Xantphos-based, silica-supported, selective, and recyclable hydroformylation catalysts: a review

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Abstract

Immobilization on silica of selective homogeneous hydroformylation catalysts based on xanthene ligands is reviewed. Various immobilized catalysts are compared, such as SAPC, sol–gel-based catalysts, silica-anchored catalysts used both in an organic phase as well as in supercritical carbon dioxide ($scCO_2$), and chemical modifications of silica-anchored catalysts. In all instances, the high selectivity of the homogeneous Xantphos ligands is retained and linear to branched ratios are 20 or higher. Formation of 2-octene from 1-octene via isomerization also remains low ($<5\%$) as in the homogeneous phase. The rates expressed in turnover frequencies drop considerably except for the experiments in $scCO_2$, which are only half of those in the homogeneous phase. Leaching of rhodium to the product is in all cases below the detection limit of ICP-AES (1 ppm). © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of well-defined catalyst systems that allow rapid and selective chemical transformations and that at the same time can be completely recovered from the product is still a paramount challenge [1]. When we look at the many applications of homogeneous catalysts today both in the laboratory and in the industrial practice, we note that there is not a single solution to separation. In fact, all "unit operations" for separation are being applied in industry, such as distillation, liquid–liquid separation or extraction, stripping, catalyst destruction, and crystallization, or no separation of the catalyst at all, just

leaving it in the product because the concentration is sufficiently low. Perhaps two-phase catalysis and immobilized catalysis have been studied most as general ways to achieve recycling of the catalyst. Two-phase catalysis finds large-scale application in the Shell Higher Olefins Process and the Ruhrchemie–Rhône Poulenc process. Immobilization, while extensively studied, has met relatively little success so far.

Improvement of rates and optimization of selectivities have been a success area of homogeneous catalysis research in the last decades. Indeed, highly active and selective catalyst systems have been reported, but key problems for many systems remain catalyst stability and selectivity on the one hand and leaching of catalytic material in the product phase on the other hand [2]. A widely studied approach to facilitate catalyst–product separation is the attachment of homogeneous catalysts to polymeric organic, inorganic or hybrid supports (for extensive reviews on polymer

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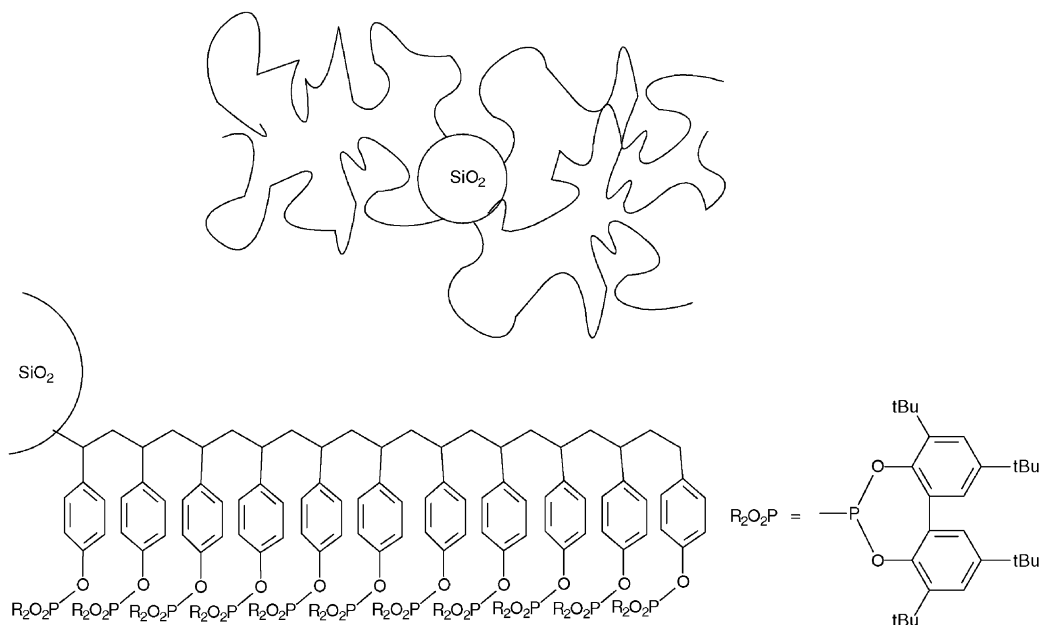(P.W.N.M. van Leeuwen).

Fig. 1. Hybrid support for rhodium-catalyzed hydroformylation [4e]. The support shown has an inorganic silica core, polystyrene-containing phosphite ligands polymerized on the surface, such that the polymeric catalyst in a solvent will behave as a homogeneous catalyst.

immobilized catalysts, see [3]; for alternative approaches toward catalyst–product separation, see Ref. [4a] aqueous biphasic catalysis; [4b] supported aqueous phase catalysis; [4c] fluorous phase catalysis; [4d] smart polymers; [4e] polymers on silica beads) (see Fig. 1) and more recently to dendrimeric [5,6] 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 functionalized monophosphine ligands have been used to tether a rhodium–phosphine complex to commercially available silica [7]. An interesting alternative for the preparation of silica-immobilized catalysts was presented by Wieland and Panster [8], who used the sol–gel process, i.e. a co-condensation of tetra-alkoxysilanes and functionalized trialkoxysilanes [9]. The sol–gel technique is an ideal method for catalyst immobilization because of its diversity and its mildness [10–13]. The selectivity of the catalyst reported in Panster's work is rather low, but metal leaching was largely suppressed. Blum et al. [14] reported a sol–gel immobilized hydroformylation catalyst that is free of metal-leaching. In the latter case no directing ligands were used which resulted in a lack of control of the selectivity.

Another interesting concept of catalyst immobilization is the supported aqueous phase catalyst (SAPC) [15]. In this system, the catalyst is immobilized in a thin water layer adhered in the pores of a high-surface-area silicate [16]. In this system, the ligands are not attached to the silica surface via a covalent bond but sulfonated ligands are used that will stay preferentially in the water layer. Since the water layer on the silica surface is very thin, a large surface area is obtained that ensures a close contact between the organic (educt) and the aqueous catalyst layer. Using this system higher alkenes can be converted at a relatively high rate. The regioselectivity, however, towards the linear aldehyde of the systems reported previous to our studies is low and surprisingly little has been reported on the recyclability and stability of these systems [17]. Virtually, all SAP hydroformylation catalysts described in literature are based on rhodium, cobalt, platinum or nickel complexes employing TPPTS as the *mono*phosphine ligand [18,19].

Only in two instances sulfonated *di*phosphines were examined [20,21].

A homogeneous system using monodentate ligands that has been optimized for a certain activity and selectivity is not likely to give the same performance after it has been immobilized on silica. It is doubtful whether the same complexes will form at all on the solid support. Thus, the use of a bidentate ligand (or oligodentate, if appropriate) that ensures the formation of the desired structure will solve this part of the problem. The bidentate nature of phosphorus ligands can have an enormous influence on the performance of a catalyst [22].

Hydroformylation forms a good example of the above; many attempts have been described but they all had their drawbacks. Catalysts containing monophosphines have proven not to be suitable and generally they gave rise to low selectivities and activities. Diphosphines will bind to rhodium in the desired fashion, but many rhodium diphosphine complexes give rise to a low selectivity in hydroformylation reactions. Since the late eighties several new bidentate diphosphines and diphosphites have been reported that give very high selectivities to the desired linear aldehyde [23]. Devon et al. [24] described a diphosphine, BISBI, that showed a very high regioselectivity for the formation of linear aldehydes. Casey et al. [25] reported that rhodium diphosphine complexes of BISBI are characterized by a large P–Rh–P (bite) angle and contain two phosphorus ligands in the equatorial plane. Especially, these complexes give rise to a high regioselectivity for the linear aldehyde. In the phosphine area, we have designed a new generation of diphosphine ligands based on xanthene backbones that also give extremely regioselective rhodium catalysts producing the linear aldehyde [26,27]. The application of catalysts with large P–Rh–P bite angles in multiphase hydroformylation reactions appeared very successful as these ligands combined a good catalyst performance with 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 several consecutive runs [21,28].

An added advantage of the use of bidentate ligands could be that the complex stability is higher and that less leaching might occur, as a single ligand-to-metal bond appeared to be too weak. If two monodentate ligands could be fixed onto the solid in the position required for favorable complex formation, this may lead to high binding constants as well, but until now this has not been achieved. In this paper, we will review the silica immobilizations we have carried using Xantphos type ligands.

2. SAPC systems

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, **1**, see Scheme 1) and its use in biphasic hydroformylation reactions [29]. The high regioselectivity obtained with this ligand stimulated us to investigate its performance as a SAPC. Both the novel Rh(**1**)/SAPC and the known Rh(TPPTS)/SAPC were studied in the hydroformylation of 1-octene. Rh(**1**)/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 1, entries 1 and 11) [21].

The rate of hydroformylation of 1-octene using Rh(**1**)/SAPC at $80\,^\circ$C in toluene as the co-solvent was found to be low ($\sim$1 turnover per hour; Table 1, entries 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 1, entries 1 and 3). Interestingly, this large concentration dependency was not found for Rh(TPPTS)/SAPC (Table 1, entries 11 and 12). We also found a 5- to 8-fold increase on performing the catalysis at a temperature of $100\,^\circ$C (turnover rate of 55 and 80 per hour, entries 9 and 13). Under optimized conditions the activity of Rh(**1**)/SAPC and Rh(TPPTS)/SAPC are in the same order of magnitude while the high selectivity of the former catalyst is retained.

The product/catalyst separation efficiency of the SAPC's was examined on performing recycling experiments (Table 1). Rh(**1**)/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 $100\,^\circ$C we even observed
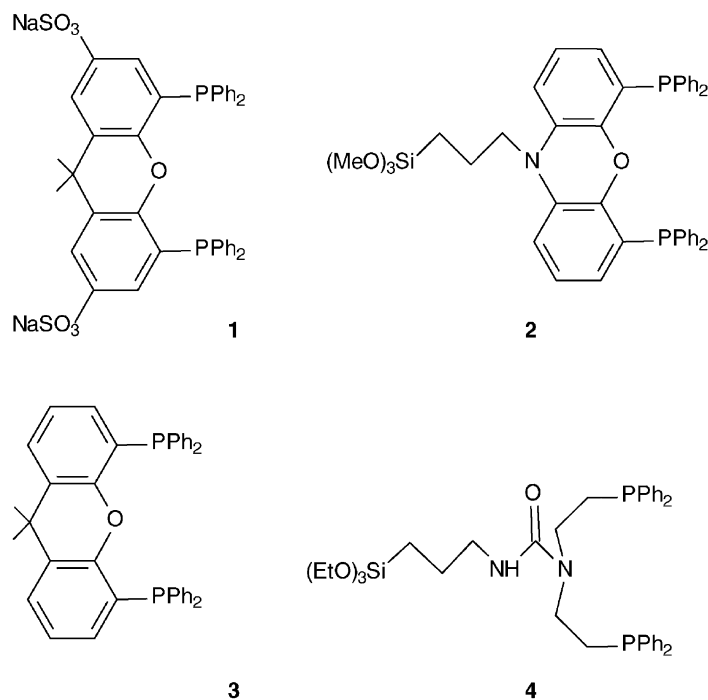
Scheme 1. Ligands used in this study.

Table 1
Results from the hydroformylation of 1-octene using Rh(**1**)/SAPC [21]

Entry	Catalyst ⟨cycle⟩[a]	Conversion after 24 h (%)	TOF[b]	Linear-to-branched ratio[c]	Alkene isomerization[c] (%)	Linear aldehyde[c] (%)
1	Rh(**1**) ⟨1⟩	7	1	38	1.9	95.6
2	Rh(**1**) ⟨2⟩	28[d]	1	44	5.7	92.2
3	Rh(**1**) ⟨3⟩[e]	14	15	46	5.0	93.0
4	Rh(**1**) ⟨4⟩[e]	14	14	42	8.7	89.2
5	Rh(**1**) ⟨5⟩[e]	12	14	40	8.5	89.3
6	Rh(**1**) ⟨6⟩[e]	10	13	40	7.7	90.0
7	Rh(**1**) ⟨7⟩[e]	24[f]	10	39	7.3	90.3
8	Rh(**1**) ⟨8⟩[g]	37	44	31	7.0	90.1
9	Rh(**1**) ⟨9⟩[g]	46	55	31	4.1	92.9
10	Rh(**1**) ⟨10⟩[g]	48	55	27	5.8	90.7
11	Rh(TPPTS) ⟨1⟩	20	15	3	7.4	67.2
12	Rh(TPPTS) ⟨2⟩[e]	3	30	3	12.3	67.2
13	Rh(TPPTS) ⟨3⟩[g]	17	160	3	7.3	70.5
14	Rh(TPPTS) ⟨4⟩[g]	90[f]	146	2	52.6	33.9

[a] Ligand to rhodium ratio is 10 for Rh(**1**) and 20 for Rh(TPPTS), catalysis performed at 80 °C and 50 bar CO/H$_2$ (1/1) in 15 ml toluene as a co-solvent using 1 ml of 1-octene.
[b] Average TOFs were calculated as (mol aldehyde)(mol catalyst)$^{-1}$ h^{-1}.
[c] Determined by means of GC-analysis using decane as an internal standard.
[d] Conversion after 96 h.
[e] Catalysis performed in 15 ml 1-octene at 80 °C.
[f] Conversion after 72 h.
[g] Catalysis performed in 15 ml 1-octene at 100 °C.

a small increase in rate in successive runs). No traces of rhodium were detected in the product phase of any of the SAPC experiments (detection limit; 1 ppm). This indicates that ligand **1** retains the rhodium on the support within the detection limits of the rhodium analysis on the product by means of ICP-AES. In contrast, Rh(TPPTS)/SAPC showed a drop in catalyst performance after three catalytic runs (Table 1, entries 11–14). In the fourth cycle, over 50% of the 1-octene isomerized and the linear-to-branched ratio drops to 2. The Rh(**1**)/SAPC is thus more robust then the TPPTS based SAPC; Rh(**1**)/SAPC could be recycled for 3 weeks, showing no deterioration of the catalyst performance, whereas under similar conditions Rh(TPPTS)/SAPC shows a reduction in hydroformylation performance after 3 days.

Thus, a stable and selective system was obtained, but the TOFs (turnover frequencies) remained about 100 times below those of the homogeneous catalyst, presumably due to transport limitations. The thickness of the water layer has not been optimized and it is known that this plays a major role [17]. For the batch reactions space–time-yields are correspondingly low, but in a fixed bed reactor a considerable improvement may be within reach.

3. Sol–gel immobilized systems

In the second approach, the hydroformylation catalyst is covalently anchored to a silicate matrix using the sol–gel technique [28a,30]. This material can be prepared by a co-condensation of tetra-alkoxysilanes and functionalized trialkoxysilanes.

$$n\text{Si(OR)}_4 + 4n\text{H}_2\text{O}$$
$$\rightarrow n\text{Si(OH)}_4 + 4n\text{ROH} \rightarrow \text{polysilicate}$$
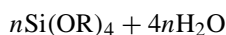
A novel xanthene-based ligand, *N*-(3-trimethoxysilane-*n*-propyl)-4,5-bis(diphenylphosphino)-phenoxazine (siloxantphos) **2**, was synthesized and immobilized as a rhodium–diphosphine complex in a sol–gel material. On stirring a solution of **2**, [Rh(acac)(CO)$_2$] and tetramethyl-orthosilicate (TMOS) in a molar ratio of 10:1:67 in 8 ml of THF/H$_2$O (3:1 volume) we found the formation of the cationic complex [Rh(**2**)CO]$^+$, immobilized in the silica (detailed investigations

concerning this process and the involvement of the support will be addressed in the next section).

Interestingly, the gelation of these mixtures takes place within 1 h without using any additive to catalyze the polycondensation of the silica monomers. This suggests that the rhodium–xanthenediphosphine complex acts as a catalyst in this process (the same mixture without **2** has a gelation time of about 7 days).

The system obtained from **2** was characterized by means of solid state ^{31}P MAS NMR and FT-IR, and it was found that both the phosphorus chemical shift and the carbonyl vibration were in good agreement with the fully characterized (homogeneous) complexes containing ligand **3**, [Rh(**3**)CO]$^+$[BF$_4$]$^-$. X-ray photoelectron spectroscopy (XPS) qualitatively identified the elements in the sol–gel complex of **2**, and the characteristic electron binding energies compared well with those of [Rh(**3**)CO]$^+$[BF$_4$]$^-$.

The catalytic performance of sol–gel-**2** in the hydroformylation of 1-octene was studied in a batch process using 1 g of polysilicate, containing 1×10^{-5} mol rhodium and 1×10^{-4} mol **2** in the presence of 1 ml *n*-propanol (the effect of the alcohol will be addressed in the next section).

The selectivity of sol–gel-**2** was found to be as high as 93% towards the linear aldehyde, which is similar to that of the homogeneous reaction (Table 2, entries 1 and 9). In the absence of **2**, the selectivity to the linear aldehyde is lowered dramatically to 26% (Table 2, entry 8). The high selectivity of sol–gel-**2** is induced by the large natural P–Rh–P bite-angle. This was proven on comparing sol–gel-**2** (bite-angle 108°) with a ligand having a much smaller bite-angle (93°): *N*-(3-triethoxysilane-*n*-propyl)-*N'*,*N'*-bis(2-(diphenylphosphino)ethyl)-urea (**4**). This ligand was sol–gel processed in the same way as **2** and immobilized. [Rh(**4**)CO]$^+$ was subsequently tested in the hydroformylation of 1-octene. The linear-to-branched product ratio using sol–gel-**4** is 15 times lower than it is for sol–gel-**2** (Table 2, entry 10). Thus, the bite-angle effect is retained in the immobilized systems.

The recyclability of catalyst sol–gel-**2** was studied by performing a series of consecutive runs (Table 2, entries 1–5). We observed no deterioration of the catalytic performance in eight cycles. The linear-to-branched ratio remained very high during all experiments and only 2% isomers of 1-alkene was formed. The decrease in rate in successive catalytic

Table 2
Results from the hydroformylation of 1-octene using sol–gel Rh(**2**) catalysts [28a]

	Catalyst (cycle)[a]	Conversion (%)	TOF[b]	l-Aldehyde (%)[c]	b-Aldehyde (%)[c]	Alkene isomerisation (%)[c]	l-Alcohol[c] (%)	l:b ratio[c]	Rh leaching (%)[d]
1	Sol–gel-**2** (1)	69	35	92.8	3.0	1.7	2.5	32	<1
2	Sol–gel-**2** (2)	69	36	94.1	2.7	2.0	1.2	36	<1
3	Sol–gel-**2** (3)	69	36	94.0	2.7	2.3	1.0	35	<1
4	Sol–gel-**2** (4)	67	35	94.5	2.7	2.2	1.3	35	<1
5	Sol–gel-**2** (8)	63	33	95.0	2.6	2.0	0.5	37	<1
6	Sol–gel-**2**[e]	92	32[f]	95.5	2.3	1.6	0.6	43	<1
7	Sol–gel-**2**[g]	63	287	95.5	2.4	1.9	0.3	40	<1
8	Rh(acac)(CO)$_2$ in sol–gel[h]	64	175	26.3	16.3	57.4	0.0	1.6	>50
9	**2**/Rh(acac)(CO)$_2$ homogeneous	19	283	93.3	2.9	3.7	0.0	32	–
10	Sol–gel-**4**	72	119	70.0	28.9	1.0	0.1	2.4	<1

[a] Ligand to rhodium ratio is 10, catalysis performed in toluene/*n*-propanol 13/1 using 1 ml of 1-octene at 80 °C and 50 bar CO/H$_2$.
[b] Initial TOFs were calculated as (mol aldehyde)(mol catalyst)$^{-1}$ h^{-1} at 10–20% conversion.
[c] Determined by means of GC-analysis using decane as an internal standard.
[d] Determined by means of AES.
[e] 3 ml of 1-octene.
[f] Average TOF.
[g] In 14 ml 1-octene and 1 ml *n*-propanol.
[h] No ligand used.

cycles is very small, indicating that ligands **2** and **4** bind strongly to rhodium. Atomic emission spectroscopy (AES) showed that leaching was below the detection limit of 1 ppm.

Compound sol–gel-**2** is remarkably stable under catalytic conditions. We were able to use the catalyst for more than 2 weeks without loss in activity and selectivity. Even a 3-day run, leaving only a few percent of the substrate unconverted, does not affect the performance (Table 2, entry 6). This long-term stability indicates that very high turnover numbers can be achieved with this system.

The rate of hydroformylation of 1-octene using sol–gel-**2** has a first-order dependency in substrate concentration and the rate is roughly 10 times lower than that of the homogeneous system. This could be compensated by increased space–time yields if the reaction were carried out in a flow system. In pure 1-octene (entry 7) a high rate was observed.

In conclusion, system sol–gel-**2** is the most selective immobilized hydroformylation catalyst up to date. Moreover, this system is one of the first examples of a heterogenized catalyst that has a metal leaching below the ppm level in the effluent.

4. Silica-supported catalyst

The immobilization of Rh(**2**) on commercially available silica was performed in four different ways [31–33]. In the first three approaches, **2** was covalently tethered to silica to obtain silica(**2**) by refluxing a suspension of **2** and silica in toluene. The subsequent complexation of the rhodium precursor was performed under three different conditions. In the first approach, the rhodium precursor [Rh(acac)(CO)$_2$] and silica(**2**) were simply mixed together and stirred in a THF suspension. In the second way, silica(**2**) was first reacted with dimethoxydimethylsilane in order to modify the acidic silanols on the silica surface.[1] To this end, a suspension of silica(**2**) and dimethoxydimethylsilane was refluxed in toluene and subsequently stirred in a solution of [Rh(acac)(CO)$_2$] in THF at room temperature. In the third approach, [Rh(acac)(CO)$_2$] was added to a pre-stirred mixture of silica(**2**) and triethylamine in THF. For the last and fourth method, the diphosphine rhodium complex Rh(**2**)(acac)(CO) was

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[1] This method was reported to be equally efficient in the modification of silica surfaces as the use of chloroalkylsilanes, see [34].

Table 3
Hydroformylation of 1-octene using polysilicate-immobilized [Rh(**2**)CO]$^+$ [28d][a]

Entry	Catalyst	Time (h)	Conversion (%)	TOF[b] (h^{-1})	Ratio of l/b	l-Aldehyde (%)	b-Aldehyde (%)	l-Alcohol (%)	2-Octene, octane (%)
1	Sol–gel-**2**	2	20	18.3	65	94.6	1.5	3.6	0.2
2	A	0.5	97	n.d.	2	40.1	22.0	0	37.9
3	B	23	24	8.0	19	85.5	4.5	0	9.9
4	C	22	18	8.7	37	96.2	2.6	1.0	0.2
5	D	22	37	13.2	37	90.7	2.6	5.1	1.6
6	Homogeneous	2	19	283	32	93.3	2.9	0	3.7
7	No ligand	2	72	119	2	70.0	28.9	0.1	1.0

[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.

[b] Average TOFs were calculated as (mol product)(mol catalyst)$^{-1}$ h^{-1}.

synthesized prior to the immobilization on pre-dried silica.

Overview of the catalyst preparation:

A: Silica(**2**) + Rh(acac)(CO)$_2$
B: Silica(**2**) + dimethylsilylation + Rh(acac)(CO)$_2$
C: Silica(**2**) + wash triethylamine + Rh(acac)(CO)$_2$
D: Silica + Rh(**2**)(acac)(CO)

The method of catalyst immobilization appeared to affect its performance in catalysis. Catalyst A showed a low selectivity in the hydroformylation of 1-octene (linear-to-branched aldehyde ratio was even lower than 2) at a very high rate (Table 3, entry 2), whereas catalyst D 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 preparation procedure of A gives rise to the ionic bonding of ligand-free rhodium cations on the slightly acidic silica surface [32,35]. If the rhodium phosphine complex is prepared prior to anchoring (D) no ligand-free rhodium is attached to the silica. The effect of the acidic silanols on the catalyst preparation can be eliminated via the chemical modification of the silica surface (B) or upon addition of a neutralizing base (C). Pre-modification of the silica using dimethoxydimethylsilane largely improved the catalyst selectivity (linear-to-branched aldehyde ratio of 19, Table 3, entry 3) at the cost of some activity [32]. The addition of triethylamine (C) also resulted in a very good hydroformylation catalyst (with a linear-to-branched aldehyde ratio of 37, Table 3, entry 4).

For comparison we show the result of sol–gel(**2**) and the homogeneous reaction (Table 3, entries 1

and 6). Also, in sol–gel(**2**) the pre-formation of the rhodium diphosphine complex avoided the formation of ligand-free rhodium-cations on the silica surface. This approach gives rise to a well-defined, very selective hydroformylation catalyst. All immobilized catalysts are 10–40 times slower than the homogeneous catalyst under the same conditions, the sol–gel catalyst being the fastest.

5. Influence of the silica on the catalyst recycling properties

Sol–gel and silica-immobilized Rh(**2**) were tested in successive hydroformylations of 1-octene to investigate the effect of the support on the recyclability of the catalyst (Table 4, entries 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 3, 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. Interestingly, we observed a small decrease in hydroformylation activity upon recycling along with an increasing formation of 1-nonanol (4–13%), especially at longer reaction times (Table 4, entries 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

Table 4
Hydroformylation of 1-octene using sol–gel and silica-immobilized catalyst [Rh(**2**)CO]$^+$ in subsequent catalytic runs [28d][a]

Entry (cycle)	Catalyst	Time (h)	Conversion (%)	TOF[b] (h^{-1})	Ratio of l/b	l-Aldehyde (%)	b-Aldehyde (%)	l-Alcohol (%)	Octene isomers/octane (%)
1 (1)	Sol–gel-**2**	2	20	18	65	94.6	1.5	3.6	0.2
2 (2)	Sol–gel-**2**	2	19	26	43	90.0	2.2	5.1	2.6
3 (3)	Sol–gel-**2**	2	19	25	35	87.6	2.7	6.7	3.0
4 (4)	Sol–gel-**2**	2	12	12	62	89.6	1.6	8.8	0
5 (1)	Sol–gel-**2**	18	38	23	22	61.0	4.1	29.6	5.3
6 (2)	Sol–gel-**2**	18	30	17	25	77.9	3.7	15.1	3.4
7 (1)	D	22	37	13	37	90.7	2.6	5.1	1.6
8 (2)	D	22	41	15	45	91.5	2.1	4.0	2.4
9 (3)	D	72	61	8	27	79.9	3.5	13.2	3.4
10 (1)	B	23	24	8	19	85.5	4.5	0	9.9
11 (2)	B	23	23	8	20	87.3	4.5	0	8.3
12 (3)	B	23	22	8	16	83.7	5.2	0	11.1
13 (4)	B	72	44	5	16	84.8	5.4	0	9.8
14	Sol–gel-**2**[c]	2.5	7	4	33	92.0	2.8	0	5.2

[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 TOFs were calculated as (mol product)(mol catalyst)$^{-1}$ h^{-1}.

[c] 1 ml of triethylamine added to the catalyst mixture.

HRh(**2**)(CO)$_2$ from [Rh(**2**)CO]$^+$ (vide infra), resulting in an increase in hydrogenation activity and a small decrease in hydroformylation activity.[2]

When the silica material with the capped (acidic) silanols was used (B) 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, entries 10–13). The modification of the surface silanols with alkylsilanes did not yield an optimal catalyst system. The overall selectivity for the linear aldehyde was slightly lower compared with the other catalysts; more isomerization and branched aldehyde was obtained.

As stated above, a more subtle method to reduce the influence of the silica comprises the addition of 1-propanol, which leads to an efficient suppression of hydrogenation activity. A high overall selectivity for the linear aldehyde was obtained in subsequent batch-wise runs (Table 2, entries 1–4). The effect of the presence of 1-propanol is in contrast with previously reported examples of hydroformylation

catalysts, where alcohols or amines were added to promote the hydrogenation of aldehydes via a transfer hydrogenation reaction [37,38]. 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, entry 14).

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 material, the immobilized cationic complex **1** completely transforms to the rhodium-hydride species **6** under a CO/H$_2$ atmosphere (Scheme 2). On dried silica, however, this conversion might not be complete since the dried support is more acidic.[3] Hence, **5** and **6** 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(**2**).

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[2] The effect of silica on the hydroformylation rate is comparable to the deleterious effect of anions like chlorides, see [36].

[3] The presence of triethylamine also slowed down the reaction rate, probably due to its co-ordination abilities.
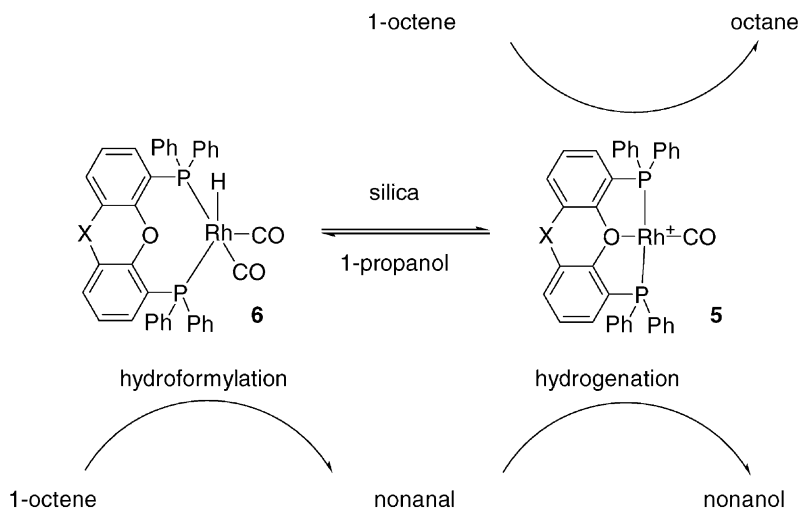
Scheme 2. Representation of the interconversion of the catalyst systems **5** [Rh(**2**)(CO)]$^+$ and **6** [HRh(**2**)(CO)$_2$] and the products generated from each catalyst species.

Experiments in the homogeneous phase including ^{31}P NMR measurements and comparison with those in the solid phase have shown that the conversion of **6**–**5** is indeed a simple protonation (Scheme 2) [28d].

6. Hydroformylation–hydrogenation cascade reaction

Under standard hydroformylation conditions, the cationic species **5** and the hydridic complex **6** co-exist on the support. Hence hydroformylation and hydrogenation will both proceed under a CO/H$_2$ atmosphere. Via a hydroformylation–hydrogenation of 1-octene using Rh(**2**), immobilized via the sol–gel process we performed a clean one-pot reaction of 1-octene to 1-nonanol. 98% of the 1-octene was converted in the hydroformylation reaction and 97% of the linear nonanal was subsequently hydrogenated to 1-nonanol resulting in an overall selectivity of 90% for the linear alcohol. 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. The hydrogenation towards the corresponding alcohol started at higher aldehyde concentrations. When approximately 90% of the 1-octene was consumed (after 60 h) 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 h, which in turn caused a decrease of the hydrogenation rate.

Such a clean, one-pot hydroformylation–hydrogenation cascade system (for a review on tandem reaction sequences under hydroformylation conditions, see [39]) producing a high yield of the linear alcohol with a high regioselectivity is uncommon for rhodium catalysts (for examples of rhodium catalyzed hydrocarbonylation, see [40]). Moreover, we can control the ratio of the two co-existing catalyst species **5** and **6** and we are able to recycle the catalyst completely because of the heterogeneous nature of the system.

We started a series of catalyst experiments on 1-octene, using polysilicate immobilized Rh(**2**), with a reaction under standard conditions, thus with the catalyst as a mixture of **5** and **6**. The reaction was stopped after 172 h, which resulted in a product mixture that consisted for 66.7% of 1-nonanol and 18.5% of 1-nonanal (Table 5, entry 1). After this reaction, we recycled the system and transformed it into a hydrogenation catalyst (**5**) just by washing it with toluene and subsequently adding a mixture of 1-octene and 1-nonanal in toluene to the catalyst

Table 5
Results from switching between hydrogenation, hydroformylation and hydroformylation–hydrogenation sequence reactions using sol–gel immobilized [Rh(**2**)CO]$^+$ [28d][a]

Entry[b]	Time (h)	Conversion octene (%)	Conversion aldehyde (%)	Ratio of l/b	l-Aldehyde (%)	b-Aldehyde (%)	l-Alcohol (%)	Octane[c] (%)
1	172	97	75	23	18.5	3.6	66.7	11.2
2	24	100	100	–	0	0	100	100
3	68	60	16	18	65.2	4.5	13.7	16.6
4	2	98	10	–	0	0	9.7	98
5	96	96	0	18	90.7	5.1	0	4.3

[a] Ligand to rhodium ratio is 10, catalysis performed at 80 °C, in 13 ml of toluene using 1 ml of 1-octene (plus 1 ml of 1-nonanal entries 2 and 4). Samples were analyzed by means of GC and GC-MS analysis.
[b] Entries 1, 3, and 5; 50 bar syngas. Entries 2 and 4; 50 bar H$_2$.
[c] Numbers include isomers of 1-octene since these are not separable from octane on GC.

mixture. After a reaction time of 24 h under an H$_2$ atmosphere only a complete hydrogenation of both substrates was observed to octane and 1-nonanol, respectively (Table 5, entry 2). We found that this modulation is reversible; in the third catalyst cycle the system was applied again as a mixed catalyst by changing the atmosphere from H$_2$ to CO/H$_2$ 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 5, 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 hydrogenation catalyst **5** was restored (Table 5, 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% alkene and 10% aldehyde was hydrogenated). From these four catalytic runs it can be concluded that the immobilized 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 5, entry 5). The atmosphere was changed from H$_2$ to CO/H$_2$ and 1 ml 1-propanol was added to the catalyst along with a fresh batch of 1-octene in toluene. After 96 h, 1-octene was almost completely converted to the linear aldehyde with a complete suppression of its hydrogenation to the alcohol!

In conclusion, the immobilized catalyst Rh(**2**) can be recycled and switched reversibly between two different states or mixtures thereof. The activities of the present catalyst are low and the most interesting features are its stability and the reversible interaction with the support.

7. Silica-immobilized catalyst and scCO$_2$ solvent

The use of scCO$_2$ is becoming increasingly important as a reaction medium in metal catalyzed reactions [41]. At Nottingham, continuous processing in scCO$_2$ has been successfully applied to hydrogenations, Friedel–Crafts alkylations and etherification reactions using heterogeneous catalysts supported on polysiloxane [42]. This technique has been effectively applied in the hydroformylation reaction using the immobilized rhodium–diphosphine described above [28c].

The catalyst used is the rhodium complex of *N*-(3-trimethoxysilane-*n*-ptpropyl)-4,5-bis(diphenylphosphino)-phenoxazine (**2**) immobilized on silica (particle size 200–500 μm). Typically 1 g of silica with a 0.4% Rh loading was loaded into a 5 ml supercritical flow reactor.

The catalyst system converted 1-octene selectively to linear nonanal. The average linear-to-branched aldehyde ratio was 40:1. 1-Octene conversions of 14% were obtained at the flow rates indicated (Table 6) and only a few percent of octene isomers and a trace amount of alcohol were observed as byproducts.

Table 6
Results from the hydroformylation of 1-octene using silica-immobilized Rh(**2**) in scCO$_2$ [28c][a]

Entry	TOF[b]	Linear aldehyde[c] (%)	Branched aldehyde[c] (%)	Alkene isomers[c] (%)	Linear alcohol[c] (%)	Linear-to-branched ratio	1-Octene conversion (%)
1[d]	39	96.1	2.4	1.5	0	40	3.6
2	87	92.9	3.0	3.8	0.3	32	9.4
3[e]	112	94.4	2.4	2.5	0.7	40	10.1
4[f]	117	92.6	3.8	2.5	1.0	24	10.3
5[g]	44	90.7	4.4	3.7	1.3	21	14.3
6[h]	160	93.5	2.8	2.9	0.8	33	4.1
7[i]	93	96.0	1.9	1.1	0.9	50	14.3
8[j]	96	91.3	4.1	4.3	0.3	23	4.6

[a] Ligand:Rh ratio is 10:1 and the catalysis was performed at 80 °C, 120 bar CO$_2$ at 0.65 l/min flow rate (at 20 °C, 1 atm), 50 bar overpressure syngas and an 1-octene flow rate of 0.05 ml/min (substrate:syngas = 1:10) unless otherwise stated. Catalyst: see text. Values shown are average numbers over a period of 3–6 h.

[b] Average TOFs were calculated as (mol aldehyde)(mol catalyst)$^{-1}$ h^{-1}.

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

[d] Reaction temperature is 70 °C.

[e] Syngas overpressure is 25 bar.

[f] 0.3 l/min CO$_2$ flow rate (at 20 °C, 1 atm).

[g] 180 bar CO$_2$.

[h] Reaction temperature is 90 °C.

[i] 1-Octene flow rate of 0.03 ml/min.

[j] 1-Octene flow rate of 0.1 ml/min.

At 70 °C with a 1-octene flow rate of 0.05 ml/min, the rate of hydroformylation is moderate (39 mol mol^{-1} h^{-1}) (Table 6, entry 1). The rate increased to 87 mol mol^{-1} h^{-1} with the catalyst bed at 80 °C (entry 2) and improved further to 112 mol mol^{-1} h^{-1} on decreasing the syngas pressure from 50 to 25 bar (entry 3). The latter effect is consistent with the negative order in CO pressure that is commonly observed in hydroformylation reactions [23]. A TOF of 117 mol mol^{-1} h^{-1} was observed on increasing the residence time of the substrate in the reactor by decreasing the CO$_2$ flow rate (entry 4). An increase of the CO$_2$ pressure resulted in a decrease in TOF to 44 mol mol^{-1} h^{-1} (entry 5). This may be explained as a higher pressure results in a higher density of CO$_2$ which will alter the transport properties in the reactor. The highest TOF (160 mol mol^{-1} h^{-1}) was observed at 90 °C (entry 6). On decreasing the 1-octene flow rate from 0.1 to 0.03 ml/min we observed an increase in the linear-to-branched ratio from 23 to 50 (entries 2, 7 and 8). Thus far, we have no explanation for this.

As the CO concentration in scCO$_2$ is relatively high, it is remarkable that the hydroformylation rate is at least four times higher than the batch reaction in toluene (see above; the rate difference may be as much as two orders of magnitude) and only half the rate of the *homogeneous* analogue. The high rate in scCO$_2$ is probably caused by enhanced mass-transport properties and the lower viscosity of the solvent medium [43].

The catalyst appeared to be very robust, as its performance is constant over at least 30 h. In Fig. 2, the turnover number (TON) is plotted against reaction time. The TON increased linearly with time at both 70 and 80 °C. Moreover, we were able to continue using the catalyst for six non-consecutive days with no observable decrease in either activity or selectivity. Furthermore, no rhodium leaching was found (detection limit of used technique (ICP-AES) is 0.2% of the total amount of rhodium of the catalyst). This demonstrates unambiguously that the rhodium–diphosphine bond in this catalyst remains stable under hydroformylation conditions.

The process is potentially interesting in the manufacture of chemicals and our approach has several advantages compared to conventional homogeneously catalyzed reactions. Firstly, scCO$_2$ is a clean, environmentally benign medium that can be easily separated
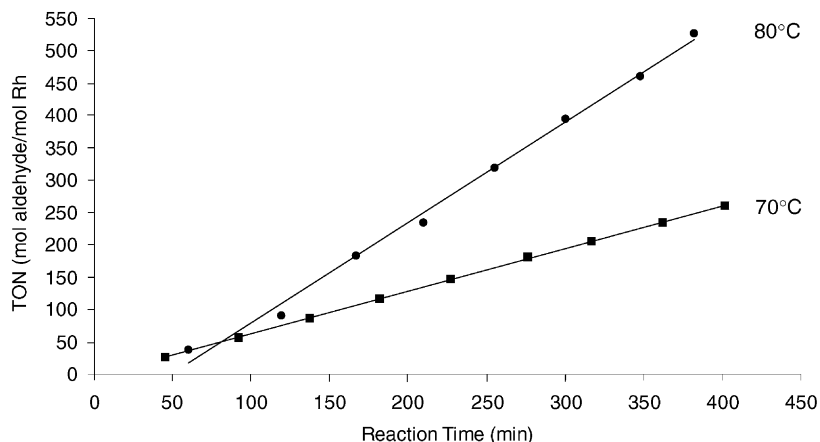
Fig. 2. Turnover number (TON) for the hydroformylation of 1-octene in scCO$_2$ at 70 and 80 °C using immobilized Rh(**2**) in a continuous run [28c].

from the organic phase. Secondly, the application of an immobilized homogeneous catalyst in the flow reactor provides a direct and quantitative separation of the products from the catalyst and avoids any solubility limitations of homogeneous catalysts [41]. Furthermore, the catalyst is very robust and leaching levels are low. The use of high pressures adds to the cost of the process, but in addition to the above benefits, it should be mentioned that the space–time yields of the immobilized system are one order of magnitude higher than those of selective homogeneous catalyst systems.

8. ROTACAT

Since the sol–gel(**2**) system is potentially interesting for the industrial production of higher linear 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 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 au-

tomotive emission control [44] and industrial off-gas purification [45]. In addition, these systems are being considered for gas–liquid–solid processes such as hydrogenations and oxidations [46]. Recently, Moulijn and coworkers [47] reported on a novel reactor configuration in which blocks of monoliths are arranged in a stirrer-like fashion. Using this setup a reasonably large surface area of the immobilized catalyst is retained, but many problems of handling a suspension of finely divided supported catalyst species are eliminated.

We have reported a concept that unites the above-described processes to obtain an immobilized homogeneous ROTAting CATalyst (ROTACAT) [28f]. Rh(**2**) was covalently anchored to monoliths and these monoliths were implemented in two hollow tubes that were constructed as blades of a mechanical stirrer (Fig. 3A 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 m^2/g vs. 0.5 m^2/g), whereas the SiC monoliths are mechanically far more stable.

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.
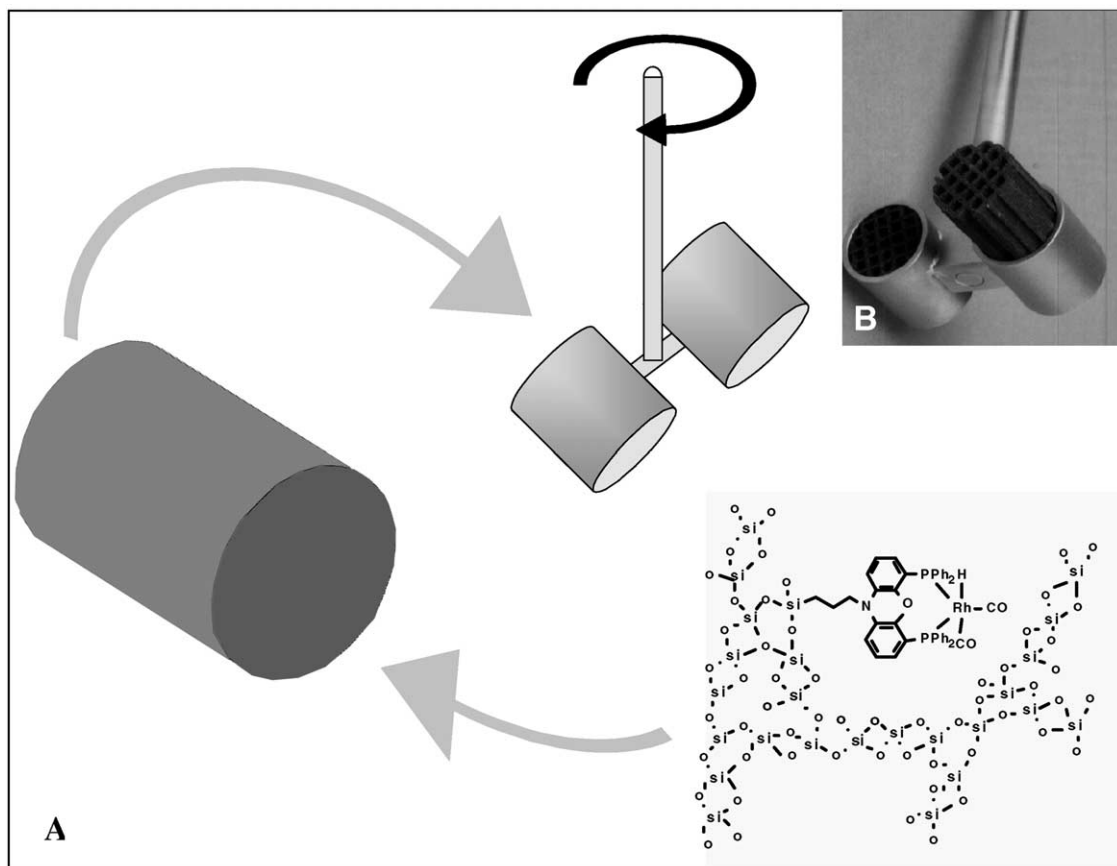
Fig. 3. A: Schematic representation of the homogeneous complex, immobilized on monoliths, and the implementation of these monoliths in the blades of a mechanical stirrer. Inset B: Picture of the silicon-carbide monoliths in the stirrer.

A sufficient amount of **2** was immobilized on the monoliths by agitation a toluene solution of **2** at 80 °C under an inert atmosphere. The immobilized ligand was subsequently functionalized with the rhodium precursor obtaining E (SiC monoliths) and F (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 h in an autoclave, equipped with the ligand functionalized 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 m^2/g according to BET surface area measurements). Only very little of ligand **2** 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 wt.% [48,49]. 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 ($\sim$0.05 mmol/g monolith).

In the hydroformylation of 1-octene, using the SiC monoliths, the overall selectivity for 1-nonanal is 89 ± 3% (Table 7). 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,

Table 7
Results from the hydroformylation of 1-octene using ROTACAT [28f]

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

[a] Ligand to rhodium ratio is 10, catalysis performed in 54 ml toluene using 3 ml of 1-octene at 80 °C under 50 bar of $CO/H_2 = 1/1$.
[b] Initial TOFs were determined as (mol aldehyde)(mol catalyst)$^{-1}$ h^{-1} at 10–20% 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 Chapter 3.
[f] In 25 ml toluene and 25 ml 1-octene.
[g] As in entry 9 but stirred back and forward.
[h] Average TOF.
[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.

the xanthene-based diphosphine effectively leads to the production of linear aldehyde. Remarkably, the selectivity for the linear product using the Si mono-liths 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 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-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, and the activity being comparable, it was decided to study this SiC system in more detail. The initial rate of hydroformy-

lation under standard conditions was found to be low (between 1 and 2 mol mol^{-1} h^{-1}). Compared to the sol–gel immobilized analogue this is about 15 times lower.

In an octene/toluene 1:1 mixture, the rate of the reaction increased to 15 mol mol^{-1} h^{-1} (Table 7, entries 1 and 9) due to the higher concentration of 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 s. This indeed resulted in a rate improvement of a factor of 2 (Table 7, 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 $94\,\text{Å}^2$ per 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. Indeed, at higher partial hydrogen pressures, the rate increased (entries 13 and 15) substantiating the existence of these dimers [23]. Under these optimized conditions, the reaction rate reached $97\,\text{mol}\,\text{mol}^{-1}\,\text{h}^{-1}$ when the catalysis was performed in neat 1-octene (entry 16).

The ROTACAT could be reused in 10 consecutive catalytic cycles showing no systematic deterioration in hydroformylation performance (Table 7, 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 AES. The catalyst showed a remarkable long-term stability. It was found that this system is reusable for over 6 months without systematic decrease in catalytic performance.

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.

In conclusion, the immobilization of a homogeneous hydroformylation catalyst on monoliths, constructed as the blades of a mechanical stirrer are a promising concept. 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 was the better catalyst in the hydroformylation of 1-octene showing an overall selectivity of $89 \pm 3\%$ for the linear aldehyde. Using optimized conditions a TOF was obtained of $97\,\text{mol}\,\text{mol}^{-1}\,\text{h}^{-1}$.

The ROTACAT system is extremely stable. The ROTACAT concept is generally applicable and it could add a new dimension to the ongoing work reported in literature on sol–gel and silica-immobilized homogeneous catalysts.

9. Concluding remarks

Many of the favorable properties of the xantphos–rhodium hydroformylation catalyst were retained after the modified xantphos ligands **1** and **2** had been immobilized. Linear-to-branched ratios of the aldehyde product ranged from 15 to 60 and 2-octene production was low. In many instances the rates dropped 10-fold or more compared to the homogeneous system. Selective systems such as this one have moderate rates even in homogeneous systems ($300\,\text{m}\,\text{m}^{-1}\,\text{h}^{-1}$, $80\,^\circ\text{C}$, 20 bar syngas, 1 M alkene). For industrial applications, this rate can be increased to acceptable values by raising the temperature and the alkene concentration. A concentration of 3 M would correspond to a conversion level of 70% for 1-octene in a continuous reactor and this alone would triple the rate.

For several silica-supported catalysts in condensed phase, including the SAPC system, the rates are disappointing. This can be assigned to slow mass transfer, and perhaps to incomplete rhodium hydride formation as we have discussed and observed. Addition of alcohol to the liquid-phase leads to complete hydride formation as we have seen. The sol–gel catalyst is relatively fast and is sometimes only a few times slower than the homogeneous one. Since only limited ways of preparation were tested, there is probably more scope for sol–gel catalysts. Space–time yields are promising at the present state of affairs.

The fastest catalysis was observed in $scCO_2$ where the rates are only half of those of the homogeneous catalyst. Expressed as space–time yields the solid catalysts are almost an order of magnitude faster, admittedly neither of them has been optimized. Thus, there is clearly a benefit in the supercritical system, which has to be weighed against the extra costs of the high pressures involved.

Leaching of the catalyst has thus far been a major problem. It turns out that the use of suitable bidentate ligands drastically reduces the leaching of rhodium. All experiments were run as batch reactions, except the $scCO_2$ experiments. The batch reactions are not necessarily representative for a continuous system, but the leaching was for all reaction that we studied below the detection limit. The detection limit was 1 ppm of rhodium in the liquid product, which might seem attractive, but for an industrial application for low-value products, this number should perhaps be two orders

of magnitude lower. On average this corresponds to a maximum loss of ∼1% of the rhodium inventory per run.

The scCO$_2$ runs, however, were continuous runs and the losses over longer periods were below 0.2%, which was again the detection limit and the actual result may be better than this. Another interesting feature that so far had little relevance is the fast heat transfer in scCO$_2$, in addition to the fast mass transfer. The hydroformylation reaction is highly exothermic and when the rates start approaching those of the homogeneous systems this certainly becomes a limiting factor in the heterogeneous hydroformylation catalysts. For lower alkenes the starting alkenes could form the supercritical phase as well, thus reducing the extra costs involved in the high pressures.

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