Tailor-made Catalysts Immobilised on Silica.
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The immobilisation of homogeneous catalysts; an important key towards sustainable chemical processes

Abstract

The immobilisation of homogeneous catalysts on solid supports may hold an important key to the development of selective and sustainable catalytic processes. In this chapter the scope of the reported approaches and examples are introduced and the perspectives are addressed. Thus far no commercial processes involving supported metal complex catalysts have been developed; most systems suffered from either metal leaching, low selectivity and/or low activity. The basic idea of the current work, described in the subsequent chapters, is to develop a general solution to these problems. The strategy is directed to the immobilisation of tailor-made homogeneous catalysts on silica or silicate derivatives.
1.1 Introduction

The phenomenal growth of both population and prosperity levels world-wide is gradually leading to an increase in the demand for energy and consumer goods. The results of a number of studies have led to the conclusion that this growth can only continue on the longterm if in the next fifty years we improve a factor of twenty in efficiency on the use of resources, space and the environment.\(^1\) Chemistry is an important key to attain this improvement. Not only does sustainable chemistry open up long-term perspectives, it also provides an integral framework for economically attractive developments, such as the use of alternative resources to replace those that are becoming scarcer and more expensive.\(^2\) Many current chemical processes, however, are not sustainable.\(^3\) Especially the production of fine chemicals generally entails the production of vast quantities of waste. In future processes, the number of synthesis steps should be minimised and the remaining process steps must be performed at the highest possible atom economy.\(^4\) Transition metal catalysts, along with enzyme technology, are important tools in these achievements.\(^5\)

1.2 Homogeneous catalysis

The replacement of stoichiometric chemical conversions with routes based on catalysis has already led to the elimination of several environmentally unacceptable processes.\(^6,7\) Nowadays, over 50 industrial processes employ homogeneous metal catalysts and the numbers are expected to increase even further. Many important investigations in homogeneous catalysis in the past decade have revolutionised conventional chemical processes, and the potential of homogeneous catalysis in new applications is even greater. Some important examples of applied homogeneous catalysts include: 1) Cobalt and rhodium catalysed hydroformylation reactions in the Shell process, Kuhlman process, Union Carbide process and the Ruhrchemie/-Rhône-Poulenc process; 2) The nickel catalysed oligomerisation of ethene and the cobalt-molybdenum metathesis reaction in the Shell Higher Olefin Process; 3) The rhodium catalysed synthesis of acetic acid in the Monsanto process; 4) Palladium catalysed oxidation of ethene in the Wacker process (Hoechst); 5) Co/Mn/Br catalysed oxidation of p-xylene in the Amoco Oxidation process towards the production of terephthalic acid. Important fine-chemicals that are produced using homogeneous catalysts include Ibuprofen (Celanese), Naproxen (Albemarle), Menthol (Takasago), Metalochlor (Novartis) and L-DOPA (Monsanto).

In a sustainable process, a catalyst system must possess several features. It should exhibit high selectivity, since otherwise the cost of purification and the atom
economy waste can be prohibitive. The catalyst must have a reasonable activity per unit volume of reactor space-time and the cost of the catalyst per unit of product should be low. In this respect, homogeneous catalysts afford better possibilities to influence the catalyst properties than heterogeneous catalysts because of a far better mechanistic understanding of its microscopic processes. A key issue, however, of the application of a homogeneous catalyst in chemical processes is the cumbersome separation of the catalyst from the product. In existing processes often applied catalyst separation methods include: 1) Precipitation and filtration of the product (terephthalic acid production); 2) Distillation of the product (Shell hydroformylation process and Monsanto acetic acid process); 3) Destructive catalyst precipitation; 4) Extraction (Kuhlmann process, Ruhrchemie/-Rhône-Poulenc process); 5) Stripping (1st generation UCC hydroformylation process, Wacker process), while in some catalysed processes, in which very high turnovers are obtained, catalysts are not removed at all (gashphase polypropene process). The catalyst selectivity achieved and the space-time yield realised in most cases still outweigh the extra effort involved in a more costly catalyst-product separation. On the contrary, there are a lot of investigations focussed on novel methods of immobilisation and reuse of homogeneous catalysts. In this chapter, we focus on the scope and limitations of interesting concepts that have been reported in this field, without the pretention, however, to give a complete overview.

1.3 Aqueous biphasic catalysis

A possible approach to facilitate the separation of a homogeneous catalyst from the products is to apply a water-soluble catalyst in aqueous biphasic systems (Figure 1.1). Rhodium(I) complexes of sulfonated arylphosphines such as the trisodium salt of tris-sulfonated-triphenylphosphine have been shown to be effective hydrogenation and hydroformylation catalysts. A process using the water-soluble HRRhCO(TPPTS)₃ (in which TPPTS is the trisodium salt of triphenylphosphine-m-trisulfonic acid) catalyst is being commercially applied by Ruhrchemie (Celanese) for the hydroformylation of propene and 1-butene. Several condensed papers review the applications and limitations of aqueous biphasic catalysts and the special role of water.

The use of aqueous two-phase catalyst systems, however, is strictly limited to substrates that are at least slightly soluble in water. Higher alkenes, an important class of compounds for the bulk chemical industry, suffer from very low rates due to mass transfer limitations. There are several ways to deal with these solubility limitations. The first one is the addition of solvents and/or co-solvents. A second approach is the
addition of surfactants or phase transfer agents to the biphasic reaction mixture. This strategy has been adopted successfully to several catalyst systems to facilitate carbonylations, C-C-coupling reactions and isomerisation reactions on hydrophobic substrates.\(^9\)\(^,\)\(^18\) The third, most sophisticated approach involves the application of amphiphilic catalysts.\(^10\) Ligands that have an amphiphilic character can combine the advantage of two-phase catalysis, i.e. easy catalyst separation, with a reasonable solubilising effect on organic substrates. Fell\(^{19,20}\) and Hanson\(^{21,22}\) reported the first compounds that combine these properties. A remarkable accelerating effect of the aggregation of catalytic sites on the catalyst activity was recently reported by Milstein and Lahav et al.\(^{23}\) Catalytically active Langmuir-Blodgett films of a rhodium complex were observed to be highly active in the hydrogenation of carbon-oxygen bonds, while the complex in an organic solution exhibited low catalytic activity.

![Figure 1.1: Schematic representation of liquid-liquid biphasic catalysis with subsequent catalyst separation. \(S = \text{substrate}, \ C = \text{catalyst} \) and \(P = \text{product}\).](image)

An alternative approach towards the aqueous phase separation of homogeneous catalysts is the extraction/re-extraction method. In this approach, homogeneous organic-phase catalysis is followed by the extraction of the metal complex into the aqueous phase and subsequent re-extraction in the organic phase where it is re-used for the next catalytic run. For many years, the extraction concept has been applied industrially in the Du Pont adiponitrile process. In this process the nickel arylphosphite catalyst that is explored in the hydrocyanation of butadiene is separated from the polar, high-boiling adiponitrile by extraction with cyclohexane.\(^{24}\) A comparable approach has also been used in the Kuhlmann process, which involves a hydroformylation reaction using HCo(CO)\(_4\) as the catalyst, followed by a catalyst recovery procedure via an acidic aqueous extraction and a subsequent basic re-extraction of the catalyst back into the organic phase. An early study on this approach reported the use of cobalt carbonyl complexes containing the diethylamino-substituted phosphine P(CH\(_2\)CH\(_2\)NEt\(_2\))\(_3\).\(^{25}\) The cobalt complex is extracted into dilute mineral acid after the reaction and it is subsequently re-extracted into the organic solvent by simply reducing the CO\(_2\) pressure. Furthermore, the adic/base
extraction/re-extraction approach was applied in the hydroformylation of 1-hexene in NMP (N-methylpyrrolidone)\textsuperscript{26} using a rhodium tris(2-pyridyl)phosphine complex and in the highly regioselective hydroformylation of 1-octene using pyridyl and diethylamino functionalised BISBI and Xantphos ligands.\textsuperscript{27,28}

1.4 Non-aqueous biphase catalysis

Although aqueous biphasic catalysts seem appealing because of the "green" image of water, the contact of organic solvents with process water can lead to the generation of large volumes of dilute aqueous organic waste streams, which are particularly difficult to treat. This environmental concern has stimulated the development of new strategies involving non-aqueous biphasic catalysis. These novel approaches concern the design of ligands that are highly and selectively soluble in specific solvents.\textsuperscript{29}

1.4.1 Fluorous biphase catalysis

Horvath and Rábai have recently introduced a new concept called "fluorous biphasic catalysis" in which fluorocarbons are used as a solvent for a homogeneous catalyst that is functionalised with highly fluorinated ligands.\textsuperscript{30} Catalysts have been functionalised with phosphine ligands containing teflon-like "ponytails" to impart high solubility in fluorocarbon solvents.\textsuperscript{31} Heating hydrocarbon/fluorocarbon mixtures containing these catalysts and organic substrates resulted in a single phase which gave rise to effective catalysis for several reactions such as hydrogenation, hydroboration, oxidation and hydroformylation.\textsuperscript{32} After completion of the reaction the system can be cooled down to give a phase separation (Figure 1.2).

![Figure 1.2: General concept of fluorous biphasic catalysis. Black area represents the fluorous phase, white area the organic phase and grey area the homogeneous mixture at elevated temperature. S = substrate, C = catalyst and P = product.](image-url)
Further optimisation of this system, i.e. the use of heavier fluorous solvents and longer ponytails, will be necessary, however, since significant leaching of catalyst and fluorous solvent in the product phase has been observed. For commercial applications the high costs and the toxicity of fluorinated solvents might be a limiting factor.

1.4.2 Supercritical carbon dioxide

Although homogeneous catalysis in supercritical reaction media is considered a relatively new field, only gaining wide attention since 1990, it has been around for a lot longer. Already in 1913, Ipatiev performed an \( \text{AlCl}_3 \) catalysed oligomerisation of supercritical ethene.\(^{33}\) One of the first examples in which supercritical carbon dioxide (\( \text{scCO}_2 \)) was used in catalysis, was reported in 1975 by Kramer and Leder who patented the isomerisation of n-hexane to methylpentane or dimethylbutane catalysed by \( \text{AlBr}_3 \) in a supercritical hexane/\( \text{CO}_2 \) mixture.\(^{34}\) The homogeneous catalysis in \( \text{scCO}_2 \), however, has not been the subject of serious study until more recently.\(^{35,36}\) Researchers in this field exhibit the properties of sc\( \text{CO}_2 \) -such as pressure-dependent density, solvent properties, lack of toxicity, nonflammability and miscibility of gases-many of which have shown to be beneficial in chromatographic and extraction applications (for example, commercial coffee decaffeination).\(^{37}\) The applicability of sc\( \text{CO}_2 \) is mainly limited by the solubility of catalysts. Homogeneous catalysts often require modification with fluorocarbons in order to increase their solubility in sc\( \text{CO}_2 \).\(^{38,39,40}\) (a notable exception is the use of rhodium trialkylphosphine complexes).\(^{41}\) \( \text{CO}_2 \) and fluorocarbons share similar solvent characteristics due to their low cohesion energy densities. Recent reports show that homogeneous rhodium complexes, containing fluorinated phosphines, catalyse the hydroformylation of higher alkenes, such as 1-octene, \( \text{trans}-3\)-hexene and 2,3-dimethyl-2-butene in sc\( \text{CO}_2 \).\(^{42,43}\) Several other homogeneous catalysed reactions, i.e. isomerisations, (asymmetric) hydrogenations, hydroisilylations, methathesis, oxidations and several C-C bond formation reactions have been performed successfully in sc\( \text{CO}_2 \).\(^{35}\) The use of homogeneous catalysts, immobilised on a solid support (see section 1.6) overcomes both solubility and catalyst recovery problems.\(^{44}\) Poliakoff \textit{et al.} utilised continuous processes using sc\( \text{CO}_2 \) as the solvent for a wide range of reactions such as hydrogenations,\(^{45,46}\) Friedel-Crafts alkylations\(^{47}\) and etherification reactions\(^{48}\) using catalysts supported on polysiloxane.

1.4.3. Ionic liquids

Another approach to non-aqueous biphasic catalysis makes use of ionic liquids.\(^{49}\) The development of these type of materials goes back to 1914 when the synthesis was reported of ethylammonium nitrate that was liquid at room
temperature. Ionic liquids, based on chloroaluminate ions were introduced in 1948 by Hurley and Wier as bath solutions for electroplating aluminum. At the end of the 1980s, this type of acidic ionic liquids were applied as effective Friedel-Crafts catalysts and at the same time Fry et al. reported on phosphonium halide melts that were used successfully in nucleophilic aromatic substitution reactions. The use of ionic liquids as solvents for homogeneous transition metal catalysts was described for the first time in 1990 by Chauvin et al. and by Carlin et al. in the Nickel catalysed dimerisation of propene and in the Ziegler-Natta catalysed ethene polymerisation, respectively. The main advantage of using ionic liquids to support homogeneous catalysts is that they generally form biphasic systems with many organic solvents, which can give rise to a straightforward recovery of homogeneous catalysts. In addition, ionic liquids have practically no vapour pressure, which also facilitates the separation of the catalyst from the product via distillation. Brennecke et al. recently showed that organic solvents can also readily be extracted from ionic liquids with the use of scCO₂. Recent examples, concerning ionic liquids as solvent for transition metal catalysed reactions include; hydrogenations, oxidations, hydroformylations and several C-C coupling reactions, mainly using ionic liquids based on imidazolium salts. Current limitations of a commercial application of ionic liquids include the limited availability and hence high costs of these materials. The production of a halogen containing wastestream is recognised as a disadvantage.

1.5 Supported liquid phase catalysis

A method of catalyst immobilisation that lies on the borderline between liquid/liquid and liquid/solid catalyst separation is the class of the supported liquid phase catalysts. After the initial work of Dawson et al. much of the work in this field was explored by the groups of Rony and Roth, Scholten and Hjortkjaer. Supported liquid phase catalysts are prepared by absorbing a catalyst in a non-volatile solvent within the pores of an inert support such as silica. The resulting system has the properties of a molecular complex but can be handled like a heterogeneous catalyst. The activity, stability and selectivity of these systems are highly dependent of the type of support, the weight percentage and polarity of the solvent and the ability of the catalyst to absorb on the support surface. This type of catalyst systems have been studied in hydrogenation, isomerisation and hydroformylation reactions in both liquid phases and gas phases. The leaching of catalyst in the product is reported as a disadvantage.
1.5.1 Supported Aqueous Phase Catalysis

A special class of supported liquid phase catalysts; "Supported Aqueous Phase Catalysis (SAPC)" was introduced by Hanson and Davis et al. This system involves a water-soluble catalyst dissolved in a film of water, adhered to the surface of silica particles (Figure 1.3). Using this system a-polar substrates that are completely insoluble in water, such as 1-heptene and oleic alcohols, were hydroformylated using the SAP catalyst. Horváth performed experiments using substrates having different solubilities in water and showed that, under optimal conditions, this solubility did not influence the catalyst activity (Table 1.1, entries 1-3). Hence it was suggested that in the SAPC system, catalysis merely takes place at the liquid-liquid interface.

The SAPC system was applied in batch and in continuous systems and in both cases no leaching of rhodium complex was detected. A drawback of the SAPC system, however, is its sensitivity towards the water content of the silica support. If the water layer is too thin (2.9 wt. %), the activity of the catalyst is a factor of ten lower compared to a SAPC containing 9 wt. % of water, which is ascribed to a decrease of the catalyst mobility (Table 1.1, entry 4-5). If the water layer becomes too thick the substrate has to diffuse into the water layer, or the catalyst has to diffuse to the interface. This results in a decrease in catalyst-product contact time leading to lower activities. The water content on the support must therefore be optimised. In a continuous flow system, however, water clearly leaches from the silica support. In a practical application, this should be compensated for by using water-containing organic solvents.
Most SAP catalysts described in literature are based on rhodium, cobalt and platinum/nickel TPPTS and show a low product selectivity in the hydroformylation of higher alkenes.\textsuperscript{14,76,77} The SAPC technique was also applied in enantioselective hydrogenation reactions using a ruthenium catalyst.\textsuperscript{78} The use of ethylene glycol instead of water as the liquid polar layer gave rise to an increase from 70% to 95% in enantiomeric excess in the asymmetric hydrogenation towards naproxen.\textsuperscript{79}

<table>
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<tr>
<th>Catalyst system</th>
<th>Substrate</th>
<th>T (°C)</th>
<th>TOF (mol.mol\textsuperscript{-1}.h\textsuperscript{-1})</th>
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<tr>
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<td>mixture\textsuperscript{b}</td>
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<td>432/432/396</td>
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<tr>
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<td>mixture\textsuperscript{b}</td>
<td>100</td>
<td>1656/1800/1800</td>
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<tr>
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<td>17/5/1</td>
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<td>SAPC (2.9 wt.% H\textsubscript{2}O)\textsuperscript{d}</td>
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<td>75</td>
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</tr>
<tr>
<td>SAPC (9 wt.% H\textsubscript{2}O)\textsuperscript{d}</td>
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<td>75</td>
<td>72</td>
</tr>
<tr>
<td>homogeneous\textsuperscript{c}</td>
<td>1-heptene</td>
<td>75</td>
<td>288</td>
</tr>
</tbody>
</table>

\textsuperscript{a} HRh(TPPTS)\textsubscript{3}CO, P = 51 bar (H\textsubscript{2}/CO = 1:1). \textsuperscript{b} The substrate was a 1:1:1 mixture of 1-hexene, 1-octene and 1-decene. Products, of which TOF's are tabulated in the far-right column are heptanals, nonanals and undecanals, respectively. \textsuperscript{c} HRh(PPh\textsubscript{3})\textsubscript{3}CO in hexane, P = 51 bar (H\textsubscript{2}/CO = 1:1). \textsuperscript{d} HRh(TPPTS)\textsubscript{3}CO, P = 7 bar (H\textsubscript{2}/CO = 1:1). \textsuperscript{e} HRh(PPh\textsubscript{3})\textsubscript{3}CO in toluene, P = 7 bar (H\textsubscript{2}/CO = 1:1).

### 1.6 Covalent anchoring onto a polymeric support

The heterogenisation of homogeneous catalysts to polymeric supports is a very active area of research. Potentially, this strategy provides the opportunity to combine the advantages (and at the same time avoiding the disadvantages) of homogeneous and heterogeneous catalysts. The use of this chemically and structurally controllable heterogenised systems can ultimately lead to the application of tailor-made homogeneous catalysts in continuously operating chemical processes (Figure 1.4).

The first work published on supported metal complexes involved [Pt(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} on sulfonated polystyrene (1969).\textsuperscript{81} After a slow start, the research in this field has rapidly expanded; up to several hundreds of papers published annually.\textsuperscript{69,82,83}

Organic and inorganic polymeric catalyst supports exhibit several differences. One of the most important differences is the temperature stability. Organic polymeric supports are often subject to considerable degradation at ca. 420 K even in the absence of oxygen, while the application of an inorganic-supported catalyst is generally limited by the thermal stability of the metal complex rather than that of the support. Another difference is the higher mechanical strength of inorganic oxides in comparison to organic polymers. Most inorganic supports are more robust and can stand higher
pressures, i.e. when used in columns, and also reduced pressures that can arise during rapid evacuation of solvents. The swelling under variable temperatures and solvent conditions is another disadvantage of organic polymers since it prohibits the practical control of diffusional variables. Inorganic supports are also more resilient with respect to changes in solvent polarity.

![Diagram](image)

Figure 1.4: Schematic representation of a continuous fixed bed reactor using a heterogenised catalyst.

### 1.6.1 Homogeneous catalysts immobilised on organic supports

Despite the disadvantages described above, the use of organic polymers as supports for organometallic complexes has been widely investigated over the last three decades. The relative ease of functionalisation and the wide range of physical properties, fine-tuned by the degree of cross-linking, have resulted in a hole range of functionalised polystyrene (and related polymers) that were applied in the immobilisation of transition metal complexes. Linear polymers have also been applied as support for various homogeneous catalysts. Bayer and Schurig showed that the immobilisation of homogeneous catalysts onto linear polymers yield catalyst systems that show a high solubility in organic solvents. The catalyst recovery, mainly performed via ultrafiltration or precipitation, however, is more troublesome. An interesting novel concept in this field, introduced by Bergbreiter *et al.*, makes use of the temperature dependency of the solubility of linear polymers in organic solvents. Homogeneous catalysts were tethered to polymers that are soluble at elevated temperatures and insoluble at room temperature. Different types of these “smart” polymers, i.e. polyethylene, polyalkene oxides, poly(N-isopropylacryl)amines and fluoropolymers were functionalised with transition metal complexes and applied in catalysis. Complete catalyst recycling has been demonstrated in the rhodium catalysed hydrogenation and in the palladium catalysed allylic amination reaction.
Another novel development in the field of homogeneous polymeric catalysis is the application of dendrimers as organic soluble support for transition metal complexes. This class of compounds enables the use of homogeneous catalysts that are separated from the reaction mixture by nano-filtration or precipitation. The former approach can be performed either batch wise or continuously.

1.6.2 Homogeneous catalysts immobilised on inorganic supports

For the anchoring of metal complexes on solid oxides one generally utilizes the surface hydroxyl groups (silanols) of the support. For many metal compounds, however, these groups do not provide a stable linker, particularly if metal complexes or organometallic compounds have to be anchored. For this purpose silanols can be derivatised with organically substituted alkoxy silanes of the type $(RO)_3Si-X-L$, in which $L$ is the ligand to co-ordinate to the transition metals and $X$ is a chemically inert spacer. Many compounds of this type are commercially available, for instance $(RO)_3Si-(CH_2)_3-L$ ($L = NH_2$, NHCH$_2$CH$_2$NH$_2$, CN), whereas others, such as $(RO)_3Si-(CH_2)_3-PR_2$ or $(RO)_3Si-(CH_2)_3-CH[C(O)CH_3]_2$, can be prepared easily. Traditionally, these ligands are anchored to commercially available inorganic materials by a simple condensation reaction between the surface OH groups and the
alkoxides of the ligand. Many catalytically active metal complexes, heterogenised via this method, have been studied in catalytic processes such as hydrogenations, hydroformylations, hydrosilylations and oligimerisations. Preparation and performance of such catalyst systems have been extensively reviewed.

An interesting alternative to this conventional method of immobilisation was presented by Panster et al. who used the sol-gel process. The sol-gel process, which is an ideal method for catalyst immobilisation because of its diversity and mildness, is a straightforward hydrolysis-polycondensation reaction sequence (Scheme 1.1). First, hydrolysis of a metal or semi-metal alkoxide precursor forms the corresponding hydroxylated analogue. Subsequent condensation between a silica-alkoxide and a silica-hydroxyl group, or between two silica-hydroxyls results in a colloidal mixture of polysilicate oligomers, which is referred to as the "sol". In the final stage, polycondensation of these oligomers eventually results in a three-dimensional polysilicate gel. Blum and Avnir et al. used the sol-gel approach in the physical encapsulation of a range of transition-metal complexes. These heterogenised compounds have been applied in isomerisation, hydroformylation and hydrogen transfer reactions and in most cases no metal leaching was observed. Thus far, however, this approach was merely successful using cationic transition-metal complexes. Probably, ionic interactions with the polar
surface of the support are involved in the recovery of the catalyst in the polysilicate matrix. Hence, it is questionable whether this method is generally applicable.

Alternatively, immobilised metal complexes are covalently anchored to the polysilicate matrix via the (co)condensation of metal complexes of the type \([ \text{(RO)}_3\text{Si-Si-X-L} \text{]}_n \text{ML}_m\) (in which \(L\) is for instance a phosphino, amino or sulfido-containing ligand) and \(\text{Si(OR)}_4\). The catalyst loading in the silicate matrix can be easily adjusted by changing the \([ \text{(RO)}_3\text{Si-X-L} \text{]}_n \text{ML}_m\) to \(\text{Si(OR)}_4\) ratio. Very high catalyst loadings have been obtained using this sol-gel route.\(^{110}\) Furthermore, the diversity of the sol-gel immobilisation technique allows the development of organic-inorganic hybrid polymers that can be tuned for the required catalytic conditions. Lindner et al. showed that the chemistry in these so called "interphases" offers a way to a subtle development of hybrid polymers to suppress the detrimental influence of the support.\(^{111}\)

In contrast to the well investigated surface heterogenisation methods, less has been reported on the immobilisation of metal complexes by sol-gel methods. Most of the reported examples include transition metal complexes using the above described ligands.\(^{112}\) A schematic overview of examples of silica immobilised transition metal complexes and their application in i.e. hydrogenation,\(^{113}\) asymmetric hydrogenation,\(^{114,115}\) asymmetric transfer hydrogenation,\(^{116}\) hydrosilylation\(^{117,118}\) and hydroformylation\(^{111}\) is listed in chart 1.1. Some of the systems that have been prepared were not applied in catalysis yet.\(^{119}\)

![Chart 1.1](image-url)
A special class of catalysts, immobilised on inorganic supports, are those that are entrapped in the structure of macroporous zeolites. Zeolites impose environmental conditions that largely differ from those on a "flat" inorganic surface. The anionic framework of zeolites and the finite size of the channels and intersections can have a major impact on the catalyst activity, product selectivity and substrate specificity. In their pioneering study, Huang and Schwartz reported that treatment of Linde 13X zeolite with tris (π-allyl)rhodium yielded a zeolite supported catalyst that preferentially hydrogenated lower alkenes above higher alkenes. Corbin et al. found that this substrate specificity improved upon poisoning unselective rhodium sites on the external surface of the zeolite. Hence, it was ensured that the catalyst is mainly operating from within the zeolite structure.

Zeolite-encapsulated complexes can be prepared in several ways: 1) by capturing the complexes in the inorganic framework during the synthesis of the zeolite, 2) by a post-synthesis sorption of complexes from either the gas or the liquid phase or 3) by a sophisticated complex preparation in the interior of the zeolite. Entrapped metal carbonyl complexes such as Fe(CO)$_5$, Rh$_6$(CO)$_{12}$, and Ni(CO)$_4$ are easily obtained via the carbonylation of transition metal exchanged zeolite. This kind of supported complexes, however, suffer from metal leaching. Moreover, thermal decomposition of the clusters often leads to ill defined systems. The first example of a molecular "ship-in-the-bottle" complex that was quantitatively retained in the zeolite support was reported by Herron. The complexation of a
bisimine-bisalcohol ligand to cobalt exchanged zeolite Y led to the formation of a CoSALEN complex inside the supercage of the zeolite that showed a remarkable stable performance in catalytic oxidation reactions. Further successful zeolite-encapsulated (oxidation) catalysts include complexes containing phthalocyanine, perfluorophthalocyanine, porphyrine and bipyridin ligands. In all cases an increase in catalyst stability was observed due to the isolation of the catalytic sites within the framework of the zeolite. In several cases, it was also observed that product distributions significantly changed upon immobilisation.

The developments of novel mesoporous polysilicate solids (MCM-41) containing large diameter channels (25-100 Å) has further expanded the abilities of immobilised homogeneous catalysts on ordered inorganic supports. The broad channels of MCM-41 allows the penetration of large organic reactants and metal complexes through the pores, while the narrow pore size distribution is reported to induce a possible shape selectivity. In the last four years MCM-41 has already been applied as a catalyst support in reactions including hydrogenations, epoxidations, oxidations, hydroxylations and several C-C coupling reactions. A significant change in regio and enantioselectivity, induced by MCM-41, was recently reported by Johnson et al. in the palladium catalysed allylic alkylation reaction. The recent developments towards inorganic materials with chiral helical pores will probably stimulate the research in this field even further.

In general, immobilised catalysts are not applied yet in industry. Catalyst deactivation due to metal leaching and/or catalyst decomposition presents the major bottleneck.

1.7 Objectives and outline of this thesis

One of the major challenges in the field of catalysis is the development of sustainable processes that combine a good catalytic performance with a facile and quantitative catalyst/product separation. In the production of fine-chemicals the recycling of catalysts becomes interesting when the costs of immobilisation are relatively low and when the system of use is generally and rapidly applicable.

Industrially, the separation of a homogeneous catalyst from the products is predominantly performed by filtration, distillation, destructive catalyst precipitation, extraction or stripping. Most of these techniques give rise to catalyst decomposition. Furthermore, distillative methods of separation are not suitable for the production of fine chemicals because of the high boiling points of the products. A widely investigated approach to facilitate catalyst-product separation is the attachment of catalysts to a polymeric support (sec 1.6). Up to date, immobilised catalysts of industrial importance are still unknown; catalyst deactivation, mostly due to metal
leaching and moderate catalyst performances are the major bottlenecks. The objective of this work is to develop sustainable catalyst systems that exhibit a high catalyst activity and selectivity and that are quantitatively and easily separated from the products and reused for numerous turnovers.

Among the options reported in literature, inorganic materials appear to be the most suitable for catalyst immobilisation. Hence, the main strategy of the work, described in this thesis, is directed to the immobilisation of tailor-made catalysts on silica or silicate derivatives.

The immobilisation of rhodium-diphosphine complexes, containing a large P-Rh-P bite-angle, via the "Supported Aqueous Phase" technique, the sol-gel approach and via the covalent anchoring to commercially available silica will be investigated and these systems are subsequently studied in the hydroformylation of 1-octene. The performance of the SAP catalyst, a rhodium complex containing a disulfonated diphosphine ligand, will be investigated in successive catalytic runs and the results are compared to that of the reported Rh-TPPTS system (Chapter 2). A second diphosphine ligand will be equipped with a trialkoxysilane moiety to enable its covalent immobilisation to a polysilicate matrix via the sol-gel process. The co-condensation of this ligand with tetramethylorthosilicate in the presence of the rhodium precursor is presented and the application of this system in successive hydroformylation runs will be addressed (Chapter 3). The nature of the covalently anchored rhodium-diphosphine catalyst and the influence of the support on the catalyst are investigated by means of solid state characterisation techniques. Small manipulations affecting the catalyst-support system are investigated and the application of the supported catalyst system in subsequent hydroformylation, hydrogenation and hydroformylation/hydrogenation cascade reactions will be stretched. (Chapter 4). Furthermore, the covalently anchored hydroformylation catalyst will be tested in a flow-reactor using supercritical carbondioxide as the dynamic phase. A continuous process for the hydroformylation of 1-octene is investigated using this set-up and the influence of the supercritical carbondioxide on the catalyst performance is discussed (Chapter 5). The multi-purpose abilities of the hydroformylation catalyst will be studied by its use in a sophisticated "drop-in" device. The catalyst will be immobilised in the channels of monoliths that are fixed in the blades of a mechanical stirrer. Hydroformylation reactions will be adopted successively to different substrates in both organic and aqueous as well as gaseous phases using the same batch of catalyst (Chapter 6).

A tailor-made homogeneous ruthenium-amino-alcohol catalyst for the asymmetric transfer-hydrogenation reaction will be described that is covalently tethered to silica. An "on-the-bead" catalyst synthesis is reported towards a rapid access to a series of supported catalysts of this type. The asymmetric transfer-
hydrogenation of acetophenone will be applied in subsequent batch-wise runs as well as in a continuous process (Chapter 7).

The application of silica immobilised palladium catalysts will be investigated in the allylic alkylation reaction, using a series of silica immobilised palladium-phosphine complexes. The influence of the morphology of the polysilicate support and the effect of silanols on the silica surface is discussed (Chapter 8).

1.8 References and notes


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