Tailor-made Catalysts Immobilised on Silica.
Sandee, A.J.

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**ROTACAT**: a rotating device containing a designed catalyst for highly selective hydroformylation*

**Abstract**

A novel concept is presented for the immobilisation of a homogeneous catalyst. A hydroformylation catalyst was covalently anchored to monoliths that were constructed as the blades of a mechanical stirrer that was used in a batch process. The catalyst was effective in the hydroformylation of both higher and lower alkenes and showed a high regio-selectivity for the linear aldehyde. The concept was proven to be useful in a liquid organic and aqueous phase as well as in the gas phase and the catalyst could be used numerous times without catalyst deterioration. No catalyst deactivation was observed in a period over half a year.

6.1 Introduction

A widely investigated approach to facilitate catalyst/product separation is the attachment of catalysts to an organic (for example polydivinylbenzene),\(^1\) inorganic (for example polysiloxane)\(^2,3\) or hybrid\(^4,5\) resin.\(^6\) There is, however, no successful commercial application of a polymer immobilised homogeneous catalyst thus far. This is mainly because there is no system yet that shows a high activity and a high selectivity and, at the same time, does not suffer from leaching of active metal catalyst.\(^7\) Our recent advances in immobilising rhodium complexes of Xanthene based diphosphine ligands in an aqueous phase,\(^8,9\) a supported aqueous phase (Chapter 2)\(^10\) and a silica matrix (Chapter 3, 4 and 5)\(^11,12\) have shown the feasibility of a catalyst that does satisfy most of these requirements.

Using the sol-gel process we were able to anchor a very active and selective hydroformylation catalyst covalently into a silicate matrix that could be recycled and that showed no deterioration in catalytic performance in numerous consecutive catalytic cycles (Chapter 3).\(^11\) The catalyst, a rhodium-complex containing a diphosphine ligand with a large “natural” bite-angle,\(^13\) \(N\)-(3-trimethoxysilane-\(n\)-propyl)-4,5-bis(diphenylphosphino)-phenoxazine \(A\), contains a trialkoxysilane unit by which the covalent anchoring on silicate surfaces has been realised. Since this catalyst system is potentially interesting for the industrial production of higher linear aldehydes, we investigated the possibility of a multi-purpose reactor, using \(A\), in which a broad range of substrates (different in boiling point and polarity) can be hydroformylated subsequently with one and the same catalyst. For this purpose a catalyst system is needed that can be easily separated from the product and that can perform reactions in gas-, liquid organic- and liquid aqueous-phases. In this perspective a slurry reactor is less favorable.

\[
\begin{align*}
\text{(MeO)}_3\text{Si} & \quad \text{PPh}_2 \\
\text{N} & \quad \text{O} \\
\text{PPh}_2
\end{align*}
\]

(A)

In recent years monolithic reactors have found wide application in gas-solid processes such as automotive emission control\(^14\) and industrial off-gas purification.\(^15\) Also, these systems are being considered for gas-liquid-solid processes such as hydrogenations and oxidations.\(^16\) Recently, Moulijn et al. reported on a novel reactor configuration in which blocks of monoliths are arranged in a stirrer-like fashion.\(^17\) Using this setup a reasonably large surface area of the immobilised catalyst is retained, but many problems of handling a suspension of finely divided supported catalyst species are eliminated.
In this paper a concept is described that unites the above described processes to obtain an immobilised homogeneous **rotating catalyst** (ROTACAT). A was covalently anchored to monoliths and these monoliths were implemented in two hollow tubes that were constructed as blades of a mechanical stirrer (Figure 6.1-A and B). Two types of monoliths (Si and SiC) were explored that differ in mechanical strength and surface area. The Si monoliths have a higher surface area (120 m²/g vs 0.5 m²/g) whereas the SiC monoliths are mechanically far more stable.

![Figure 6.1 A: Schematic representation of the homogeneous complex, immobilised on monoliths, and the implementation of these monoliths in the blades of a mechanical stirrer. Inset B: Picture of the silicon-carbide monoliths in the stirrer.]

**6.2 Results and discussion**

**6.2.1 ROTACAT preparation**

The mechanical stirrer of a 200 ml autoclave, consisting of two parallel cylindrical tubes, was charged with two monoliths. SiC monoliths were gently forced in the tubes by means of a teflon socket. Since Si monoliths are far more brittle, its positioning was more troublesome. To this end the tubes of the rotor were cut in two half-pipes and after positioning of the monoliths, the two halves were carefully screwed together.
A sufficient amount of A was immobilised on the monoliths by agitation a toluene solution of A at 80°C under an inert atmosphere. The immobilised ligand was subsequently functionalised with the rhodium precursor obtaining 1 (SiC monoliths) and 2 (Si monoliths) by incubating a toluene solution of [Rh(acac)(CO)₂] at 80°C under 50 bar of CO/H₂ (1:1) for 1 hour in an autoclave, equipped with the ligand functionalised rotor.

The SiC monoliths were found to need a special treatment since the surface area of this type of monoliths is too low (less than 0.5 m²/g according to BET surface area measurements). Only very little of ligand A could be loaded on a SiC monolith of 3.5 g. To increase the surface area the SiC monoliths were first wash-coated with a porous silica top-layer of approximately 15 weight percent. To this end monoliths were dipped in a colloidal silica solution in water. After the excess of liquid was removed the silica-layer was casted at elevated temperature. This silicon top layer, causing an increase in surface area to 17 m²/g (determined by BET surface area measurements) allowed a sufficient ligand loading (0.02-0.04 mmol/g monolith). The Si monoliths could be charged with a sufficient amount of ligand without pre-treatment (~0.05 mmol/g monolith).

### 6.2.2 Catalysis

In the hydroformylation of 1-octene, using the SiC monoliths, the overall selectivity for 1-nonanal is 89 ± 3 percent (Table 6.1). As was found previously for the homogeneous system (entry 4) and the silica immobilised system (entry 5), the linear-to-branched aldehyde ratio is very high (ranging from 20 to 46). Also in this case the Xanthene-based diphosphine effectively leads to the production of linear aldehyde. Remarkably, the selectivity for the linear product using the Si monoliths is lower (72 %) (entry 2). The regioselectivity for the linear aldehyde is rather high (1/b ratio of 14) but alkene isomerisation was observed to a large extent (18 %). Furthermore, significant hydrogenation of 1-nonanal to the alcohol was observed (4.8 %). The hydrogenation was completely suppressed by the addition of a small amount of 1-propanol during catalysis (entry 3). We assume that the lower catalyst selectivity of the Si-monolith immobilised catalyst is a result of the higher acidity of this material.

Since the SiC ROTACAT was found to be superior in mechanical strength and selectivity, the activity being comparable, it was decided to study this SiC system in more detail. The initial rate of hydroformylation under standard conditions was found to be low (between 1 and 2 mol.mol⁻¹.h⁻¹). Compared to the sol-gel immobilised analogue this is about 15 times lower.

Analogous to the sol-gel immobilised system there is a first order rate dependency of the hydroformylation rate on the substrate concentration (Figure 6.2). As a result, hydroformylations performed at a high octene concentration led to a major increase in reaction rate. This is important since ROTACAT is applicable at very high substrate concentrations as it is not limited by the solubility of the catalyst. In an octene/toluene 1:1 mixture the rate of the reaction increased to 15 mol.mol⁻¹.h⁻¹ (Table 6.1 entries 1 and 9).
Table 6.1: Results from the hydroformylation of 1-octene at 80°C and 50 bar CO/H₂.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (cycle)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>TOFb</th>
<th>Linear aldehyde (%)</th>
<th>Branched aldehyde (%)</th>
<th>Alkene isomerisation (%)</th>
<th>Linear to branched ratio</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>96</td>
<td>26</td>
<td>2</td>
<td>92.5</td>
<td>2.0</td>
<td>5.5</td>
<td>46</td>
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<tr>
<td>2</td>
<td>2</td>
<td>48</td>
<td>19</td>
<td>3</td>
<td>71.5</td>
<td>5.6</td>
<td>18.1</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>2(2)</td>
<td>48</td>
<td>12</td>
<td>2</td>
<td>77.2</td>
<td>3.8</td>
<td>19.0</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>A/Rh&lt;sup&gt;e&lt;/sup&gt; {homog.}</td>
<td>2</td>
<td>19</td>
<td>283</td>
<td>93.3</td>
<td>2.9</td>
<td>3.7</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>A/Rh&lt;sup&gt;e&lt;/sup&gt; {sol-gel}</td>
<td>24</td>
<td>69</td>
<td>35</td>
<td>92.8</td>
<td>3.0</td>
<td>1.7</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>1(1)</td>
<td>96</td>
<td>24</td>
<td>1</td>
<td>86.4</td>
<td>1.5</td>
<td>12.1</td>
<td>57</td>
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<tr>
<td>7</td>
<td>1(2)</td>
<td>96</td>
<td>23</td>
<td>1</td>
<td>87.6</td>
<td>3.7</td>
<td>8.7</td>
<td>23</td>
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<tr>
<td>8</td>
<td>1(3)</td>
<td>168</td>
<td>38</td>
<td>1</td>
<td>86.7</td>
<td>3.2</td>
<td>10.1</td>
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<td>18</td>
<td>15</td>
<td>88.0</td>
<td>4.0</td>
<td>8.0</td>
<td>22</td>
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<tr>
<td>10</td>
<td>1(5)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>96</td>
<td>14</td>
<td>13</td>
<td>95.2</td>
<td>2.8</td>
<td>1.9</td>
<td>34</td>
</tr>
<tr>
<td>11</td>
<td>1(6)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>96</td>
<td>15</td>
<td>13</td>
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<td>28</td>
<td>21</td>
<td>84.2</td>
<td>4.2</td>
<td>11.5</td>
<td>20</td>
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<tr>
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<td>1(8)&lt;sup&gt;g&lt;/sup&gt;</td>
<td>389</td>
<td>76</td>
<td>21</td>
<td>87.3</td>
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<td>23</td>
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<tr>
<td>14</td>
<td>1(9)&lt;sup&gt;g&lt;/sup&gt;</td>
<td>645</td>
<td>90</td>
<td>9&lt;sup&gt;h&lt;/sup&gt;</td>
<td>87.0</td>
<td>3.2</td>
<td>9.7</td>
<td>26</td>
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<td>15</td>
<td>1(10)&lt;sup&gt;l&lt;/sup&gt;</td>
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<td>14</td>
<td>97</td>
<td>87.9</td>
<td>4.1</td>
<td>8.0</td>
<td>22</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ligand to rhodium ratio is 10,  catalysis performed in 54 ml toluene using 3 ml of 1-octene under 50 bar of CO/H₂=1/1.  <sup>b</sup> Initial turnover frequencies were determined as (mol aldehyde)(mol catalyst)⁻¹h⁻¹ at 10-20 percent conversion.  <sup>c</sup> Determined by means of GC-analysis using decane as an internal standard.  <sup>d</sup> In 54 ml toluene and 1 ml 1-propanol.  <sup>e</sup> Data taken from chapter 3.  <sup>f</sup> In 25 ml toluene and 25 ml 1-octene.  <sup>g</sup> As in entry 9 but stirred back and forward.  <sup>h</sup> Average turnover frequency.  <sup>i</sup> As in entry 12 but 35 bar H₂ and 15 bar CO.  <sup>j</sup> As in entry 13 but in 50 ml 1-octene.
One of the possible causes of the difference in reaction rate of the ROTACAT compared to the slurry reactor is a poorer accessibility of the substrate to the catalytic active sites due to an inefficient mixing. We studied this by changing the one-way stirring mode into one that inverts the direction every 5 seconds. This indeed resulted in a rate improvement of a factor of 2 (Table 6.1, entries 11 and 12). Another possible cause of the lower reaction rate is the relatively low surface area compared to the sol-gel immobilised catalyst (17 m$^2$/g vs. 500 m$^2$/g). The immobilised catalytic sites are densely packed on the monolith. The average surface area, available per molecule of ligand, was estimated at 94 Å$^2$/molecule. This close proximity of catalytic sites possibly promotes the formation of carbonyl bridged rhodium dimers, which give no hydroformylation activity. The partial hydrogen pressure is known to have a strong influence on the equilibrium between the rhodium hydride dicarbonyl and the carbonyl bridged rhodium dimer (in Chapter 2 it was reported that this effect was clearly observed in solution with an analogous complex). On performing the catalysis under an atmosphere of CO/H$_2$: 15/35, the reaction rate was increased from 21 to 50 mol.mol$^{-1}$h$^{-1}$ compared to the CO/H$_2$: 1/1 experiment (entries 13 and 15) substantiating the existence of these dimers. Under these optimised conditions the reaction rate reached 97 mol.mol$^{-1}$h$^{-1}$ when the catalysis was performed in neat 1-octene (entry 16).

The ROTACAT could be reused in a series of consecutive catalytic cycles showing no systematic deterioration in hydroformylation performance. (Figure 6.3, Table 6.1 entries 6-16). Clear colorless product solutions were drawn from the autoclave, which did not contain rhodium or phosphine, as was indicated by means of Atomic Emission Spectroscopy. The catalyst showed a remarkable long-term stability. It was found that this system is reusable for over six months without systematic decrease in catalytic performance. We did, however,
observe a fluctuation in the percentage of alkene isomers (7 ± 5 percent). We ascribe this fluctuation to differences in catalyst induction period between subsequent catalytic runs.\textsuperscript{22}

![Figure 6.3: Schematic representation of the product distribution in the hydroformylation of 1-octene. Representing (from the back to the front): n-aldehyde, isomers, i-aldehyde.](image)

The ROTACAT is one of the most stable hydroformylation systems reported in literature. The bond-strength of the chelating diphosphine to the rhodium is very high and the rhodium-diphosphine complex is solidly anchored on the monolithic rotor. The system enables a straightforward recycling procedure (compared to slurry reactions) in which adequate washings do not damage the catalyst.

### 6.2.3 Multiphase catalysis

We further explored the ROTACAT concept in the application of gas- and aqueous phase reactions in order to investigate its multi purpose feasibility. The hydroformylation of propene in the gas-phase was studied on agitating the ROTACAT in a mixture of propene/CO/H\textsubscript{2} of 8/25/25. The product mixture, collected at the bottom of the autoclave, was investigated by means of GC analysis (Table 6.2, entries 1-3). The selectivity towards the linear aldehyde was 93% with a linear to branched aldehyde ratio of 14 which is slightly lower than the selectivity found for 1-octene.

The application of the ROTACAT in the aqueous phase was also investigated. Although propene is only moderately soluble in water it is well known to be a suitable substrate for aqueous phase catalysis.\textsuperscript{23} The autoclave was charged with 50 ml water, 50 bar syn gas and 8 bar of propene. The separate organic layer, formed during catalysis, was found to consist of 93 percent 1-butanal and 7 percent of 2-methylpropanal (Table 6.2, entry 4-6) which is the same as found in the gas-phase reaction. After several phase changes the ROTACAT was used for reactions in an organic phase again. The hydroformylation of propene in toluene showed a comparable selectivity for the linear aldehyde (Table 6.2, entry 7-9).
Table 6.2: Results from the hydroformylation of propylene at 80°C and 50 bar CO/H₂.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate phase</th>
<th>Catalyst (cycle)</th>
<th>Aldehyde Yield (mmol*10⁻²)</th>
<th>Linear aldehyde (%)</th>
<th>Linear to branched ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>gaseous</td>
<td>1 (1)</td>
<td>3 93.5</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>gaseous</td>
<td>1 (2)</td>
<td>1 89.7</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>gaseous</td>
<td>1 (3)</td>
<td>2 93.2</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>water</td>
<td>1 (4)</td>
<td>0.4d 91.9</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>water</td>
<td>1 (5)</td>
<td>1 92.7</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>water</td>
<td>1 (6)</td>
<td>0.4 92.4</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>toluene</td>
<td>1 (7)</td>
<td>2 86.7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>toluene</td>
<td>1 (8)</td>
<td>1 91.7</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>toluene</td>
<td>1 (9)</td>
<td>1 90.6</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

*a Ligand to Rhodium ratio is 10, catalysis performed in 50 ml solvent (except for entry 1 to 3) at 8 bar of propene and 50 bar of CO/H₂=1/1. b Acurate data on conversion and turnover frequency are not available due to the gaseous nature of the substrate, yields stated were obtained after 3-4 days reaction time unless otherwise stated. c Determined by means of GC-analysis using decane as an internal standard. d Yield after 1 day of reaction time.

The ROTACAT concept was shown to be applicable in a range of two-phase hydroformylation processes. Organic substrates can be converted in an organic-liquid/solid process both in organic solvent or in pure substrate. Water-soluble substrates can be hydroformylated in an aqueous-liquid/solid two-phase system and gaseous substrates can be processed in the gas phase. The high catalyst stability enables unlimited switching between the different systems and substrates on the same catalyst batch without notable catalyst deterioration.

6.3 Conclusion

The immobilisation of a homogeneous hydroformylation catalyst on monoliths, constructed as the blades of a mechanical stirrer, is reported as a novel concept towards sustainable catalyst systems. A rhodium-complex containing a Xanthene based diphosphine
The SiC ROTACAT performed as the better catalyst in the hydroformylation of 1-octene showing an overall selectivity of 89 ± 3 percent for the linear aldehyde. The catalysis is first order rate dependent on the substrate concentration and is significantly influenced by changes in the CO/H$_2$ ratio and the stirring mode. Using optimised conditions a turnover frequency was obtained of 97 mol.mol$^{-1}$h$^{-1}$.

The ROTACAT system is extremely stable. Numerous subsequent experiments were performed using only one batch of catalyst showing no catalyst deterioration within 6 months, moreover, the catalyst can be stored at room temperature for weeks. The ROTACAT concept is in principle applicable for a whole range of substrates since catalysis can be performed both in pure substrate as well as in liquid organic-, liquid aqueous- and gas-phase reactions within one reactor and with the same batch of catalyst. This combination of properties makes it potentially interesting for the use as multi-purpose reactor in the fine chemical industry despite the fact that the activity of the system is a factor of 100 lower compared to the homogeneous system. We believe the ROTACAT concept is generally applicable and that it could add a new dimension to the ongoing work reported in literature on sol-gel and silica immobilised homogeneous catalysts.

6.4 Experimental section

Wash-coating procedure
The SiC monoliths were dried at 1000°C for 18 hours and were subsequently dipped into a 40% colloidal silica solution in water (Ludox AS 40) for 30 minutes. The excess of liquid was carefully blown out of the channels and the monoliths were dried at room temperature for 24 hours. Finally, the monoliths were heated to 400°C at a rate of 1°C/min and dried for 3 hours.

Catalyst preparation
Two monoliths were dehydrated under vacuo at 180°C for 2 hours. The monoliths were placed in cylindrical shaped tubes forming the stirring blades of a mechanic stirrer using a teflon socket (For the Si-monoliths the stirring blades were cut in two and after placement of the monoliths the parts were carefully put together). A stainless-steel 200 ml autoclave was equipped with the above-described stirrer, a substrate vessel, a cooling spiral and a sample outlet. In the autoclave a solution of 200 mg of ligand A in 60 ml toluene was stirred for 20 hours at 80°C under an inert atmosphere. 50 to 75 percent of the ligand was immobilised on the monoliths. After the autoclave was washed with several portions of toluene a solution of 3 mg [Rh(acac)(CO)$_2$] in 60 ml of toluene was brought in the autoclave and the catalyst was allowed to incubate for 1 hour at 80°C under 50 bar CO/H$_2$. The catalysis was performed after washing the catalyst with toluene.
Chapter 6

Catalysis procedure

A mixture of 3 ml of 1-octene, 3 ml of decane and 54 ml of toluene was added to the autoclave and the mixture was pressurised to 50 bar CO/H₂ (1:1) and stirred for 24 hours at room temperature (this induction period was needed for good catalyst performance). The reaction mixture was heated to 80°C. After 4 (or more) days the autoclave was cooled down to 10°C and the pressure was reduced to 2 bar. Using this small overpressure the liquid was slowly removed from the autoclave with a 1.2 mm needle. After this the catalyst was washed in the autoclave under controlled atmosphere with toluene, the next cycle was performed.

6.5 References and notes

20 The total surface area of two dip-coated monoliths of 3.5 g is 2*3.5*17*10²⁰ = 119*10²⁰ Å². Using 150 mg ligand (1.27*10²⁰ molecules) the estimated surface area per molecule becomes 119/1.27 = 94 Å²/molecule.

It was observed that catalyst performance improved significantly when the reaction mixture was stirred at room temperature before starting a novel catalytic cycle. For this purpose we added a 24 h induction period to the catalysis procedure (see experimental section). In some cases a further extension of the induction period led to a further increase in catalyst selectivity.

E.G. Kuntz *Chemtech* 1987, 570.