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Immobilized Catalysts

Solid Phases, Immobilization
and Applications

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Immobilized Catalysts

Solid Phases, Immobilization and Applications

Volume Editor: Andreas Kirschning

With contributions by

W. Bannwarth · D. E. Bergbreiter · B. Desai · N. End · R. Haag ·
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Preface

Over the last decade the environmental setup has changed for synthetic organic chemists to a considerable degree. So far synthetic organic chemistry had focussed on methodology development which mainly deals with the development of new reactions as well as new reagents and catalysts. These ought to be able to perform preferentially highly selective (chemo-, regio- and stereoselective) synthetic transformations, often applied in the context of complex and highly functionalized molecules.

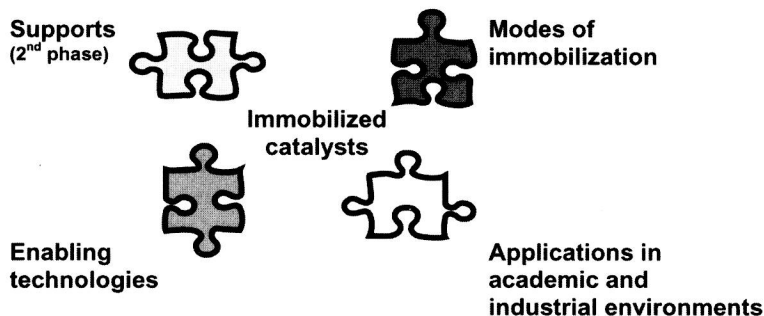
Except for the synthesis of peptides and oligonucleic acids, little attention has been spent on the question of how synthesis can be carried out in an environment of sophisticated technologies which includes improved hardware. While peptides and oligonucleotides are conveniently prepared by Merrifield's solid phase technique, solution phase synthesis of most other synthetic targets have not been substantially replaced by this solid phase approach. Without discussing this aspect in detail it is obvious that today a renaissance of sophisticated solution phase synthesis can be noted. Immobilization of reagents and particularly catalysts, an old concept indeed, recently returned back onto the stage and this is addressed in this volume of *Topics in Current Chemistry* in a broader sense.

The volume consists of eight chapters and is intended to introduce the reader to various aspects of immobilizing catalysts. Particular focus was spent on the concept that immobilization is only one out of many new enabling technologies introduced to organic synthesis and that the future of intelligent use of enabling technologies is associated with the clever and successful combination and integration of these techniques. As enabling techniques ionic liquids or perfluorinated solvents need to be listed, as well as the use of microwave assistance and continuous flow devices, and these aspects have been incorporated into this volume. In fact, immobilization of homogeneous catalysts not only requires detailed knowledge on the performance and properties of homogeneous catalysts. Successful applications of homogeneous catalysts in an heterogeneous environment must take the second phase and the mode of immobilization into account, often underscored by synthetic organic chemists.

Thus, this volume tries to tell a story. Definitely, it is not the only story to be told on immobilized catalysts. Our story starts with the phase to which the catalyst is attached to and further proceeds to the question of how homogeneous

catalysts can best be fixed to a second phase. From there the journey proceeds to actual synthetic applications of catalytic processes with particular focus on Pd-catalyzed transformations before two contributions will show how immobilized catalysts can conveniently be combined with other enabling technologies, namely microwave assistance and continuous flow reactors.

Finally, the breakthrough of new technologies can clearly be spotted when they have paved their way into industrial applications. Then such technologies are versatile and economical enough to create products or improve processes on larger scales. Little details on these aspects can be found in the literature, as chemical and pharmaceutical companies tend to be vague about the introduction of new concepts into process engineering. This volume covers two reports on immobilized catalysts in industrial settings. From these reports one can conclude that immobilized biocatalysts have reached the production lines already while solid phase attached chemical catalysts are still struggling through a jungle composed of lack of efficiency, leaching problems and finally recyclability of these catalytic systems as well as attitudes and closely defined perceptions among those who deal with process engineering. However, it is only a matter of time before immobilized catalysts will become a common tool outside the academic world.



Finally, I have to thank all contributing authors and colleagues who made this volume possible. It has been a great privilege and honour to assemble a magnificent crew of outstanding scientists who put a lot of effort into the production of state of the art manuscripts and who at the same time ideally held all deadlines set by the editor. Particular thanks are directed to Springer Verlag and Frau Marion Hertel as well as Frau Birgit Kollmar-Thoni who always gave support and encouragement when required.

Hannover, August 2004

Andreas Kirschning

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Polymeric Supports for the Immobilisation of Catalysts

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Abstract This chapter summarises the most frequently used polymeric supports for catalysis and highlights some recent developments in the field. Two classes of polymers, crosslinked solid phase supports and non-crosslinked soluble polymeric supports, are discussed with the focus on covalently attached catalysts. In addition, for soluble polymeric supports the different separation techniques are critically compared and evaluated for their application in catalysis.

Keywords Solid phase supports · Soluble polymeric supports · Hybrid supports · Dendrimers · Separation techniques · Homogeneous catalysis

Abbreviations

<i>BET</i>	Brunauer–Emmett–Teller adsorption isotherm
<i>BINAP</i>	2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl
<i>DB</i>	Degree of branching
<i>DCM</i>	Dichloromethane
<i>DMF</i>	<i>N,N</i> -dimethylformamide
<i>DVB</i>	Divinylbenzene
<i>GPC</i>	Gel permeation chromatography
<i>Leu</i>	Leucine
<i>MPEG</i>	Monomethylated poly(ethylene glycol)
<i>MWCO</i>	Molecular weight cut-off
<i>SEC</i>	Size exclusion chromatography
<i>PAMAM</i>	Poly(amido amine)
<i>PD</i>	Polydispersity
<i>PEG</i>	Poly(ethylene glycol)
<i>PEI</i>	Poly(ethylene imine)
<i>PPI</i>	Poly(propylene imine)
<i>PS</i>	Polystyrene
<i>ROMP</i>	Ring opening metathesis polymerisation
<i>TADDOL</i>	$\alpha,\alpha,\alpha',\alpha'$ -Tetraaryl-1,3-dioxolane-4,5-dimethanol
<i>TLC</i>	Thin layer chromatography

1**Introduction**

Polymeric supports revolutionised organic synthesis and catalysis at the end of the twentieth century and became a major driving force for lab automation and modern separation techniques [1]. Investigations on polymer-supported catalysts have been ongoing for many decades [2–4] but it wasn't until the explosion of interest in the field of combinatorial chemistry that the subject became an area of intense research activity [5–8]. Also in the last decade, a rapidly increasing number of new polymeric supports, crosslinked (insoluble) [9–12] and non-crosslinked (soluble) polymers [13–17], have been published and used for polymer-supported catalysis. The reader should be aware of the fact that there is no polymeric support for general application in organic synthesis and catalysis. Every polymer has its drawbacks (e.g. chemical stability, polarity etc.) and hence can be used only within a certain range of reaction conditions.

In this chapter, we will describe the structure and the properties of the most frequently used polymeric supports as well as the effects of different spacer molecules (Fig. 1). Spacer molecules, as compared to linker or ligand molecules, are used to provide more accessible catalytic sites and to modify the properties of the polymer matrix (e.g. polarity, swelling characteristics). The two major classes of polymeric supports, solid and soluble polymers, will be discussed with respect to their application in catalysis. Detailed examples will be found in the chapters by Bergbreiter and Uozumi. This chapter will focus on cova-

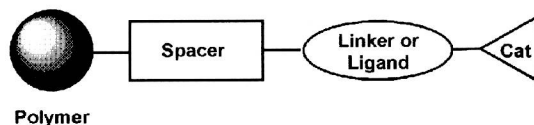


Fig. 1 General structure of a polymeric support for catalysis application

lently attached catalysts and will not cover immobilised enzymes, molecular imprinted polymers (MIPs) or inorganic supports [18, 19].

2

Polymeric Solid Phase Supports for Catalysts

2.1

Polystyrene-Based Resins

Functionalised polystyrenes are available as linear non-crosslinked and as crosslinked polymers. The latter ones, generally referred to as PS resins, are among the most commonly used solid supports for solid-phase organic synthesis and catalysis. Nowadays, numerous types of polystyrene resins are commercially available. They can be obtained in different sizes, loading capacities (amount of functionalisation) and different degrees of crosslinking. In addition resins with a large variety of different linker groups, reagents and catalysts have been commercialised over the last 5–10 years [20].

Macroporous and microporous polystyrene resins are typically prepared by suspension polymerisation [21, 22]. The basis of this process is the dispersion of an organic phase (constituted of a monomer, a radical initiator, a crosslinking agent and eventually a comonomer) into an aqueous phase [23, 24]. The size of the initial droplets is adjusted by emulsifying the organic phase under stirring in the presence of a polymeric surfactant, which governs the final size and the final size distribution of the beads after polymerisation [21, 22]. The different bead sizes are then separated by a multiple sieving process. Resin beads used for solid-phase synthesis and catalysis are spherical particles, typically in the range of 50 to 500 μm , which can be easily handled.

In order to obtain insoluble resins, a crosslinking agent has to be used for the synthesis of the beads by suspension polymerisation [9, 10, 22]. A crosslinking agent is generally a bi- or multifunctional molecule that can be incorporated in two or more growing chains during the polymerisation process, leading to interconnected chains. The most popular crosslinking agent, used in the presence of styrenic monomers, is divinylbenzene (DVB) but many other crosslinkers have also been used to obtain special effects (see below).

For chemists working with polymeric supports, it is of great importance to have a good knowledge of the internal structure and morphology of the mi-

microbeads, because they strongly influence the physical properties and as a consequence the reactivity of the functional sites. For example, if active sites are located in highly crosslinked microdomains, as can be the case in macroporous resins, they will remain inaccessible for reactions and the effective loading will be lower than the theoretical one [25].

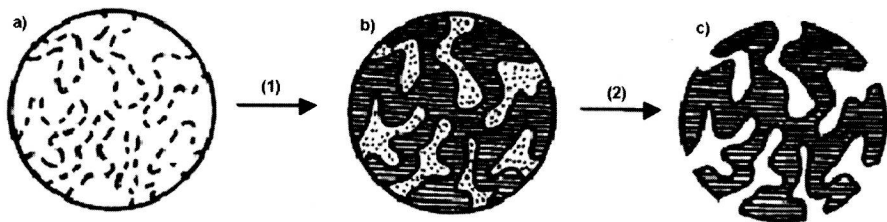
Even in microporous resins, one can expect some heterogeneities due to the different reactivities of the monomers and crosslinking mixtures involved in the suspension polymerisation process [22, 26]. However, it has been demonstrated experimentally that the distribution of reactive sites is homogenous throughout the whole bead [27–30]. Based on geometrical considerations, one should also be aware of the fact that in microbeads with a diameter of 100 μm , 50% of the active sites are within the first 10 μm of the outer shell [27].

2.1.1

Macroporous Resins

Macroporous resins are generally highly (>5%, typically 20–25%) crosslinked polystyrene microbeads [9, 10, 21]. The term “macroporous” refers to their inner skeleton, which is made of a permanent porous structure even in the dry state (cf. Scheme 1c). Historically, functionalised macroporous resins have mainly been used for ion exchange and separation. Nowadays, many new applications, especially in the field of polymer-supported reagents [31, 32] and catalysts [5, 7], have been developed.

Macroporous resins are prepared by suspension polymerisation of monomers such as styrene, vinyl pyridine, acrylamide or glycidyl methacrylate with a porogen agent, such as a low boiling solvent (Scheme 1) [21, 33]. Thus, a mixture of monomer with eventually a comonomer and a crosslinking agent is copolymerised after dispersion in aqueous medium in the presence of the porogen, which remains within the beads during the polymerisation and acts as a template for the formation of the permanent internal porous structure of the final resin. After completion of the polymerisation the porogens are re-



Scheme 1a–c Synthesis and structure of macroporous resins. **a** Polymer network forming; **b** porogen phase acts as pore template; **c** dry macroporous resin with large interconnected pores. (1) Porogen and network start to phase separate; (2) porogen phase removed to yield pores (hatched area=crosslinked polymer, dots=porogen phase)

moved depending on their characteristics and a hard opaque bead with a rough surface remains. The opacity of the macroporous resins, as compared to the glassy appearance of the microporous beads, is due to their heterogeneous structure made of highly crosslinked polymeric microdomains and pores devoid of polymer.

2.1.1.1

Structure and Physical Properties of Macroporous Resins

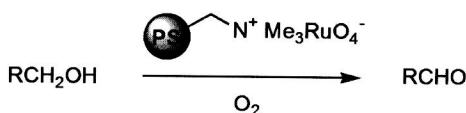
Due to their mode of preparation, macroporous microbeads are constituted on the one hand of a permanent macroporous internal structure and on the other hand of highly crosslinked areas (Scheme 1c). The porous areas are made of numerous interconnected cavities of different sizes leading to a large internal surface available for functionalisation, whereas the crosslinked areas provide the rigidity to such structures [22, 33]. This high internal surface area, typically ranging from 50 to 1,000 m²/g (determined by N₂ BET), is accessible even in the dry state. In general, macroporous resins show very low swelling in organic solvents due to the very highly crosslinked areas. For that reason, macroporous beads remain unaffected by changes in the direct environment, even in the presence of “good” solvents. Another consequence is that the pores can accommodate a large variety of solvents including polar solvents as water and low molecular weight alcohols. Because of the pore size and the presence of channels interconnecting these cavities, solvents can diffuse rapidly in and out of these pores.

One drawback of these heterogeneous structures is the very low accessibility of the solvents and reagents to the very crosslinked areas, with the consequence of limited loading capacities with a typical range of 0.8 to 1.0 mmol g⁻¹ [12]. However, some commercial ion-exchange resins, also used for immobilisation of organic reagents and catalysts, have loading capacities up to 4.5 mmol g⁻¹ [32]. Generally, macroporous resins display lower reactivities than microporous swollen beads. In contrast to microporous resins, they show high resistance towards osmotic shock [22], but they can be brittle when not manipulated carefully [23].

2.1.1.2

Applications of Macroporous Resins in Catalysis

The most extensively used macroporous resins are polystyrene-based ion-exchange resins. They are made of poly(styrene-*co*-divinylbenzene) with subsequent modification to arylsulphonic acids, quaternary ammonium salts or other derivatives mainly located on the internal surface of the pores [33, 34]. This renders them accessible to numerous organic solvents including water and alcohols. Recently, these ion-exchange resins have had a revival for the immobilisation of ionic reagents [31, 32] in automated synthesis. Macroporous beads have also been used for the immobilisation of catalysts [5, 7]; however, leach-



Scheme 2 Perruthenate oxidation catalyst supported on an ion-exchange resin

ing may be problematic in some cases due to the weak ionic interaction. A powerful example is the polymer-supported perruthenate (Scheme 2) introduced by Ley et al., which converts primary alcohols in the presence of oxygen selectively to the corresponding aldehydes [35, 36].

2.1.2

Microporous Resins

Microporous beads are weakly crosslinked resins obtained by suspension polymerisation of styrene and divinylbenzene in the absence of any porogen agent. This process leads to the formation of a homogeneous network evidenced by a glassy and transparent appearance. The most commonly used supports for solid-phase organic synthesis and catalysis are styrene-divinylbenzene copolymers crosslinked with only 1–2% DVB. Many of their derivatives are commercially available [20].

The loading capacity is controlled by the yield of the electrophilic aromatic substitution. Typically loading values are between 0.2 and 4.0 mmol g⁻¹, and a loading capacity of 1.5 mmol g⁻¹ (for the most commonly used Merrifield resins) [37] corresponds approximately to 20% substituted aromatic groups. Higher loading Merrifield resins (4 mmol g⁻¹) have also been used in organic synthesis [38]. However, the highest possible loading of 6.55 mmol g⁻¹, which corresponds to 100% chloromethylstyrene, would not be useful in practice [10].

2.1.2.1

Crosslinkers and their Effects on the Matrix Properties

For microporous resins the exact degree of crosslinking and the nature of the crosslinker are even more important than for macroporous resins, due to the severe effect on the swelling properties and matrix effects. The most common microporous resins are 1 to 2% crosslinked, but resins with less crosslinkage have also been studied [39]. They are mechanically weak and consequently easily subject to damage [9]. However, increased reaction rates have been observed for these more flexible polymer networks. It is important to keep in mind that the divinylbenzene used for crosslinking is usually a technical grade product with a composition that can vary from one batch to another and influence the properties of the beads. The consequences are variable amounts of crosslinking agents incorporated in resins depending on the different polymerisation

batches, which generally lead to relatively high error values ($\pm 0.5\%$) in the degree of crosslinking.

Alternative crosslinkers are ethylene glycol dimethacrylate (EGDMA), *N,N*-methylene bisacrylamide (MBA) and trimethylolpropane trimethacrylate (TRIM) and, more recently, novel crosslinkers have been introduced like 1,4-bis(vinylphenoxy)-butane [40] and bis(vinylphenoxy)-PEG [41, 42], which present the advantage of having a strong influence on the swelling properties due to the increased flexibility between the two crosslinking units and their compatibility with polar or even protic solvents. Crosslinkers with a higher degree of functional groups, and especially those with ligands incorporated, have also been used in solid-phase catalysis (Fig. 2).

Styryl-terminated Fréchet-type dendrimers have been introduced as novel polymer crosslinkers by Seebach et al. [43–45]. They are constituted of four to 16 peripheral styryl units attached to aryl end branches of dendritic TADDOL, BINOL or Salen ligands and were copolymerised with styrene by suspension polymerisation. The catalytic performance of the polymer-bound catalyst was identical to that of the homogeneous analogues; however, the supported catalysts could be used in many consecutive catalytic runs with only small loss in catalytic activity. A major drawback of fixing the catalytic unit in the core of the crosslinker is the poor loading capacity of the final polymer ($0.13\text{--}0.20\text{ mmol g}^{-1}$), especially when high amounts of catalysts ($10\text{--}20\text{ mol}\%$) are needed.

2.1.2.2

Physical Properties of Microporous Resins

In contrast to macroporous resins, microporous beads have a low internal surface area in the dry state of less than $10\text{ m}^2/\text{g}$ (determined by N_2 BET) [22], due

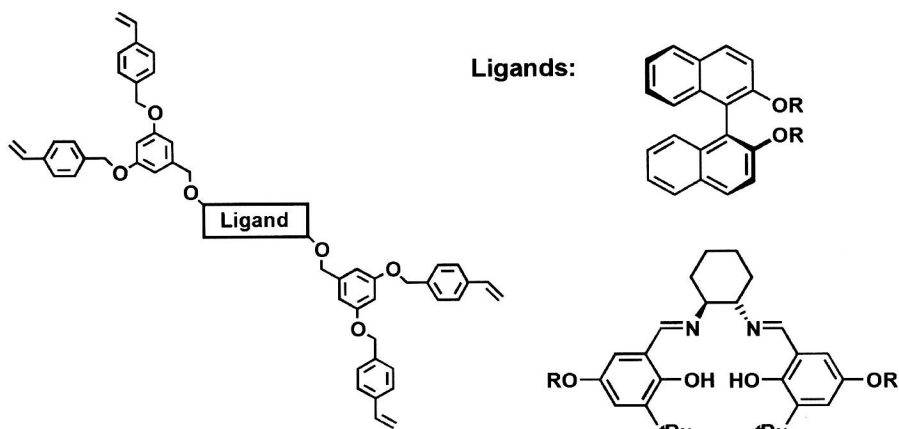


Fig. 2 Dendritic crosslinkers for the immobilisation of chiral ligands