Tailor-made Catalysts Immobilised on Silica.

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A silica supported, switchable, and recyclable hydroformylation-hydrogenation catalyst

Abstract

A homogeneous hydroformylation catalyst, designed to produce selectively linear aldehydes, was covalently tethered to a polysilicate support. The immobilised transition-metal complex \([\text{Rh}(\text{A})\text{CO}]^+\) (I), in which \(\text{A}\) is \(N-(3\text{-trimethoxysilane-n-propyl})-4,5\text{-bis(diphenylphosphino)}\text{-phenoxazine}\), was prepared both via the sol-gel process and by covalently anchoring to silica. Polysilicate immobilised \(\text{Rh}(\text{A})\) performed as a selective hydroformylation catalyst showing an overall selectivity for the linear aldehyde of 95 %. In addition 1-nonanol, obtained via the hydrogenation of the corresponding aldehyde, was formed as an unexpected secondary product. Under standard hydroformylation conditions, \(1\) and \(\text{HRh}(\text{A})(\text{CO})_2\) (I') co-exist on the support. This dual catalyst system performed as a hydroformylation/hydrogenation sequence catalyst (Z), giving selectively 1-nonanol from 1-octene. The addition of 1-propanol completely changes Z in a hydroformylation catalyst (X), which produces 1-nonanal with an overall selectivity of 93 %, and complete suppresses the reduction reaction. If the atmosphere is changed from CO/H\(_2\) to H\(_2\) the catalyst system is switched to the hydrogenation mode (Y) which shows a clean and complete hydrogenation of 1-octene and 1-nonanal within 24 hours. The immobilised catalyst can be recycled and the system can be switched reversibly between the three “catalyst modes” X, Y and Z, completely retaining the catalyst performance in each mode.

4.1 Introduction

The development of well-defined catalyst systems that allow rapid and selective chemical transformations and at the same time can be completely recovered from the product is still a paramount challenge. Although highly active and selective reusable catalyst systems have been reported, key problems for many systems comprise catalyst stability and leaching of catalytic material in the product phase. An intensively studied and promising approach to facilitate catalyst-product separation is the attachment of homogeneous catalysts to polymeric organic, inorganic or hybrid supports, and more recently to dendritic supports. Inorganic materials such as silica are particularly suited as heterogeneous catalyst support because of their high physical strength and chemical inertness.

In the past three decades much research has been devoted to recyclable catalyst systems for the hydroformylation of higher alkenes. In the late seventies, alkoxysilane functionalised monophosphine ligands have been used to tether a rhodium-phosphine complex to commercially available silica. An interesting alternative for the preparation of silica-immobilised catalysts was presented by Panster et al. who used the sol-gel process, i.e. a co-condensation of tetraalkoxysilanes and functionalised trialkoxysilanes. The sol-gel technique is an ideal method for catalyst immobilisation because of its diversity and its mildness. The selectivity of the catalyst reported in Panster's work is rather low, but metal leaching, was suppressed to a large extent. Blum et al. reported a sol-gel immobilised hydroformylation catalyst that is free of metal-leaching. In the latter case no directing ligands were used, which resulted in a lack of control over the product distribution. Immobilised hydroformylation catalysts that combine a high selectivity and activity with the absence of leaching of the catalytic material in the product phase have not been reported yet. For this purpose, catalysts containing monophosphines have proven not to be suitable thus far. A single ligand-to-metal bond appeared to be too weak and monophosphines generally give rise to a low selectivity. Diphosphines bind more strongly to rhodium than monophosphines due to the chelate effect. Many rhodium diphosphine complexes give rise to a low selectivity in hydroformylation reactions, but Devon et al. described a diphosphine, BISBI, that showed a very high regioselectivity for the formation of linear aldehydes. Casey et al. reported that rhodium diphosphine complexes with a large P-Rh-P (bite) angle can give rise to a high regioselectivity for the linear aldehyde. In our group, a new generation of diphosphine ligands was designed based on xanthene backbones that give extremely regioselective rhodium catalysts producing the linear aldehyde.

The application of catalysts with large P-Rh-P bite angles in multiphase hydroformylation reactions appeared very successful as with these ligands a good catalyst performance was combined with a high ligand-to-metal bond strength. These properties resulted in selective two and three-phase catalyst systems that were completely separated from the product-phase and reused in numerous consecutive runs. Preliminary results
showed that under proper conditions a polysilicate immobilised rhodium complex, containing a xanthene based diphosphine, gave rise to a very selective and sustainable hydroformylation process. In this chapter we report a detailed study showing that the performance of such an immobilised catalyst is largely dependent on the conditions applied. Under standard conditions the system performed as a regioselective hydroformylation-hydrogenation cascade catalyst, which yielded a clean one pot synthesis of 1-nonanol from 1-octene. Furthermore we will show that with small and simple manipulations, which affect the catalyst-support interactions, the system can be switched between three different catalyst modes. Depending on the conditions applied, the catalyst system can either function as a hydroformylation, a hydrogenation or as a hydroformylation/hydrogenation sequence catalyst. Moreover, upon recycling and reusing the system we can reversibly switch between these catalyst modes, thus using the same batch of catalyst for different types of reactions.

\[ \text{Chart 4.1} \]

4.2 Results and discussion

4.2.1 Catalyst immobilisation

The rhodium-diphosphine complex Rh(A) was immobilised on silica using the sol-gel technique and by a direct anchoring to commercially available silica. The latter method has been studied using different conditions. Both techniques are relatively straightforward procedures. Via the sol-gel process, Rh(A) was immobilised on a polysilicate support by stirring a solution of A, \([\text{Rh(acac})(\text{CO})_2]\) and tetramethyl orthosilicate (TMOS) in THF/H\textsubscript{2}O to obtain \([\text{Rh(A)CO}]^+\) (I) (Scheme 4.1-I). The resulting gel was dried and crushed into a free flowing silica.

The immobilisation of Rh(A) on commercially available silica was performed in four different ways (Scheme 4.1-II to V). In the first three approaches, A was covalently tethered to silica (to obtain silica(A)) by refluxing a suspension of A and silica in toluene for 2 h. The subsequent complexation of the rhodium precursor was performed under three different conditions. In the first approach the rhodium precursor \([\text{Rh(acac})(\text{CO})_2]\) and silica(A) were simply mixed together and stirred in a THF suspension (Scheme 4.1-II). In the
second way, silica(A) was first reacted with dimethoxydimethylsilane in order to modify the acidic silanols on the silica surface.21 To this end a suspension of silica(A) and dimethoxydimethylsilane was refluxed for 2 h in toluene and subsequently stirred in a solution of [Rh(acac)(CO)₂] in THF at room temperature for 30 min (Scheme 4.1-III). In the third approach, [Rh(acac)(CO)₂] was added to a pre-stirred mixture of silica(A) and triethylamine in THF. The resulting suspension was stirred for 30 min at room temperature (Scheme 4.1-IV). For the last method the diphosphine rhodium complex was synthesised prior to the immobilisation by adding [Rh(acac)(CO)₂] to a solution of A in THF and stirring it for 30 min at room temperature. Predried silica was added to this reaction mixture and the suspension was stirred for 18 h (Scheme 4.1-V). All above described catalyst systems were washed thoroughly and dried under reduced pressure before use.

![Scheme 4.1: Schematic representation of different routes to prepare silica immobilised [Rh(A)(CO)]^+](image)

4.4.2 Catalyst characterisation

As was reported in Chapter 3, system I was characterised by means of solid state ^3¹P MAS NMR, FT-IR and X-ray Photoelectron Spectroscopy and the data were in good agreement with the fully characterised (homogeneous) cationic complexes 2(OTf) and 2(BF₄); 2 = [Rh(B)CO]^⁺, in which B = 9,9-dimethyl-4,5-bis(diphenylphosphino)-xanthene (Chart 4.1).22 The formation of the cationic complex during the sol-gel process, which was obtained by mixing B and [Rh(acac)(CO)₂] in a TMOS/H₂O/THF solution, was monitored using liquid state ^3¹P NMR spectroscopy (Figure 4.1).23 After [Rh(B)(acac)CO] was formed, as indicated by a broad doublet at 10 ppm; J_P,Rh = 92 Hz, this complex quantitatively transformed into
[Rh(B)CO]⁺ (2) (doublet at 37 ppm; \(J_{\text{Rh}} = 122\ \text{Hz}\)) during the gelation process (Figure 4.1-A, B and C), having a siloxate as its counterion.²⁴

![Figure 4.1: \(^{31}\text{P}\) NMR spectra obtained during the sol-gel processing of [Rh(B)(acac)(CO)]. A) [Rh(B)(acac)(CO)] in soluble pre-polymer mixture. B) Transformation from [Rh(B)(acac)(CO)] to [Rh(B)(CO)]⁺. C) Transformation has been completed to [Rh(B)(CO)]⁺ (the polymer has gelled at this stage). D) HRh(B)(CO)₂ in a wet polymer gel, obtained from [Rh(B)(CO)]⁺ upon applying a CO/H₂ atmosphere.](image)

On exposing the gel containing 2 to one bar of CO/H₂ (1:1) the color of the gel changed from orange to yellow.³¹\(^{31}\text{P}\) NMR studies elucidated the quantitative transformation of 2 to [HRh(B)(CO)]₂ (2') (doublet at 22 ppm; \(J_{\text{Rh}} = 123\ \text{Hz}\)), which is the key intermediate for a selective hydroformylation catalyst in a homogeneous phase (Figure 4.1-D).¹⁵

Since Si(OMe)₄ (Q elements) was used as the major silica precursor with only 5 percent of RSi(OMe)₃ (T elements) a dense silicate network was expected to be formed.⁹ The presence of a rhodium complex in the sol-gel matrix can even give rise to a further increase in network density.²⁵ The composition of the sol-gel manufactured silica was investigated by means of \(^{29}\text{Si}\) MAS NMR (Figure 4.2). With this technique, the ratio of Si-O-Si versus Si-OH and Si-OR groups can be determined and the density of the network can be estimated from the ratio of silica atoms having a branching point of 4, 3, 2 or 1 (Q₄, Q₃, Q₂, Q₁ resp.) by deconvoluting the relative peak areas.¹⁰ For the silica material, prepared in the presence of 1, we found a relative ratio of Q₄, Q₃, Q₂ of 49.0/40.5/10.2. (no terminal Q₁ was observed, and the amount of T elements was too low to detect, Figure 4.2-A). For the silica material, prepared in the presence of 2, comparable results were obtained; a Q₄, Q₃, Q₂ ratio of 57.5/37.5/4.9 was observed (Figure 4.2-B).²⁶ These results indicate that the network density
of these systems is indeed very high and the copolymerisation of 5 percent of RSi(OMe)₃ (A) yields only slightly less dense networks.

Figure 4.2: $^{29}$Si MAS NMR spectra of the Si-support of the sol-gel immobilised [Rh(A)(CO)]⁺ (A) and [Rh(B)(CO)]⁺ (B).

4.4.3 The impact of the catalyst preparation procedure on catalysis

The method of catalyst immobilisation appeared to effect its performance in catalysis. When the catalyst was synthesised via route II the catalyst showed a low selectivity in the hydroformylation of 1-octene (linear to branched aldehyde ratio was even lower than 2) (Table 4.1, entry 2), whereas the route V catalyst is highly selective towards the linear aldehyde (with a linear to branched ratio of 37) (entry 5). In accordance with examples from literature it is likely that the former preparation procedure gives rise to the ionic bonding of ligand-free rhodium cations on the slightly acidic silica surface.¹⁹²⁷ If the rhodium phosphine complex is prepared prior to anchoring (route V) no ligand-free rhodium is attached to the silica. We also succeeded in eliminating the interference with the acidic silanols on the catalyst preparation via the chemical modification of the silica surface (route III) or upon addition of a neutralising base (route IV). Pre-modification of the silica using dimethoxydimethylsilane (III) largely improved the catalyst selectivity (linear to branched aldehyde ratio of 19, Table 4.1, entry 3) at the cost of some activity.¹⁹ The addition of
A silica supported, switchable, and recyclable...  

triethylamine (IV) also resulted in a very good hydroformylation catalyst (with a linear to branched aldehyde ratio of 37, Table 4.1, entry 4).

System 1, immobilised via the sol-gel process, (Scheme 4.1-I) performed very well in the hydroformylation of 1-octene. The selectivity for the linear aldehyde of 1 was found to be as high as 94.6 %, which equals that of its homogeneous analogue (Table 4.1, entries 1 and 6). Again, the pre-formation of the rhodium diphosphine complex before immobilisation avoided the formation of ligand free rhodium-cations on the silica surface. This approach gives rise to a well-defined, very selective hydroformylation catalyst.

Table 4.1: Hydroformylation of 1-octene using polysilicate immobilised [Rh(A)CO] +.

<table>
<thead>
<tr>
<th>Entry/ (method of preparation)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>TOFb (h⁻¹)</th>
<th>l/b Ratio</th>
<th>l-aldehyde (%)</th>
<th>b-aldehyde (%)</th>
<th>l-alcohol (%)</th>
<th>Octene isomers/octane (%)</th>
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</thead>
<tbody>
<tr>
<td>1/ (I)</td>
<td>2</td>
<td>20</td>
<td>18.3</td>
<td>65</td>
<td>94.6</td>
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<td>3/ (III)</td>
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<td>4.5</td>
<td>0</td>
<td>9.9</td>
</tr>
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<td>4/ (IV)</td>
<td>22</td>
<td>18</td>
<td>8.7</td>
<td>37</td>
<td>96.2</td>
<td>2.6</td>
<td>1.0</td>
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<tr>
<td>5/ (V)</td>
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<td>37</td>
<td>13.2</td>
<td>37</td>
<td>90.7</td>
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<td>1.6</td>
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<td>6/ (homog.)</td>
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<td>0.1</td>
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*a Ligand to rhodium ratio is 10, catalysis performed in 13 ml of toluene using 1ml of 1-octene as the substrate at 80 °C and 50 bar CO/H₂. Samples were analyzed by means of GC and GC-MS analysis. b Average turnover frequencies were calculated as (mol product/mol catalyst)/h⁻¹. 

The high network density of immobilised 1, obtained via the sol-gel process, was expected to have implications on the catalysis; it can result in a good recyclability due to its rigidity, but at the same time it might decrease the catalyst activity due to the blocking of catalyst sites. The sol-gel immobilised catalyst, however, was slightly faster than the silica immobilised analogue (Table 4.1, entry 1 and 5) indicating that the catalytic sites are fully accessible.

4.4.4 Influence of the silica on the catalyst recycling properties

Sol-gel and silica immobilised Rh(A) were tested in successive hydroformylations of 1-octene to investigate the effect of the support on the recyclability of the catalyst (Table 4.2, entry 1-6 and 7-9, respectively). For both systems the ratio of linear aldehyde, branched aldehyde and octene isomers was found to be comparable with the homogeneous analogue (Table 4.1, entry 6). Upon recycling, the high regioselectivity for the linear aldehyde was maintained (linear to branched ratios ranging from 22 to 65) while only a few percent of...
alkene isomers was formed as a side product (ranging from 0 to 3.4 %). Interestingly, we observed a small decrease in hydroformylation activity upon recycling along with an increasing formation of 1-nonanol (4-13 percent), especially at longer reaction times (Table 4.2, entry 5 and 6). We have not observed this phenomenon in analogous homogeneous hydroformylation reactions, suggesting that the silica support plays a key role in this secondary reaction. We suggest that the acidic silica increasingly blocks the formation of HRh(A)(CO)$_2$(1') from [Rh(A)CO]$_2$(1) (for figures of 1 and 1' see Scheme 3.1), resulting in an increase in hydrogenation activity and a small decrease in hydroformylation activity.

When the silica material with the capped (acidic) silanols was used (Scheme 4.1-III) the influence of the silica on the recyclability of the hydroformylation catalyst was largely suppressed. No hydrogenation of the aldehyde was observed as a secondary reaction in any of the successive catalytic runs (Table 4.2, entry 10-13). The modification of the surface silanols with alkylsilanes did not yield an optimal catalyst system. The overall selectivity for the linear aldehyde (ranging from 83.7 to 87.3 %) was slightly lower compared with the other catalysts; more isomerisation (8.3 to 11.1 %) and branched aldehyde (4.5 to 5.4 %) was obtained.

Interestingly, we found a more subtle method to reduce the influence of the silica. In the presence of 1 ml of 1-propanol, which is approximately 7 % of the total volume of the reaction mixture, an efficient suppression of hydrogenation activity has been realised; a high overall selectivity for the linear aldehyde (ranging from 92.8 to 94.5 %) was obtained in subsequent batch-wise runs (Table 4.2, entry 14-17). The effect of the presence of 1-propanol is in contrast with previously reported examples of hydroformylation catalysts, when alcohols or amines were added, to promote the hydrogenation of aldehydes via a transfer hydrogenation reaction. In the present case the presence of alcohol prevents the formation of the hydrogenation catalyst from the hydroformylation catalyst by deactivating the acidic silanols on the silica surface. The addition of triethylamine as a base also enabled the suppression of the hydrogenation activity (Table 4.2, entry 18).

It is evident that the silica support influences the catalytic performance and in the following part we describe experiments that provide a better insight in the processes involved. In the sol-gel state the immobilised cationic complex 1 completely transforms to the rhodium-hydride species 1' under a CO/H$_2$ atmosphere (Figure 4.1). On dried silica, however, this conversion might not be complete since the dried support is more acidic. Hence, 1 and 1' probably co-exist on the silica support. To investigate the effect of dried silica on this type of complexes, several experiments in solution were performed using Rh(B).

Upon the addition of predried silica to a yellow solution of 2' in toluene, the solution slowly decolourised and the silica turned orange. This silica "adsorbed" rhodium diphosphine complex indeed appeared to be the cationic species 2 as indicated by the carbonyl vibration at 1972 cm$^{-1}$ in the IR spectrum. The rhodium-hydrido complex 2' is converted to 2 by the silica, probably via a protonation of the rhodium hydride. Upon the addition of 20 μL of trifluoroacetic acid to a mixture of 2' in d$_6$-benzene a similar protonation resulted in the
formation of 2(CF₃COO⁻), as indicated by ³¹P NMR that showed a broad doublet at 38 ppm; \(J_{P,RH} = 111\) Hz.³⁴ This supports the idea that the conversion of 2\(^{1}\) to 2 indeed occurs via a simple protonation.

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<th>1/b Ratio</th>
<th>l-aldehyde (%)</th>
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</table>

\(^a\) Ligand to rhodium ratio is 10, catalysis performed in 13 ml of toluene using 1 ml of 1-octene as the substrate at 80 °C and 50 bar CO/H\(_2\). Samples were analyzed by means of GC and GC-MS analysis. \(^b\) Average turnover frequencies were calculated as (mol product)(mol catalyst)\(^{-1}\)h\(^{-1}\). \(^c\) 1 ml of 1-propanol added to the catalyst mixture. \(^d\) Initial turnover frequency. \(^e\) 1 ml of triethylamine added to the catalyst mixture.
The catalytic performance of 2 is significantly different from that of the rhodium-hydride analogue, 2'. The activity of 2(CF3COO\textsuperscript{-}) in the hydroformylation of 1-octene was investigated by monitoring a mixture of 2', CF\textsubscript{3}COOH and 1-octene in toluene under standard hydroformylation conditions (Table 4.3, entry 1). After 2 hours, 12 percent of 1-octene was converted; 75 % of the products were aldehydes (TOF = 21 mol.mol\textsuperscript{-1}.h\textsuperscript{-1}) while the remaining 25 % was octane, obtained by hydrogenation of 1-octene. Compared to 2', the hydroformylation rate of 2 was a factor ten lower, but the hydrogenation activity was significantly higher. The hydrogenation activity of both 2(CF3COO\textsuperscript{-}) and 2' was further compared in the hydrogenation of 1-nonanal under 50 bar of H\textsubscript{2}. Catalyst 2(CF3COO\textsuperscript{-}) showed a significant hydrogenation of the aldehyde to the corresponding alcohol (16 % conversion within 2 h reaction time, Table 4.3, entry 2), whereas the rhodium-hydride complex 2' is completely inactive in this reaction (Table 4.3, entry 3). The presence of both complexes on the silica support thus explains the observed cascade of a hydroformylation followed by a hydrogenation reaction. These experiments substantiate that in the silica immobilised system 1 and 1' co-exist on the polysilicate surface and that 1 must be formed from 1' by a protonation of the rhodium-hydride by the silica support since this is the only acid present in the reaction mixture (Scheme 4.2).

Table 4.3: Hydroformylation (X) and hydrogenation (Y) activities of [Rh(B)(CO)\textsubscript{2} (CF\textsubscript{3}COO\textsuperscript{-}) (2) and HRh(B)(CO)\textsubscript{2} (2')]\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst (Reaction)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>TOF\textsuperscript{b} (h\textsuperscript{-1})</th>
<th>L/b Ratio</th>
<th>l-aldehyde (%)</th>
<th>b-aldehyde (%)</th>
<th>l-alcohol (%)</th>
<th>Octane/Octene isomers\textsuperscript{c} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (X)</td>
<td>2</td>
<td>12</td>
<td>21</td>
<td>&gt;50</td>
<td>75.3</td>
<td>0</td>
<td>0</td>
<td>24.7\textsuperscript{d}</td>
</tr>
<tr>
<td>2' (Y)</td>
<td>2</td>
<td>16</td>
<td>22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>2 (X)</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ligand to rhodium ratio is 10, catalysis performed in 13 ml of toluene using 1 ml of 1-octene (in case of X) or 1 ml of 1-nonanal (in case of Y) as the substrate at 80 °C and 50 bar of CO/H\textsubscript{2} (in case of X) or H\textsubscript{2} (in case of Y). Samples were analyzed by means of GC and GC-MS analysis. \textsuperscript{b}Average turnover frequencies were calculated as (mol product)(mol catalyst)\textsuperscript{-1}.h\textsuperscript{-1}. Octane and alkene isomers are not quantitatively separable on GC. \textsuperscript{c}Of which approximately 50 percent octane.

The neutralising effect of alcohols on the silica supported cationic rhodium species was illustrated by the addition of 1-propanol (under 1 atm of CO/H\textsubscript{2}) to a suspension of silica "adsorbed" 2 in toluene. This resulted in a decolorisation of the silica while the toluene turned yellow; Rh(B) was "desorped" from the silica under formation of the rhodium-hydride 2' as indicated by the appearance of a doublet at 21 ppm; \textit{J}_{Rh,p} = 125 Hz in the \textsuperscript{31}P NMR spectrum. The presence of alcohol sufficiently decreases the acidity of the silica, which becomes unable
to protonate the rhodium-hydride species.\textsuperscript{32} Hence 2 is completely transformed to the rhodium-hydride 2' under a CO/H\textsubscript{2} atmosphere in the presence of alcohol.\textsuperscript{34} Consequently, the catalytic performance using Rh(A), immobilised on polysilicates, can be controlled by the addition of a sufficient amount of alcohol (Scheme 4.2).

\begin{center}
\includegraphics[width=\textwidth]{scheme_4.2.png}
\end{center}

\textbf{Scheme 4.2: Representation of the interconversion of the catalyst systems [Rh(A)(CO)]\textsuperscript{+} and [HRh(A)(CO)\textsubscript{2}] and the products generated from each catalyst species.}

4.4.5 Hydroformylation-hydrogenation cascade reaction

Under standard hydroformylation conditions, the cationic species 1 and the hydridic complex 1' co-exist on the support. Hence hydroformylation and hydrogenation will both proceed under a CO/H\textsubscript{2} atmosphere. Via a hydroformylation-hydrogenation of 1-octene using Rh(A), immobilised via the sol-gel process (Scheme 4.1-I) we performed a clean one-pot reaction of 1-octene to 1-nonanol. 98 percent of the 1-octene was converted in the hydroformylation reaction and 97 percent of the linear nonanal was subsequently hydrogenated to 1-nonanol resulting in an overall selectivity of 90 percent for the linear alcohol.\textsuperscript{35} Importantly, no heavy-end side-products were observed in this reaction owing to the mild conditions applied.

On monitoring such a cascade reaction, mainly the hydroformylation of 1-octene to the aldehyde was observed in the first few hours (Figure 4.3). The hydrogenation towards the corresponding alcohol started at higher aldehyde concentrations. When approximately 90 \% of the 1-octene was consumed (at 60 hours) the hydroformylation activity had decreased significantly, which is in line with the first order rate dependency in substrate. In contrast, the
hydrogenation of the aldehyde product proceeded. As a result the aldehyde concentration decreased again after approximately 40 hours, which in turn caused a decrease of the hydrogenation rate.\textsuperscript{36}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.3}
\caption{Course of the hydroformylation-hydrogenation sequence reaction of 1-octene using sol-gel immobilised Rh(A). Black line represents the 1-octene concentration, black dotted line 1-nonanal, grey line the sum of 1-nonanal and 1-nonanol and grey dotted line 1-nonanol. For detailed information about the conditions applied, see experimental section.}
\end{figure}

Such a clean, one-pot hydroformylation-hydrogenation cascade system,\textsuperscript{37} producing a high yield of the linear alcohol with a high regioselectivity is uncommon for rhodium catalysts.\textsuperscript{38} Moreover, we can control the ratio of the two co-existing catalyst species 1 and 1' and we are able to recycle the catalyst completely as a result of the heterogeneous nature of the system. The combination of these properties can be utilised for a multi-purpose system that can be switched between a pure hydroformylation catalyst (X), a pure hydrogenation catalyst (Y) and a hydroformylation-hydrogenation (Z) sequence catalyst (Scheme 4.3).
4.4.6 Modulation of the catalyst functionality

We started a series of catalyst experiments on 1-octene, using polysilicate immobilised Rh(A), with a reaction under standard conditions, thus with the catalyst system in the Z mode. The reaction was stopped after 172 h, which resulted in a product mixture that consisted for 66.7 percent of 1-nonanol and 18.5 percent of 1-nonanal (Table 4.4, entry 1). After this reaction we recycled the system and transformed it into a hydrogenation catalyst (Y) just by washing it with toluene and subsequently adding a mixture of 1-octene and 1-nonanal in toluene to the catalyst mixture. After a reaction time of 24 h under an H2-atmosphere a complete hydrogenation of both substrates was observed to octane and 1-nonanol, respectively (Table 4.4, entry 2). This shows that the switch from the Z to the Y mode was accomplished by simply replacing the CO/H2 for an H2 atmosphere. More importantly, we observed that this modulation is reversible; in the third catalyst cycle the system was applied again as a Z-sequence catalyst by changing the atmosphere from H2 to CO/H2 and using 1-octene as the substrate. This resulted in a switch of the catalyst from the hydrogenation mode back to the hydroformylation-hydrogenation sequence mode. The regioselectivity for the linear aldehyde and alcohol (overall linear to branched ratio of 18) was largely restored (Table 4.4, entry 3). This evidences that the catalyst did not decompose upon switching between these two modes, since even a few percents of decomposed rhodium catalyst would result in a dramatic drop in regioselectivity.

In the fourth cycle, once more the system was switched back from the Z to the Y mode (Table 4.4, entry 4). This time, the hydrogenation reaction of a 1:1 mixture of 1-octene and 1-nonanal was stopped after 2 h and a chemoselectivity for the alkene reduction over aldehyde reduction was observed (96 percent alkene and 10 percent aldehyde was hydrogenated). From these four catalytic runs it can be concluded that the immobilised catalyst system is
switched easily and repeatedly between the hydrogenation mode and the hydroformylation-hydrogenation cascade mode. We subsequently investigated, in the fifth run, the switch of the system to a pure hydroformylation catalyst (Table 4.4, entry 5). The atmosphere was changed from H₂ to CO/H₂ and 1 ml 1-propanol was added to the catalyst along with a fresh batch of 1-octene in toluene. After 96 hours 1-octene was almost completely converted to the linear aldehyde with a complete suppression of its hydrogenation to the alcohol! Hence, the catalyst modulation between all three catalyst functionalities was successfully accomplished upon small changes of the reaction conditions.

Table 4.4: Results from switching between hydrogenation (Y), hydroformylation (X) and hydroformylation-hydrogenation sequence (Z) reactions using sol-gel immobilised [Rh(A)CO].

<table>
<thead>
<tr>
<th>Entry/ (Reaction)</th>
<th>Time (h)</th>
<th>Conversion Octene (%)</th>
<th>Conversion Aldehyde (%)</th>
<th>l/b</th>
<th>l-aldehyde (%)</th>
<th>b-aldehyde (%)</th>
<th>l-alcohol (%)</th>
<th>Octane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/ (Z)</td>
<td>172</td>
<td>97</td>
<td>75</td>
<td>23</td>
<td>18.5</td>
<td>3.6</td>
<td>66.7</td>
<td>11.2</td>
</tr>
<tr>
<td>2/ (Y)</td>
<td>24</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3/ (Z)</td>
<td>68</td>
<td>60</td>
<td>16</td>
<td>18</td>
<td>65.2</td>
<td>4.5</td>
<td>13.7</td>
<td>16.6</td>
</tr>
<tr>
<td>4/ (Y)</td>
<td>2</td>
<td>98</td>
<td>10</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>9.7</td>
<td>98</td>
</tr>
<tr>
<td>5/ (X)</td>
<td>96</td>
<td>96</td>
<td>0</td>
<td>18</td>
<td>90.7</td>
<td>5.1</td>
<td>0</td>
<td>4.3</td>
</tr>
</tbody>
</table>

* Ligand to rhodium ratio is 10, catalysis performed in 13 ml of toluene using 1 ml of 1-octene (X and Z) (plus 1 ml of 1-nonanal in case of Y) as the substrate(s) at 80 °C and 50 bar of CO/H₂ (X and Z) or H₂ (Y). Samples were analyzed by means of GC and GC-MS analysis. Numbers include isomers of 1-octene since these are not separable from octane on GC.

4.5 Conclusion

We have developed a polysilicate immobilised homogeneous catalyst system that can act both as a hydrogenation and a regioselective hydroformylation catalyst. This system has been used for a clean one-pot synthesis of 1-nonanol from 1-octene via a hydroformylation-hydrogenation cascade reaction and could be quantitatively recovered from the product. The catalyst-support interactions were fully controlled and easily manipulated by simple changes in the reaction conditions. This enabled a reversible switching of the catalyst mode between a hydroformylation, a hydrogenation and a hydroformylation/hydrogenation cascade catalyst. In view of the increasing demand for greener chemical processes the current system exhibits several important properties; 1) it affords a quantitative and straightforward separation of the catalyst from the products, 2) it is reusable in numerous catalytic cycles without any deterioration of the catalytic activity, and 3) it enables clean and selective reactions for different important catalytic processes using only one catalyst system.
4.6 Experimental Section

Materials
The synthesis of N-(3-trimethoxysilane-n-propyl)-4,5-bis(diphenylphosphino)-phenoxazine (A) was reported in chapter 3 and 9,9-dimethyl-4,5-bis(diphenylphosphino)-xanthene (B) were synthesised according to literature procedures.\textsuperscript{15} 1-octene was purified over neutral alumina prior to its use. All other chemicals were purchased commercially and used without further purification. Solvents were dried prior to their use. Hexane, pentane, diethyl ether, THF, toluene and benzene were distilled from sodium. Dichloromethane and triethylamine were distilled from calcium hydride. All solutions and solvents not stated above were degassed under argon prior to their use. All reactions were performed under Schlenk conditions.

Analytical Techniques
NMR spectra were recorded on a Bruker AMX 300 or DRX 300 spectrometer. Chemical shifts are in ppm relative to TMS as external standard unless otherwise stated. Solid state \textsuperscript{29}Si MAS NMR chemical shifts are relative to Zeolite A (at –89 ppm) and Q\textsubscript{s}M\textsubscript{s} (at 11.85 ppm). The correct pulse delays were determined at 5 min for the \textsuperscript{29}Si MAS NMR at a spinning rate of 10.000-11.000 Hz. FT-IR spectra were obtained on a Bio-Rad FTS-7 spectrophotometer. Mass spectra (FAB) were recorded on a JEOL JMS SX/SX102A. Elemental Analysis were performed on a Elementar Vario EL apparatus (Foss Electric).

Synthesis of silica immobilised catalyst
A typical catalyst immobilisation procedure on silica; 2 g of silica, which is stored at 180 °C, was predried at 180 °C under reduced pressure for 2 h. 250 mg A was added to a suspension of the silica in 20 ml toluene and the resulting mixture was refluxed for 2 h. The silica(A) was washed with toluene, dried under reduced pressure and stored under an inert atmosphere. The silica modification (Scheme 1-III) was performed by refluxing a mixture of 2 g silica(A) and 2 ml of dimethoxydimethylsilane in 20 ml of toluene for 2 h. The resulting modified silica(A) was washed with toluene, dried under reduced pressure and stored under an inert atmosphere.

Catalysts were prepared freshly before use for catalysis. 1 g of silica(A) and 1*10\textsuperscript{5} mol [Rh(acac)(CO)\textsubscript{2}] was stirred in 5 ml of THF for 30 min. at room temperature. The resulting catalyst-support system was washed with THF and dried under reduced pressure (Method II). Method III was performed, on modified silica, similar to that of method I. For method IV, 1 g of silica(A) was suspended in a mixture of 1 ml of triethylamine and 5 ml of THF and stirrer at room temperature for 30 min. After 1*10\textsuperscript{5} mol [Rh(acac)(CO)\textsubscript{2}] was added the reaction mixture was stirred for another 30 min at room temperature. Work-up was analogues to other methods. For method V, A and [Rh(acac)(CO)\textsubscript{2}] were stirred in 10 ml of THF for 30 minutes. Predried silica was added to the yellow reaction mixture and the
resulting suspension was stirred for 18 h at room temperature. The resulting yellow-brown catalyst-support system was washed with THF and dried under reduced pressure.

**Synthesis of sol-gel immobilised [Rh(A)CO]**

A mixture of 5 mg (0.01946 mmol) Rh(acac)(CO)₂ and 138.7 mg (0.1946 mmol) A was dissolved in 6 ml of THF. 2 ml of H₂O and 2 ml of TMOS were subsequently added and a red-brown two-phase system was formed. MeOH was added until a clear red-brown solution was formed. Gelation took place within 1 hour. After 36 hours the gel was carefully dried under reduced pressure. The dried gel was powdered and thoroughly washed with MeOH, THF and Et₂O. The resulting pink-red silica’s were stored at -20°C. FT-IR (KBr); ν(CO) 2011 cm⁻¹, ³¹P MAS NMR (121.4 MHz, versus NH₄H₂PO₄ = 0.8 ppm); δ 38 br (some phosphine oxide (δ 26) br and protonated phosphine (δ 51) was observed).

**Effect of silica on HRh(B)(CO)**

CO/H₂ was bubbled through a solution of 5 mg [Rh(acac)(CO)₂] and 20 mg B in 5 ml of toluene for 10 min. 250 mg predried silica was added to the yellow reaction mixture. As a result the solution decolorised and the silica turns orange. FT-IR (KBr); ν(CO) 1972 cm⁻¹. Under continuous bubbling of CO/H₂, 1 ml of 1-propanol was added to the reaction mixture. The solution slowly became yellow. After 20 min an ³¹P NMR spectrum was acquired; δ 21 (d, J(P,Rh) = 125 Hz).

**Effect of CF₃COOH on HRh(B)(CO)**

CO/H₂ was bubbled through a solution of 5 mg [Rh(acac)(CO)₂] and 20 mg B in d₆-benzene for 10 min. 20 µl of CF₃COOH was added to the reaction mixture under continuous bubbling of CO/H₂. ³¹P NMR; δ 38 (br d, J(P,Rh) = 111 Hz). A hydroformylation and a hydrogenation experiment were performed using a catalyst mixture of 1*10⁻⁵ mol [Rh(acac)(CO)₂], 1*10⁻⁴ mol B and 20 µl of CF₃COOH in toluene (see below for details).

**Hydroformylation of 1-octene**

A typical catalysis experiment: A stainless steel 50 ml autoclave, equipped with a mechanical stirrer, a substrate vessel, a cooling spiral and a sample outlet was charged with 1 g of 1*10⁻⁵ mol rhodium-catalyst containing silica in 10 ml of toluene. The suspension was incubated for 1 hour at 80 °C under 20 bar CO/H₂ (1:1). A mixture of 1 ml of 1-octene and 1 ml of decane in 3 ml of toluene was added and the CO/H₂ pressure was brought to 50 bar. The mixture was stirred for 24 hours. The autoclave was cooled down to 10 °C and the pressure was reduced to 1.8 bar. With this small overpressure the liquid is slowly removed from the catalyst with a 1.2 mm syringe. After the catalyst was washed with 5 ml of toluene, 10 ml of toluene is added
and the pressure was brought to 20 bar. Finally the mixture was heated to 80 °C and the second cycle was performed.

**Switching of catalyst functionality**

Hydroformylation-reduction sequence reactions were performed as described above. Hydroformylations were also performed under the same conditions, but 1-ml of propanol was added to the reaction mixture. Hydrogenations were performed on a reaction mixture of 1 ml of 1-octene, 1 ml of 1-nonanal and 1 ml of decane in 12 ml of toluene under 50 bar of H₂ at 80°C. The catalyst recycling procedure was performed as described above.

### 4.7 References and notes

Chapter 4


21 This method was reported to be equally efficient in the modification of silica surfaces as the use of chloroalkylsilanes; D.W. Sindorf, G.E. Marciel J. Am. Chem. Soc. 1983, 105, 3161.

22 It was observed that the stretch frequency of the carbonyl is slightly influenced by the counterion of the complexes. Non-immobilised complexes can be studied easily during the sol-gel process by means of liquid-state NMR. This is not possible for the immobilised rhodium(A) complex.


25 A transition metal can serve as extra junction in the silica network and it can also catalyse the polycondensation process. This was previously observed by Lambert et al.; C.K. Lambert, R.D. Gonzalez Microporous Mat. 1997, 179.

26 The resolution of Figure 2A is better than that of 2B due to a difference in the number of scans.


28 The effect of silica on the hydroformylation rate is comparable to the deleterious effect of anions like chlorides; P.W.N.M. van Leeuwen in Rhodium Catalyzed Hydroformylation (Ed. P.W.N.M. van Leeuwen, C. Claver), Kluwer Acedemic Publishers, Dordrecht, 2000, 233.


31 The presence of triethylamine also slowed down the reaction rate, probably due to its co-ordination abilities.

32 The decrease in the capacity of silica to form hydrogen bridges on drying, gives rise to an increase in acidic sites on the silica surface; A.J. van Roosmalen, J.C. Mol J. Phys. Chem. 1979, 83, 2485. The addition of a protic solvent (water or alcohol) to dried silica will facilitate hydrogen bond formation and thereby neutralise the acidity.

33 The bonding of a rhodium phosphine carbonyl complex to a silica surface was previously applied via the protonation of a rhodium-methyl bond; S.L. Scott, M. Szpakowicz, A. Mills, C.C. Santini J. Am. Chem. Soc. 1998, 120, 1883.

34 The reversible protonation and hydrogenation of a comparable rhodium-hydride viz. HRh(CO)(TPPTS), was previously observed; W.A. Herrmann, J.A. Kulpe J. Organomet. Chem. 1990, 389, 85.
This result was obtained using a reaction mixture of 14 ml of toluene, 0.5 ml of 1-octene and 0.5 ml of decane after 328 hour. The exact product distribution obtained was: 1-nonanol (89.8 %), octane (4.5 %), 1-nonanal (2.3 %), b-nonanal (0.7 %) and b-alcohol (0.7 %).

The decreased hydrogenation activity at higher conversions is most probably caused by the increased alcohol concentration; the silica becomes less acidic and the hydrogenation catalyst I transforms to I'. Full conversion to the alcohol is obtained at lower substrate concentration, see ref 35.


This is in contrast with Rh(A) performing as a Z-sequence catalyst with which the aldehyde is preferentially reduced. The preference of aldehyde hydrogenation under a CO/H_2 atmosphere has previously been observed on different cationic complexes; see ref 38e and 38g. It is assumed that under hydroformylation conditions aldehyde co-ordination to the cationic species will be kinetically favored over alkene co-ordination.