Tailor-made Catalysts Immobilised on Silica.
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A stable and recyclable Supported Aqueous Phase Catalyst for highly selective hydroformylation of higher alkenes

Abstract

A highly regioselective supported aqueous phase hydroformylation catalyst is presented that is completely and conveniently separated from the products and reused in numerous consecutive catalytic cycles.

Chapter 2

2.1 Introduction

Hydroformylation is one of the mildest and cleanest methods to produce aldehydes and is therefore widely applied in the petrochemical industry. The cleanest and most important industrial hydroformylation process is the aqueous biphasic process, developed by Ruhrchemie, affording a straightforward separation of the organic products from the catalyst. The applicability of this system, however, is strictly limited to substrates that are slightly water-soluble, such as propene and but-1-ene. The industrial hydroformylation of higher olefins is carried out in a single, organic phase from which the catalyst is mostly separated by extraction, precipitation or distillation, which may result in catalyst decomposition. Furthermore, distillative techniques are not suitable for the separation of heavier products or fine chemicals because of the high boiling points of the products.

An interesting novel concept of catalyst immobilisation is the Supported Aqueous Phase Catalyst (SAPC). In this system the catalyst is immobilised in a thin water layer adhered in the pores of a high-surface-area silicate. Using this system higher alkenes can be converted at a relatively high rate without metal leaching. The regioselectivity, however, towards the linear aldehyde of the reported systems thus far is very low and surprisingly little has been reported on the recyclability and stability of these systems. Virtually all SAP hydroformylation catalysts described in literature are based on rhodium, cobalt or platinum/nickel complexes with TPPTS as the ligand. Only in a single case sulfonated diphosphines were examined. Diphosphines with a large P-M-P bite angle have a beneficial influence on the regioselectivity of homogeneous hydroformylation catalysts. Our group recently reported on the synthesis of a water-soluble ligand with a large bite-angle, the disodium salt of 2,7-bissulfonate-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Sulfoxantphos) (A), and its use in biphasic hydroformylation reactions. The high regioselectivity obtained with this ligand stimulated us to investigate its performance as a SAPC.

2.2 Results and discussion

2.2.1 Complex study

It was recently shown that the rhodiumhydride HRh(A)(CO)₂ (1), the precursor to the active species in hydroformylation reactions, was formed quantitatively under a CO/H₂ (1:1) atmosphere in DMSO-δ6. When 1 is exposed to 1 bar of CO it completely transforms to the rhodium dimer [Rh(A)(CO)(μ-CO)]₂ (2) (Scheme 2.1), which could be isolated and characterised by means of NMR, FT-IR and FAB-MS. The ³¹P NMR spectrum of 2 is consistent with an AA’BB’XX’ spin system (J_RHP = 129, 135, 155 and 164 Hz, J_RHP = 8 Hz, J_PP = 18 Hz, J_PP = 2 and 5 Hz, see Figure 2.1).
The equilibrium between 1 and 2 can be forced completely to either side by changing hydrogen pressure.\textsuperscript{12} A similar experiment in D\textsubscript{2}O revealed that the formation of both 1 and 2 is much slower in aqueous media.

Silica immobilised 1 was prepared by adding one equivalent of Rh(acac)(CO)\textsubscript{2} to a suspension of A, impregnated on silica (CPG-240 Å), in diethylether under a CO/H\textsubscript{2} atmosphere. The \textit{in situ} formation of 2 in the resulting mixture was clearly observed using NMR techniques.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.1.png}
\caption{Observed and calculated \textsuperscript{31}P NMR spectrum of [Rh(A)(\textmu-\textit{CO})(CO)]\textsubscript{2} (2).}
\end{figure}

### 2.2.2 Catalysis

Both the novel Rh(A)/SAPC and the known Rh(TPPTS)/SAPC were studied in the hydroformylation of 1-octene. Rh(A)/SAPC is very selective towards the linear aldehyde;
a linear to branched aldehyde ratio of 40 was obtained. This is an increase in regioselectivity, compared to Rh(TPPTS)/SAPC, of a factor of at least 10 (Table 2.1, entries 1 and 11). This proves that indeed ligand A plays a key role in the regulation of the regioselectivity in the hydroformylation of immobilised homogeneous catalysts.

The rate of hydroformylation of 1-octene using Rh(A)/SAPC at 80 °C in toluene as the co-solvent was found to be low (~1 turnover per hour; Table 2.1, entry 1 and 2). When the catalysis was performed in pure 1-octene, however, the rate increases to a turnover rate of 15 per hour (Table 2.1, entry 1 and 3). Interestingly, this large concentration dependency was not found for Rh(TPPTS)/SAPC (Table 2.1, entries 11 and 12). We also found a 5- to 8-fold increase on performing the catalysis at a temperature of 100 °C (turnover rate of 55 and 80 per hour, entries 9 and 13). Under optimised conditions the activity of Rh(A)/SAPC and Rh(TPPTS)/SAPC are in the same order of magnitude while the high selectivity of the former catalyst is retained.

### Table 2.1: Results from the hydroformylation of 1-octene at 80/100 °C and 50 bar CO/H\(_2\) (1:1).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst [cycle](^b)</th>
<th>Conversion after 24 hour (%)</th>
<th>TOF(^b)</th>
<th>Linear to Branched Isomerisation(^c) (%)</th>
<th>Linear Aldehyde(^c) (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Rh(A) [1]</td>
<td>7</td>
<td>1</td>
<td>38</td>
<td>1.9</td>
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<tr>
<td>2</td>
<td>Rh(A) [2]</td>
<td>28(^d)</td>
<td>1</td>
<td>44</td>
<td>5.7</td>
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<tr>
<td>3</td>
<td>Rh(A) [3](^e)</td>
<td>14</td>
<td>15</td>
<td>46</td>
<td>5.0</td>
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<tr>
<td>4</td>
<td>Rh(A) [4](^e)</td>
<td>14</td>
<td>14</td>
<td>42</td>
<td>8.7</td>
</tr>
<tr>
<td>5</td>
<td>Rh(A) [5](^e)</td>
<td>12</td>
<td>14</td>
<td>40</td>
<td>8.5</td>
</tr>
<tr>
<td>6</td>
<td>Rh(A) [6](^e)</td>
<td>10</td>
<td>13</td>
<td>40</td>
<td>7.7</td>
</tr>
<tr>
<td>7</td>
<td>Rh(A) [7](^e)</td>
<td>24(^e)</td>
<td>10</td>
<td>39</td>
<td>7.3</td>
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<td>8</td>
<td>Rh(A) [8](^e)</td>
<td>37</td>
<td>44</td>
<td>31</td>
<td>7.0</td>
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<tr>
<td>9</td>
<td>Rh(A) [9](^e)</td>
<td>46</td>
<td>55</td>
<td>31</td>
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<td>55</td>
<td>27</td>
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<tr>
<td>11</td>
<td>Rh(TPPTS) [1]</td>
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<td>15</td>
<td>3</td>
<td>7.4</td>
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<tr>
<td>12</td>
<td>Rh(TPPTS) [2](^e)</td>
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<td>30</td>
<td>3</td>
<td>12.3</td>
</tr>
<tr>
<td>13</td>
<td>Rh(TPPTS) [3](^e)</td>
<td>17</td>
<td>160</td>
<td>3</td>
<td>7.3</td>
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<tr>
<td>14</td>
<td>Rh(TPPTS) [4](^e)</td>
<td>90(^f)</td>
<td>146</td>
<td>2</td>
<td>52.6</td>
</tr>
</tbody>
</table>

\(^a\) Experiments performed at a ligand to rhodium ratio is 10 for Rh(A) and 20 for Rh(TPPTS), catalysis performed at 80 °C and 50 bar CO/H\(_2\) in 15 ml toluene as a co-solvent using 1 ml of 1-octene. \(^b\) Average turnover frequencies were calculated as mol aldehydemol catalys\(_1\) (h\(^{-1}\)). \(^c\) Determined by means of GC-analysis using decane as an internal standard. \(^d\) Conversion after 96 hours. \(^e\) Catalysis performed in 15 ml 1-octene at 80 °C. \(^f\) Conversion after 72 hours. \(^g\) Catalysis performed in 15 ml 1-octene at 100 °C.
The product/catalyst separation efficiency of the SAPC's was examined on performing recycling experiments (Table 2.1). Rh(A)/SAPC could be recycled numerous times without deterioration of the catalyst performance (entries 1–10). The selectivity towards the linear aldehyde remained high during all experiments and the decrease in rate of hydroformylation is very small (at 100 °C we even observe a small increase in rate in successive runs). This indicates that ligand A retains the rhodium quantitatively on the support which is confirmed by rhodium analysis, performed on the product, by means of I.C.P. Atomic Emission Spectroscopy. No traces of rhodium were detected in the product phase of any of the SAPC experiments (detection limit; 1 ppm). In contrast, Rh(TPPTS)/SAPC showed a drop in catalyst performance after three catalytic runs (Table 2.1, entries 11-14). In the fourth cycle, over 50 percent of the 1-octene isomerised and the linear-to-branched ratio drops to 2. The Rh(A)/SAPC is thus far more robust then the TPPTS based SAPC; Rh(A)/SAPC could be recycled over at least three weeks, showing no deterioration of the catalyst performance whereas under similar conditions Rh(TPPTS)/SAPC shows a strong reduction in hydroformylation performance after three days.

Importantly, Rh(A)/SAPC is stable in the absence of substrate as it can be transformed into the dimer \([\text{Rh(A)}(\mu\text{-CO})(\text{CO})]_2\) which is stable over weeks when properly stored under 1 bar of CO. The reversible switching between the catalytically active species 1 and the stable dimeric species 2 in between two consecutive catalytic runs did not influence the catalytic performance.

### 2.3 Conclusion

We can conclude that the introduction of rigid bidentate diphosphines with a large ‘natural’ bite angle in the Supported Aqueous Phase Catalysis improves the regioselectivity towards the linear aldehyde enormously compared to the SAPC’s known thus far. The application of A in SAP catalysed hydroformylation gives a 100 percent retaining of the catalyst activity and selectivity in at least 10 cycles. To the best of our knowledge this Supported Aqueous Phase Catalyst is the first example of an immobilised homogeneous catalyst that is highly selective and robust and shows no metal leaching in numerous consecutive catalytic runs. Since the catalyst activity is lowered with a factor of 20 with respect to the homogeneous system this concept does not satisfy the demands for an industrial application however.
2.4 Experimental Section

Synthesis of [Rh(Sulfoxantphos)(μ-CO)(CO)]₂
A solution of 20 mg (0.078 mmol) Rh(acac)(CO)₂ and 61 mg (0.078 mmol) Sulfoxantphos in 1.5 ml DMSO was purged with CO/H₂ (1:1) for 10 minutes and stirred for 18 hours. The yellow solution was purged for 10 minutes with CO and stirred for another 18 hours. A yellow precipitate was formed when 10 ml of THF was slowly added. The yellow powder was collected by filtration, washed with THF and dried under a gentle stream of CO. The product was stored under a CO atmosphere (yield; 54.3 mg, 74%).

\[ ^{31}P{^1}H \text{NMR (121 MHz, [D}_6^0\text{DMSO, 20°C, reference to external H}_3^3P0_4): } \delta = 2.0 \text{ and } 8.0 \text{ (see text for details).} \]

\[ ^1H \text{NMR (300 MHz, [D}_6^0\text{DMSO, 20°C, TMS): } \delta = 7.86 \text{ (br.d, 4H, ArH), 7.34-6.49 (m, 44H, ArH), 1.92 (s, 3H, CH}_3, \text{ 1.40 (s, 3H, CH}_3). FT-IR (KBr): } \nu = 1968 \text{ cm}^{-1} (\text{C=O}), 1733 \text{ cm}^{-1} (\mu\text{-C=O). FAB(+)MS: } m/z(%) = 1882(1)[M^+] , 1803(3)[M^+-Na-2(CO)], 918(76) [(M^+-2(Na))/2].

Preparation of Rh(Sulfoxantphos)/SAPC
Sulfoxantphos was impregnated on CPG-240 Å using a literature procedure. One equivalent of Rh(acac)(CO)₂ was added to a suspension of Sulfoxantphos/CPG-240Å in diethylether. The suspension was purged with CO/H₂ (1:1) for 10 minutes. During this period the solution discolored and the silica turned yellow. The suspension was stirred for 18 hours and subsequently purged with CO for 10 minutes and stirred for another 18 hours. The SAPC was collected by filtration and partly dissolved in CO-saturated DMSO-d₆. \(^{31}P\) NMR experiments clearly showed the formation of 2.

Catalyst preparation
The Rh(Sulfoxantphos)/SAPC precursor was prepared by mixing 1 g of CPG-240Å to a solution, containing approximately 3×10⁻⁵ mol Rh(acac)(CO)₂ and 3×10⁻⁴ mol A in 10 ml of MeOH on mechanically stirring for 1h. The MeOH was removed in vacuo until a free flowing, pink silica remained. Rh(TPPTS)/SAPC was prepared according to a literature procedure.

Catalysis procedure
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 the SAPC in 10 ml toluene. The suspension was incubated for 1 hour at 80°C under 20 bar CO/H₂ (1:1). A mixture of 1 ml 1-octene and 1 ml decane in 3 ml toluene was added and the CO/H₂ pressure was
brought to 50 bar. Catalyst runs of 24 hours were performed. The autoclave was cooled down to 15°C and the pressure was reduced to 2 bar. With the small overpressure the liquid was slowly removed from the catalyst with a 1.2 mm syringe. After the catalyst was washed with 5 ml toluene, 10 ml of toluene was added and the pressure was brought to 20 bar. Finally the mixture was heated to 80°C and the next cycle was performed.

2.5 References and notes

1. E.G. Kuntz Chemtech 1987, 570.
13. We also observed this increase in rate of hydroformylation in successive catalytic runs in the biphasic Rh(A) system (reference 10). We suggest that at this temperature remaining catalytically inactive species are slowly transformed in the active form (the inactive species is most probably the carbonyl bridged rhodium dimer).
15. Water content on the SAPCs was 4 weight percent (thermogravimetrically determined).
Chapter 2

Catalyst preparation

The Rh(Sulfoximine)(HCOO) catalyst was prepared in the following solution, containing approximately 2 g of NBSOff, mechanically stirring the solution for 1 hour. The black precipitate solidified, and the catalyst was isolated using a fine-mesh sieve.

Catalysis procedure

A stainless steel 50 ml reactor, equipped with a magnetic stirring bar and a cooling jacket, was charged with 10 ml of acetone. The reactor was heated to 100°C under a nitrogen atmosphere and the 5 mg catalyst was added. The reaction was allowed to proceed for 1 hour, and the product was isolated and characterized.