ROTACAT: A Rotating Device Containing a Designed Catalyst for Highly Selective Hydroformylation

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Abstract: A novel concept is presented for the immobilization of a homogeneous catalyst. A hydroformylation catalyst was covalently anchored to monoliths that were constructed as the blades of a mechanical stirrer and used in a batch process. The catalyst was effective in the hydroformylation of both higher and lower alkenes and showed a high regioselectivity 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.

Introduction

Since decades, the hydroformylation of alkenes has been recognized as a clean and efficient chemical process for the production of aldehydes and, therefore, it is applied widely in the petrochemical industry. In the cleanest industrial hydroformylation process, developed by Ruhrchemie/Rhône-Poulenc, the catalyst [HRhCO(TPPTS)$_3$] is located in a water phase affording a straightforward separation of the organic products and the catalyst.[1] The applicability of this biphasic system is, however, strictly limited to substrates that are slightly water soluble, such as propene and 1-butene.

A widely investigated approach to facilitate catalyst/product separation is the attachment of catalysts to an organic (for example, polydivinylbenzene),[2] inorganic (for example, polysiloxane)[3,4] or hybrid[5,6] resin.[7] There is, however, no successful commercial application of a polymer-immobilized 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.[8] Our recent advances in immobilizing rhodium complexes of xanthene-based diphosphine ligands in an aqueous phase,[9,10] a supported aqueous phase[11] and a silica matrix[12,13] 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.[12] The catalyst is a rhodium-complex containing a diphosphine ligand with a large "natural" bite-angle,[14] *N*-(3-trimethoxysilane-*n*-propyl)-4,5-bis(diphenylphosphino)phenoxazine, **A** (Scheme 1), which contains a trialkoxysilane unit by which the covalent anchoring on silicate surfaces has been realized. Since this system seems generally applicable and explicitly interesting for the industrial production of fine chemicals or high boiling aldehydes, we investigated the possibility of a multi-purpose reactor 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 very stable 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.

In recent years *monolithic* reactors have found wide application in gas-solid processes such as auto-

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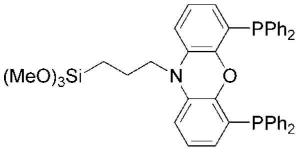
motive emission control[15] and industrial off-gas purification.[16] Also, these systems are being considered for gas-liquid-solid processes such as hydrogenations and oxidations.[17] Recently, Moulijn et al. reported on a novel reactor configuration in which blocks of monoliths are arranged in a stirrer-like fashion.[18] Using this setup a reasonably large surface area of the immobilized catalyst is retained, but many problems of handling a suspension of finely divided catalyst are eliminated.



A

Scheme 1. Structure of ligand **A**.

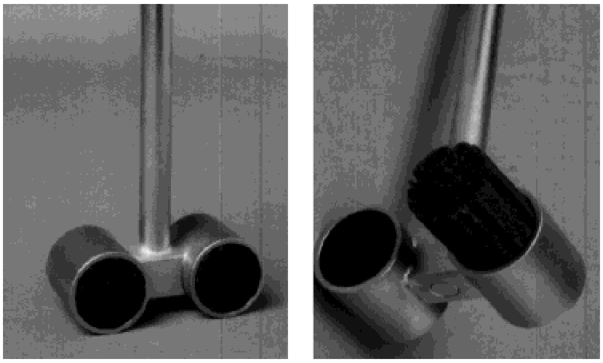


Figure 1. A picture of the stirrer and silicon-carbide monoliths.

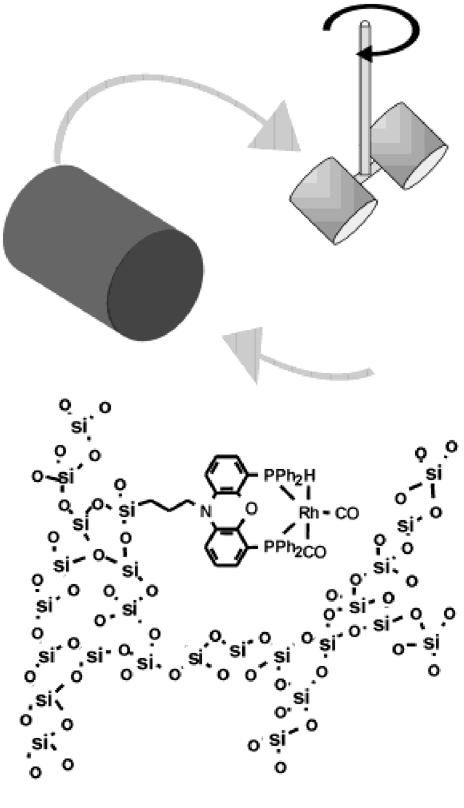


Figure 2. A schematic representation of the homogeneous complex, immobilized on monoliths that are implemented in the blades of a mechanical stirrer.

In this paper a concept is described that unites the above described processes to obtain an immobilized homogeneous rotating catalyst (ROTACAT). Ligand **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 1 and Figure 2). 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 m^2/g vs. 0.5 m^2/g) whereas the SiC monoliths are mechanically far more stable.

Results and Discussion

Catalyst 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, their 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 immobilized on the monoliths by agitation of a toluene solution of **A** at 80 °C under an inert atmosphere. The immobilized ligand was subsequently functionalized 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/H$_2$ (1 : 1) for 1 hour in an autoclave, equipped with the ligand functionalized rotor.[19]

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 m^2/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.[20,21] 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 m^2/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 (0.11 mmol/g monolith).

Catalysis

In the hydroformylation of 1-octene, using the SiC monoliths, the overall selectivity for 1-nonanal is 89 ± 3% (Table 1). As was found previously for the homogeneous system (entry 4) and the silica-immobilized 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 (l/b ratio of 14) but alkene isomerization was observed to a large extent (18%). Furthermore, significant reduction of 1-nonanal to the alcohol was observed (4.8%). The reduction 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 immobilized 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/h). Compared to the sol-gel immobilized analogue this is about 15 times lower. We explored several studies to investigate the reaction rate.[22]

Analogous to the sol-gel immobilized system there is a first order rate dependency of the hydroformylation rate on the substrate concentration. As a result, hydroformylations performed at a high octene concentration led to a major increase in reaction rate. This is important since the 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/h (entries 1 and 9).

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 catalytically 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 1, entries 11 and 12). Another possible cause of the lower reaction rate is the relatively low surface area compared to the sol-gel immobilized catalyst (17 m^2/g vs. 500 m^2/g). The immobilized catalytic sites are densely packed on the monolith. The average surface area, available per molecule of ligand, was estimated at 94 $Å^2$/molecule.[23] This close proximity of catalytic sites promotes the formation of

Table 1. Results from the hydroformylation of 1-octene at 80 °C and 50 bar CO/H_2

Entry	Catalyst (cycle)[a]	Time (h)	Conversion (%)	TOF[b]	Linear aldehyde[c] (%)	Branched aldehyde[c] (%)	Alkene isomerization[c] (%)	Linear to branched ratio[c]
1	**1**	96	26	2	**92.5**	2.0	5.5	46
2	**2**	48	19	3	**71.5** (+ 4.8% nonanol)	5.6	18.1	14
3	**2** (2)[d]	48	12	2	**77.2**	3.8	19.0	20
4	A/Rh[e] {homog.}	2	19	283	**93.3**	2.9	3.7	32
5	A/Rh[e] {sol-gel}	24	69	35	**92.8**	3.0	1.7	32
6	**1** (1)	96	24	1	**86.4**	1.5	12.1	57
7	**1** (2)	96	23	1	**87.6**	3.7	8.7	23
8	**1** (3)	168	38	1	**86.7**	3.2	10.1	27
9	**1** (4)[f]	96	18	15	**88.0**	4.0	8.0	22
10	**1** (5)[f]	96	14	13	**95.2**	2.8	1.9	34
11	**1** (6)[f]	96	15	13	**93.0**	3.8	3.1	24
12	**1** (7)[g]	96	28	21	**84.2**	4.2	11.5	20
13	**1** (8)[g]	389	76	21	**87.3**	3.7	9.0	23
14	**1** (9)[g]	645	90	9[h]	**87.0**	3.2	9.7	26
15	**1** (10)[i]	24	14	50	**87.3**	3.6	9.1	24
16	**1** (11)[j]	24	14	97	**87.9**	4.1	8.0	22

[a] Two monoliths (for **1**; 3.5 g each, containing a total amount of 0.174 mmol ligand and for **2**; 1.5 g each, containing a total amount of 0.164 mmol ligand) were used with a ligand to rhodium ratio of 10. Catalysis was performed in 54 mL toluene using 3 mL of 1-octene under 50 bar of CO/H_2=1/1.

[b] Initial turnover frequencies were determined as (mol aldehyde)(mol catalyst)$^{-1}$ h^{-1} at 10–20 percent conversion.

[c] Determined by means of GC-analysis using decane as an internal standard.

[d] In 54 mL toluene and 1 mL 1-propanol.

[e] Data taken from ref. [12]

[f] In 25 mL toluene and 25 mL 1-octene.

[g] As in entry 9 but stirred back and forward.

[h] Average turnover frequency.

[i] As in entry 12 but 35 bar H_2 and 15 bar CO.

[j] As in entry 13 but in 50 mL 1-octene.

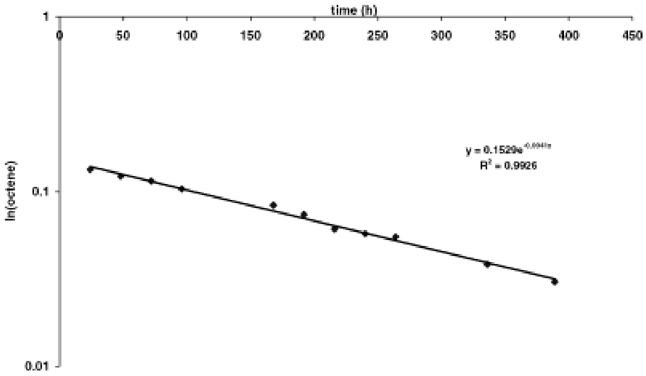


Figure 3. Plot of the logarithm of the 1-octene concentration in time during the hydroformylation reaction.

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 (we previously reported that this effect was clearly observed in solution with an analogous complex).[11] On performing the catalysis under an atmosphere of CO/H_2: 15/35, the reaction rate was increased from 21 to 50 mol/mol/h compared to the CO/H_2: 1/1 experiment (entries 13 and 15) substantiating the existence of these dimers.[24] Under these optimized conditions the reaction rate reached 97 mol/mol/h, performing the catalysis 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 4, Table 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 a systematic decrease in catalytic performance. We did, however, observe a fluctuation in the percentage of alkene isomers (7 ± 5%). We ascribe this fluctuation to differences in catalyst induction period between subsequent catalytic runs.[25]

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.

We further explored the ROTACAT concept in the application of gas and aqueous phase reactions in order to investigate its multipurpose feasibility. The hydroformylation of propene in the gas phase was studied on agitating the ROTACAT in a mixture of propene/CO/H_2 of 8/25/25. The product mixture, collected at the bottom of the autoclave, was investigated by means of GC analysis (Table 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.

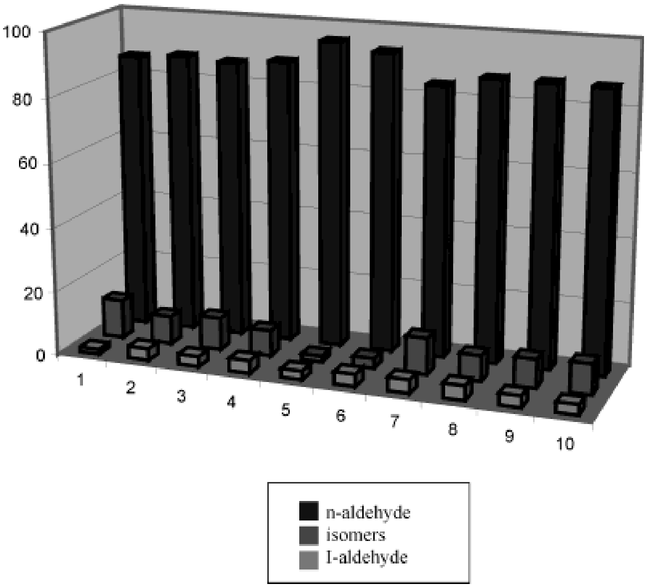


Figure 4. Schematic representation of the product distribution in the hydroformylation of 1-octene.

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.[1] 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% 1-butanal and 7% 2-methylpropanal (Table 2, entries 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 2, entries 7–9). Importantly, we did not observe catalyst leaching in any of the catalytic runs.

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.

Table 2. Results from the hydroformylation of propylene at 80 °C and 50 bar CO/H_2

Entry	Substrate phase	Catalyst (cycle)[a]	Aldehyde Yield[b] (mmol$\times 10^{-2}$)	Linear aldehyde[c] (%)	Linear to branched ratio[c] (%)
1	gaseous	**1** (1)	3	**93.5**	14
2	gaseous	**1** (2)	1	**89.7**	9
3	gaseous	**1** (3)	2	**93.2**	14
4	water	**1** (4)	0.4[d]	**91.9**	11
5	water	**1** (5)	1	**92.7**	13
6	water	**1** (6)	0.4	**92.4**	12
7	toluene	**1** (7)	2	**86.7**	7
8	toluene	**1** (8)	1	**91.7**	11
9	toluene	**1** (9)	1	**90.6**	10

[a] Two 3.5 g SiC monoliths, containing a total amount of 0.174 mmol ligand were used with a ligand to rhodium ratio of 10. Catalysis was performed in 50 mL solvent (except for entries 1 to 3) at 8 bar of propene and 50 bar of $CO/H_2=1/1$.
[b] Accurate data on conversion and turnover frequency are not available due to the gaseous nature of the substrate, yields listed are 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.

Conclusions

The immobilization 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 ligand was covalently anchored directly (to Si-monoliths) or via a silica coating (to SiC monoliths). The SiC ROTACAT performed as the better catalyst in the hydroformylation of 1-octene showing an overall selectivity of 89 ± 3% 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 optimized conditions a turnover frequency was obtained of 97 mol/mol/h.

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. 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-immobilized homogeneous catalysts.

Experimental Section

Monolith Preparation

The monoliths were cylindrically shaped and had the following dimensions: SiC monoliths of 3.46 g were 20.5 mm in length with a diameter of 15.5 mm and a channel diameter of 1.9 mm. Si monoliths of 1.53 g were 19.9 mm in length with a diameter of 14.9 mm and an average channel diameter of 1.1 mm. The wash-coating procedure on the SiC monoliths was performed as follows. 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 vacuum 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 immobilized 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.

The Catalytic 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 pressurized to 50 bar CO/H_2 (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 the catalyst was washed in the autoclave under controlled atmosphere with toluene, the next cycle was performed.

Acknowledgements

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[19] The ligand to rhodium ratio of ten was adopted from the experiments on the analogous slurry reaction (ref. [12]) for which we observed a decrease in catalyst stability on lowering this ratio.

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[22] Detailed studies towards heat and mass transport parameters are of great importance to fully understand the performance of this concept. These facts, however, are beyond the scope of this study and will be discussed later in a separate technical report.

[23] The total surface area of two dip-coated monoliths of 3.5 g is $2 \times 3.5 \times 17 \times 1020 = 119 \times 1020$ Å^2. Using 150 mg ligand (1.27×10^{20} molecules) the estimated surface area per molecule becomes $119/1.27 = 94$ Å^2/molecule.

[24] The increase in reaction rate might be partly caused by the lower partial CO pressure, since rhodium-phosphine complexes show a small negative order in CO: P. W. N. M. van Leeuwen, C. Claver, *Rhodium Catalyzed Hydroformylation*, Kluwer Academic Publishers: Netherlands, **2000**, pp. 63–105.

[25] 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.