisation is simultaneously realised. Catalyst leaching remains a challenge.

The second class consists of 'membrane-assisted processes', also referred to as 'inert catalytic membrane reactors' (CMRs) where 'catalytically passive' membranes are used, the membrane merely retaining the catalyst in the reactor volume. The membrane thus simply serves as a barrier to drain off reactants and/or to supply products.

An appropriate selection of polymer materials or the implementation of small modifications (such as cross-linking) allows the use of polymeric membranes in many chemical reactions (Scheme 40).



Scheme 40. Catalytically passive (**a**) and catalytically active membranes: homogeneous (**b**), heterogeneous (**c**) and homogeneous with additive (shown as ellipses) (**d**).

11.1 Catalyst Encapsulation

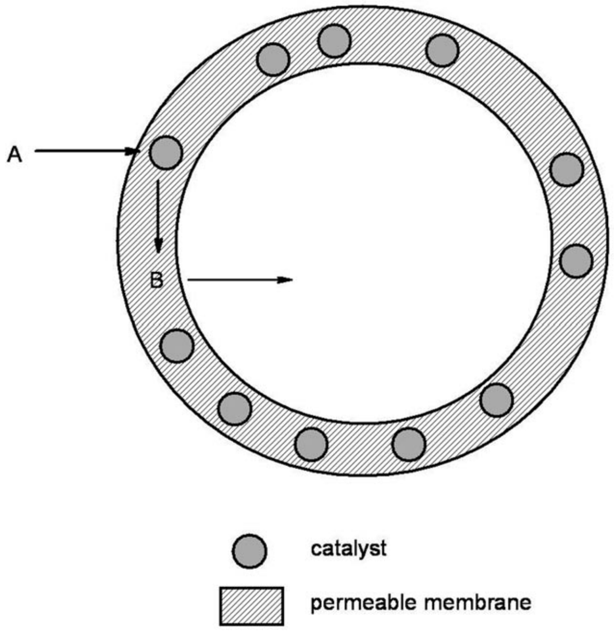
Encapsulation refers to the confinement of a liquid solution within small capsules enclosed by a polymer or a surfactant containing the catalyst.[178] A potentially high interfacial specific area is thus created and the recovery of the catalyst is facilitated.

The concept of capsule membrane-supported phase-transfer catalysts (CM-PTC) was introduced by grafting PTCs onto the surface of an ultrathin, porous capsule membrane.[179] Nylon capsules were prepared by adding dropwise an amine solution to a terephthaloyl chloride solution, containing a trimesoyl chloride cross-linker.[180] The tetraalkylammonium PTCs were supported on the obtained capsules. Capsules have no way to a provide fresh organic phase to the inner portion of the capsule or to remove continuously product from that phase. Pd and Au nanoparticles were introduced in the shell of hollow polyelectrolyte-based capsules. The $CaCO_3$ core was removed after formation of the polyelectrolyte layer (Scheme 41). Some metal leaching appeared in the Sonogashira reaction when applying DMF as the solvent.[181]

11.2 Incorporation of Heterogeneous Catalysts

To decrease Pd consumption, hydrogen-permeable membranes were prepared using a silicone matrix, *via* ligation to an organosilicon compound covalently bound to a silica surface.[182] Similar types of CMs were tested in a variety of reactions with different kinds of catalysts.[183,184]

A zeolite Y with Fe-phthalocyanine (FePc) complexes immobilised in its cages was the first PDMS incorporated catalyst.[185] In the cyclohexane oxidation, the PDMS-membrane formed an optimal 'solvent phase' contacting both immiscible reagent phases. Solvent thus became redundant in such a set-up, and water molecules, present in the peroxide phase, were excluded from the hydrophilic catalyst, while the re-



Scheme 41. Catalyst encapsulation (after ref.[181]).

agents were sorbed excessively in the PDMS to form an abundant reservoir of reagents. The concept was claimed to be applicable to any catalyst applied in reactions that involve immiscible reagent phases, provided that the appropriate polymer was selected with respect to selective sorption and diffusion of reagents and products.[183] Whereas the formed cyclohexanol and cyclohexanone were found in both the aqueous and the organic phase,[186] products from an *n*-dodecane oxidation appeared at one membrane side only, thus integrating reaction and full separation in one single process unit.[186]

The versatility of the PDMS-occluded membrane systems was further proven with the Ti-containing catalysts TS-1[187] and Ti-MCM-41.[188] In the absence of a solvent, undesired blank reactions were suppressed and the absence of water in the catalyst pores limited the epoxide ring opening in epoxidations.[189,190] However, consecutive oxidation reactions gained importance as no solvent was present to remove the products from the catalyst pores.[189] Reaction rates could be increased by adding modifiers to the membrane[191] or by blending hydrophilic polymers with the PDMS, improving the balance between the sorbed amounts of peroxide and alkane.[192]

Whereas ethyl acrylate-based pseudo-interpenetrating networks as polymer systems used for catalyst incorporation, avoided membrane cracks upon zeolite incorporation, active sites were more blocked by the penetrated polymer chains.[193,194]

Heteropolyacids (HPA)s like $H_3PMo_{12}O_{40}$ were incorporated in polyphenylene oxide[195,196] and polysulphone, leading to a drastically changed reaction selectivity.[197] The incorporated catalyst was much more active due to the enlarged active surface, created by the fine distribution of the filler. The high permeability of the membrane for acetone was suggested to further increase the selectivity for acetone. α-Pinene was hydrated efficiently after incorporation of the HPAs in a cross-linked PVA[198] after hydrophobisation with acetic anhydride.[199] When incorporating other heterogeneous acid catalysts in PDMS for the same hydration,[200,201] the hydrophobic matrix decreased the activity, due to reduced water sorption.

Gas permeable ionic liquid (IL)/polymer gels were used to incorporate Pd/carbon catalysts. The IL[202] and the Pd catalyst were thus incorporated simultaneously and the resulting membrane was applied as a contactor.[203]

11.3 Heterogenisation of Homogeneous Catalysts

An important problem occurring in liquid phase reactions with membrane occluded homogeneous catalysts is leaching of the complex and/or the incorporated additive. In most cases, the catalyst/polymer interaction is believed to be a combination of mere van der Waals interactions and some steric constraints of the surrounding polymer chains on the catalyst.[204] Solvents in which the complex does not dissolve, are preferred to perform the reactions.[204,205] Alternatively, leaching could be greatly reduced by placing bulky groups on the catalyst, by preparing its dimeric or oligomeric forms or by selecting more appropriate reaction conditions, *viz.*, using solvents that combine moderate membrane swelling with low solubility of the complex.[206] Adaptations at the level of the polymeric matrix could also restrict leaching, *viz.*, increasing the degree of cross-linking of the membrane, decreasing the MW of the polymer chains, or blending with other polymers to change the affinity.[207] In discontinuous reaction modes, the polarity of the reaction medium, and thus the solubility of the transition metal complex (TMC), changes as products are formed and reagents are consumed.

Ru-BINAP, with co-incorporation of acids,[208] and Jacobsen catalyst were the first homogeneous TMCs to be occluded in PDMS.[209] The results indirectly confirm the preservation of the intact structure of a TMC in PDMS, since an excessively strong interaction between the polymer and the complex would have destroyed the chiral induction. PVA was later reported as a useful alternative for PDMS. Its very different sorption characteristics open perspectives for reactions with more polar substrates that suffer from low sorption in PDMS.[210]

With some Me-phthalocyanine complexes in PDMS a significantly increased activity upon occlusion was reported for oxidation reactions,[211] a clear correlation being found between the PDMS sorption and the reactivity of different oxidised alcohols.[212,213] In the epoxidation of deactivated substrates, like hydroxyalkenes, ketone formation can be suppressed by electron-donating axial ligands, like imidazole. With this additive co-incorporated in PDMS, the ketone formation was completely absent. The 20-fold increased activity was attributed to the lowered mobility of the axial ligand in the restrictive PDMS phase, resulting in a prolonged co-ordination to the active centre, and to the PDMS influence on better balanced concentrations of alkene, ligand and peroxide around the metal centre.[214,215]

Homogeneous Ti-catalysts have been incorporated in polyvinylidene difluoride for the oxidation of secondary amines with successful catalyst recycling and activities comparable to the homogeneous system.[216]

Recently, TMCs have also often been immobilised in polymeric membranes through the co-heterogenisation of the ionic liquids in which the reactions run. The catalyst/IL combination can either be loaded in the pores of an existing membrane,[217,218] or can be mixed with the membrane forming polymer. In the latter, improved mass transfer in liquid-phase hydrogenations induced higher activities than with the unsupported system.[219]

Polymer incorporated metals or metal clusters show specific metal/polymer interactions, sometimes leading to exceptional catalytic behaviour.[220] Pd incorporated in polymeric membranes has been used to hydrogenate a wide set of substrates. Pd can be brought inside the membrane by refluxing a Pd solution in a solvent that made the membrane swell excessively.[221] A nylon-6 membrane was functionalised with a $Pd_3(OAc)_6$ cluster to suppress trans-isomerisation in the hardening of oil by using a regime of forced flow through the membrane pores. This technique also improved other processes where internal diffusion limitation was important and the use of finely dispersed catalysts was not desired.[222,223] Pd anchored on polymers, subsequently retained in the micropores of hollow fibres, was used in a CMR set-up with the diene at the inner side of the fibre and H_2 permeating from the outer side. Conversion and monoene selectivity were higher than in a similar fixed-bed reactor, since the CMR succeeded in creating a concentration gradient of hydrogen between the inlet and outlet of the reactor, matching that of the diene at the other side of the hollow fibre. Incorporated Pd and Pd-bimetallic clusters in polyamidoimide (PAI), where cluster sizes varied with the solvent used and the stirring time of the metal salt/polymer solution. When silicones were used instead of PAI, larger aggregates were obtained, due to the higher mobility of the atoms in the silicone matrix.[224,225] *In situ* preparation of the Pd clusters in the PDMS matrix from Pd acetate precursors was found to lead to more efficient catalysts *via* incorporation of clusters that were heterogenised already on inorganic supports before incorporation. Later on, clusters were prepared in polyether block amide[226] (PEBA) and PEBA modified by blending with polyvinylpyrrolidone and silica.[227] The latter composition proved better in the hydrogenation of 4-chlorophenol due to improved substrate diffusion through the polymer matrix and the smaller size of the Pd clusters formed. In still another approach, membranes were first dipped into a solution of tetraethyl titanate.[228] After hydrolysis, TiO_2 remained deposited in the pores to which Pd acetate was subsequently introduced from solution. In a so-called ‘infusion approach’ in which the free volume elements in solid polymers are used to disperse metal based nanoparticles,[229] a volatile metal precursor is infused in the evacuated free volume elements of the polymer and subsequently reduced. Pd nanoparticles were immobilised in polyelectrolyte films *via* 2 concepts. Either the nanoparticles served as polycation or polyanion during the film deposition, or metal ions were incorporated into the film and then reduced to form the nanoparticles.[230] An interesting application of Pd-containing membranes consisted of the controlled synthesis of hydrogen peroxide directly from mixtures of molecular hydrogen and oxygen with compositions outside the explosion range.[231]

Entrapped bi-metallic catalysts in a variety of polymers[232,233] referred to as ‘Lentikats’ were commercialised. Lentikats have a lenticular shape with dimensions of 1.5–5 mm diameter and a thickness of 200–400 μm, thus showing minimised diffusion limitations. Catalyst enlargement was realised by linking them to chitosan.[234,235] The particles can be hydrogels, like in the case of PVA, or cross-linked elastomers.[232]

Similar PDMS spheres were formed *via* suspension polycondensation of TEOS with oligomeric pyridine containing Si to retain Mo species. Their epoxidation activity was superior to both that of soluble $MoO_2(acac)_2$ and of poly(benzimidazole)-supported Mo.[236]

11.4 Membrane-Assisted Catalysis

Membrane-assisted catalysis bridges the gap between homogeneous and heterogeneous catalysis combining the advantages of both. The key success factor is the choice of an appropriate membrane that allows full catalyst retention and complete product passage. In contrast with a fixed-bed reactor, membrane-assisted catalysis has the advantage that fresh catalyst can be supplemented easily, even in a continuous process.

Stable catalysts and short reaction times to realise high space-time yields should be involved.[237] In the continuous mode, where the reactor permanently operates at high conversion levels, the educt concentration is kept low. Since remaining free ligands are washed out during the initial phase of the membrane-assisted process,[238] catalyst purification prior to reaction can be shortened. Membrane processes, like pervaporation (PV) and NF, have been combined already with catalysis.

By far the most studied reaction in pervaporation-assisted catalysis, is the esterification as a typical example of an equilibrium limited reaction.[239] The thermodynamic equilibrium can be easily shifted using a large excess of one of the reagents, or by removing one of the products. PV offers an interesting alternative since the separation is not limited by relative volatility. Moreover, energy consumption is generally lower, because only a fraction of the feed is permeating to undergo the liquid to vapour phase change. PV can also be operated at lower temperatures, which can better match the optimal conditions for reaction, an aspect of high importance in biotransformations.[240] Modelling is important for these processes because, e.g., membrane permeability may change with temperature and composition of the mixture. A complex situation arises since such parameters influence the rate of ester production. In general, a highly permeable membrane with long-term stability is the main requirement,[241] together with the correct membrane surface area/volume ratio.[242] No solvent at all was permeated with esterifications in ionic liquids, since no driving force exists for the solvent to permeate, due to the low partial pressure.[243] Using PVA membranes coupled to esterifications, the secondary alcohol groups in the PVA could also become esterified by the acid, leading to the loss of the separative properties of the membrane.[244] Solutions to solve the problem of unwanted esterification of PVA functional groups, are the so-called catalytically active PV membranes, i.e., 'bi-functional' membranes endowed with both catalytic and separative properties, made from blends of strongly acidic and highly hydrophilic polymers. Better separations were realised by preparing multilayer membranes by casting the catalytically active polymer mixture on top of a PVA membrane.[245,246] H-Nafion tubes were used as alternative one-layered 'bi-functional' membranes.[247] Coupled to a homogeneous Diels–Alder alkylation, the reaction temperature was maintained to the desired low temperature[248] thanks to the heat of evaporation needed for the compounds to permeate. Finally, pervaporation has been applied to stabilise microemulsions during oxidations with hydrogen peroxides. Whenever large amounts of peroxides are required, the microemulsions become destabilised by the simultaneous addition of large amounts of water. This water can be drained by pervaporation.[249]

Vapour permeation instead of pervaporation coupled esterifications have been used when the applied membranes were too much plasticised when contacting the liquid state feed.[250] In the gas phase methyl-*tert*-butyl ether (MTBE) decomposition, methanol was selectively removed *via* gas separation.[251]

When rather small catalysts, like TMCs, have to be retained in pressure driven membrane processes, several approaches are possible. The catalyst can be enlarged to dendrimers[252–254] or hyperbranched polymers[255] so that it can be retained by UF membranes. The catalyst can be covalently bound to soluble polymers or insoluble supports,[256–258] or membranes with a lower molecular weight cut-off (MWCO) can be selected, possibly at the expense of membrane flow. A decrease in the MWCO of the membranes can be achieved by selecting tighter membranes or by changing the reaction conditions that influence this MWCO.[259] Another approach to enlarge TMCs, is to add micelle forming amphiphiles that encapsulate the catalyst,[260] leading to the so-called micellar enhanced ultrafiltration.

In an attractive CMR concept, called 'cascade CMR', two reactions with different optimal reaction conditions were carried out in series, separated by a UF membrane to retain both (bio)-catalysts in their appropriate reactors and allow both reactors to work in optimal conditions.[261,262]

Photocatalysis with dispersed TiO_2 particles is commonly integrated with membrane separation, either with MF, UF, NF or even RO.[263,264] In order to avoid membrane fouling, TiO_2 catalysed photocatalytic degradation of dyes was combined with membrane distillation. Such processes can only be viable if waste heat is available.[265]

Nanofiltration is a relatively new membrane process with a nominal MWCO in the range of 200–1000 Da. Its application in water treatment has been growing rapidly over the past decade. Only in a few cases did these aqueous applications involve catalysis to remove endocrine disruptors[266] or sulphides[267] *via* catalytic oxidation. Wet air oxidation was combined with aqueous NF and biological treatment to treat PEG-containing waste waters. The integrated process thus showed a much higher treatment efficiency than any of the single optimised processes.[268] Non-aqueous applications [often referred to as solvent-resistant nanofiltration (SRNF) or organic solvent nanofiltration (OSN)] are an emerging, but increasingly popular, field as the number of possible new applications is amplifying. With the advent of better performing membranes, commercially available,[269] or limited to laboratory preparation,[270,271] combined reasonable solvent fluxes with high catalyst rejection are achievable.[272–275] Sometimes, a trade-off exists when the best conditions for catalysis are incompatible with those for filtration.[276,277] The introduction of high-throughput membrane testing[278] and combinatorial synthesis techniques[279] for SRNF membranes might speed up developments. SRNF has recently been coupled to nanocolloid-catalysed reactions to realise the first efficient recycling of this type of pseudo-homogeneous catalysts for which filtration remained problematic.[280] Also ionic liquids, used to stabilise homogeneous catalysts and avoid Pd black formation in Suzuki reactions, were very well retained.[281]

Extrapolation from laboratory scale low volume, dead-end nanofiltration to larger systems, e.g., cross-flow nanofiltration, may be difficult.[282] SRNF-coupled catalysis can either be run continuously or batch-wise. Concentration polarisation (due to insufficient stirring of the feed at high solvent fluxes and high retentions), increasing osmotic pressure and fouling (e.g., due to precipitation of retained compounds due to their high retention) can all induce flux decline, in addition to compaction of the membrane.[283]

12 Catalyst Immobilisation on Silica and Related Inorganic Supports

Although it is not the aim to treat exhaustively the immobilisation of metal complexes on inorganic supports, its comparison with what precedes is obvious, as in most cases similar concepts have been used to perform the same type of catalytic reaction. In many cases, mesoporous and macroporous silica gel have been used. As far as the anchoring of catalytic moieties is concerned, the key step consists of the functionalisation of the silica surface, populated with silanol groups. The pretreatment temperature of the parent silica determines the nature of the hydroxy groups (isolated, geminal, hydrogen bound), their location and reactivity. In nanostructured mesoporous silica of the MCM-41-type, the reactivity of the siloxanes is considered to be sufficient for covalent linking with a tether.[284] The transformation of the silica surface is possible *via* a pleiade of commercially available silylating agents, yielding the same functionalities mentioned also for polymeric supports. Concomitant or subsequent silylation with trimethylchlorosilane is possible to ensure the neutralisation of residual hydroxy groups.

Functionalised silica surfaces can undergo chemical grafting in the same way as polymeric supports with the same pendant group. An exhaustive review with all successfully prepared organic-silica hybrids is available.[285] Good and stable activity is obtained in a majority of the cases, which is of the same order of magnitude as in the homogeneous case. Recyclability, at least for a limited number of cases, is mostly not an issue. Just as in the case of polymers, the support causes site isolation, although it sometimes imposes its sorption properties on the catalytic system.[286] The latter is often determined as a key parameter to rationalise the observation of enhanced TOFs. The available pore size of ordered mesoporous materials (OMM), *viz.*, silicas, can be controlled over a range extending from 2 to 30 nm with uniform hexagonally arranged one-dimensional pores, or with a tri-dimensional cubic pore structure.[287]

Microporous molecular sieves have received much attention for their specific immobilisation potential of catalyst complexes *via* entrapment or encapsulation. The procedure, if successful, yields isolated complexes in cages of molecular dimensions. The term “ship-in-a-bottle” immobilisation has been coined to this technique.[288] The claims of the zeolite encapsulated complexes are well supported spectroscopically. Next to site isolation, pronounced zeolite sorption effects determine the activity. Adaptation of a rather flexible host complex in a rigid matrix mostly causes tight fitting, sometimes resulting in complex distortion and even incomplete coordination. Mainly in oxidation reactions with (hydrogen) peroxide, the latter phenomena are at the basis of selectivity for allylic oxidation pathways or initiate radical chain reactions. Compared to the homogeneous phase, well fitting zeolite encapsulated complexes oxidise alkane and alkene substrates *via* a kind of oxygen rebound mechanism, inhibiting strongly the occurrence of radical chains.[289]

13 Conclusions

In this article the authors have attempted to make a tutorial review on catalyst immobilisation from the viewpoint of the catalyst designer, emphasising the use of promising concepts in this area, rather than trying to be exhaustive.

The use of polymeric catalyst supports is covered in a much more exhaustive way than that of siliceous supports. However, the similarity in the approach and the results is striking. The polymers allow the use of an extended range of functional groups *via* straight organic synthesis for linking metal complexes. On functionalised silica surfaces very related chemistry occurs after correct functionalisation of the surface silanols, *viz.*, after neutralisation of residual acidity. The catalytic behaviour on such systems can be manipulated by the creation of permanent porosity during cross-linking or of temporary porosity during swelling of a polymer gel. Microencapsulated polymers often suffer from a lack of tight fitting between a flexible host and a flexible guest. The use of siliceous pores, often causes a tighter fit between the catalytic host and guest, sometimes causing stereochemical strain on the catalyst. Both types of supports show advantages and disadvantages, when the behaviour of specific catalytic complexes, supports and reaction types are combined.

One heavily searched for goal consists in the direct transfer of chirality from surfaces to the catalyst. The use of bio-polymers in this respect seems promising.

Most of the studied hybrid catalysts show, according to the authors, absence of metal/ligand leaching and sufficient stability for successful use in batch operations. Unfortunately, the successful data mostly refer to less than 10 successive reuses. Continuous operation for a few thousand turnovers is never achieved and no information is available on the ultimate stability of the catalyst (support) in such conditions. Probably, the best properties of both classes of supports, will be present in so-called hybrid nanocomposites, consisting of the fixation of thin layers of an organic polymer on an inorganic (porous) support.

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