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Catalysis Today 42 (1998) 431–440

CATALYSIS TODAY

Various approaches to transfers improvement during biphasic catalytic hydroformylation of heavy alkenes

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Abstract

The [HRh(CO)(TPPTS)$_3$] precursor, where TPPTS is the water-soluble P(m-C$_6$H$_4$SO$_3$Na)$_3$ ligand, has opened a large area for the Supported-Aqueous-Phase (SAP) catalysed functionalisation of heavy substrates. We investigated several ways to increase the efficiency of heavy alkenes hydroformylation by [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(TPPTS)$_2$]. Addition of a cosolvent was shown to lead to a significant leaching of rhodium in the organic phase. Promising results were obtained. First, the Delmas–Chaudhari method of adding small amounts of PPh$_3$ to [HRh(CO)(TPPTS)$_3$] to maintain the complex at the interface, was examined for [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(TPPTS)$_2$]. Here [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(PPh$_3$)$_2$] was rapidly formed and is operating classically in the organic phase. Moreover, β-cyclodextrin was used as a phase-transfer agent allowing the inclusion of the substrate and its transport to the aqueous phase where the reaction is occurring. Finally, the use of silica with various hydration ratios in SAP catalysis led us to propose that the microreactors containing water, complex and extra TPPTS operate on the surface of the support. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The use of the highly water-soluble tris(meta-sulfonatophenyl)phosphine ligand, TPPTS, to maintain the rhodium complex in the aqueous phase led to a breakthrough for the hydroformylation of propene [1]. This low pressure biphasic process which provides high chemo- and regio-selectivities allows the elegant and efficient separation of the catalyst from the products by a simple decantation operation [2]. Extending this aqueous biphasic process to higher olefins has shown that a minimum solubility of the reactants in the aqueous phase is required [3]. With light olefins the reaction occurs in the catalyst phase [4]; for instance using [HRh(CO)(TPPTS)$_3$] as a precursor, the hydroformylation of propene takes place with the apparent activation energy of a homogeneous reaction. For heavy substrates, which of course, present a reduced solubility in water, the reaction rate is mainly governed by the mass transfer between the organic and aqueous phases. In fact many efforts have been devoted during the last few years to find subtle means either to improve the mass transfer of the reactants or to maintain the active species at the interface, mainly by using a cosolvent [5–7], a cyclodextrin [8,9], an amphiphilic ligand [10,11] or by Supported Aqueous Phase Catalysis (SAPC) [12,13].

This paper deals with the use of [Rh$_2$(μ-StBu)$_2$(CO)$_2$(TPPTS)$_2$] catalyst precursor for the low-pressure hydroformylation of 1-octene or 1-decene as models of heavy alkenes. Three means have been

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PII S0920-5861(98)00125-4

utilized to increase the reaction rate of this catalyst system: interfacial catalysis, use of cyclodextrins and SAPC.

2. Experimental section

2.1. General comments

All syntheses were carried out under an atmosphere of nitrogen using Schlenk tube techniques. Reagents and toluene were purchased from Aldrich and used without further purification. Other solvents were purchased from SDS and used without further purification too. Silica Sipernat 22 (generous gift from Degussa) is a high surface area (S_{BET}=162 $m^2 \cdot g^{-1}$) hydrophilic support, with an average pore diameter of 25 Å and a granulometry of 100 μm. Hydration percentage of this silica is 5.1 wt%. Rhodium trichloride trihydrated is a generous loan from Comptoir Lyon-Alemand-Louyot. Tris (*m*-sodiumsulphonatophenyl)phosphine (TPPTS) is a generous gift from Rhône-Poulenc Chimie. Wacker Chimie S.A. generously gave us cyclodextrins.

2.2. Syntheses

Complexes [HRh(CO)$(TPPTS)_3$] [14] and $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ [5] were prepared as described in the literature.

2.3. Catalytic tests

Hydroformylation experiments were carried out in a 150 ml Sotelem stainless steel autoclave, equipped with mechanical stirring.

2.3.1. Biphasic catalysis

In a typical run, in a Schlenk tube, 0.20 g (11.86×10^{-5} mol) of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ and 1.4 g (22.7×10^{-4} mol) of TPPTS are dissolved in 40 ml of deaerated water, then 10 ml (6.4×10^{-2} mol) of 1-octene is added. The reactor is put under vacuum and the solution is introduced by suction, then the reactor is heated to 80°C (preheated oil bath) under mechanical stirring (1870 rpm). When the temperature of 80°C is reached, the autoclave is pressurised with 10 bar of an equimolar CO/H_2 mixture. During the catalytic test, the pressure is kept constant and equal to 10 bar inside the reactor. After 21 h, the gas mixture feeding is stopped and the reactor is cooled at room temperature. Then the gas present inside the autoclave is evacuated. After reactor's opening, the biphasic solution is transferred by suction into a round-bottom flask and placed under nitrogen.

2.3.2. Supported aqueous phase catalysis

In a typical run, 0.038 g (2.26×10^{-5} mol) of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$, 0.141 g ($2.27\times10^{-4}$ mol) of TPPTS and 2.3 g of silica are placed in the autoclave. The solids are covered with 57 ml of toluene. Then, 2.86 g (2.55×10^{-2} mol) of 1-octene and the quantity of permuted water necessary to reach the desired hydration percentage are added before closing the autoclave. The reactor is pressurised three times with 4.5 bar of an equimolar mixture of hydrogen and carbon monoxide. After these operations, the autoclave is pressurised with 2 bar of the same gas mixture, then the reactor is heated to 80°C (preheated oil bath) under mechanical stirring (1870 rpm). When this temperature is reached, the reactor is pressurised with 5 bar of gas mixture. During the catalytic test, the pressure is kept constant and equal to 5 bar inside the reactor. After 15 h, the gas mixture feed is stopped and the reactor is cooled to room temperature. Then the pressure present inside the autoclave is released. After opening the reactor, the suspension of silica is transferred by suction into a round-bottom flask and placed under nitrogen.

2.4. Analytical techniques

2.4.1. NMR spectroscopy

Solid state ^{31}P NMR experiments were performed on a Brüker spectrometer (121.44 MHz) at the Laboratoire de Chimie de la Matière Condensée de l'Université Pierre et Marie Curie in Paris. Liquid phase ^{31}P NMR spectra were recorded on a Brüker AM 250 spectrometer (101.26 MHz) and on a Brüker AMX 400 (161.99 MHz) calibrated with H_3PO_4 as the external standard. Liquid phase and ^1H, ^{13}C spectra were recorded on a Brüker AM 250 spectrometer (250.13 MHz for ^1H spectra and 62.90 for ^{13}C spectra) and on a Brüker AMX 400 (400.14 MHz for ^1H spectra and 100.62 for ^{13}C spectra) calibrated with

TMS as external standard. Liquid phase ^{103}Rh spectra were recorded on a Brüker AMX 400 (3.16 MHz).

2.4.2. *Infrared spectroscopy*

Infrared spectra were recorded on a Perkin Elmer 1710 FTIR apparatus.

2.4.3. *ICP spectrometry*

Rhodium content of organic solutions after catalysis was determined by ICP on a JY 24 apparatus.

2.4.4. *TGA*

Hydration percentage of silica was determined by the thermal gravimetric analysis on a Setaram B 60 apparatus coupled with a temperature regulator Setaram PRG 64. Manipulations were carried out under helium 4.6 atmosphere.

2.4.5. *GPC*

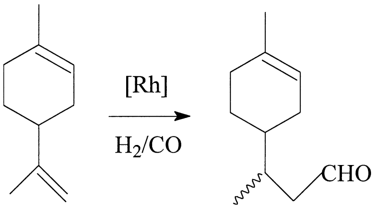
After catalysis the organic phases were analysed by gas phase chromatography on a Carlo Erba HRGC 5160 apparatus equipped with a flame ionisation detector and a capillary column Alltech Econocap FFAP (30 m; 0.53 mm; 1.2 μm), $T_{det.}$=200°C, P_{H_2}=0.45 bar.

3. Interfacial catalysis exploration through exchange of ligands

As far as the hydroformylation of 1-octene is concerned, Delmas, Chaudhari and Bhanage [15] very recently have reported that the spectacular improvement in the reaction rate takes place when small amounts of triphenylphosphine are added to the complex [HRh(CO)(TPPTS)$_3$]. This study detailed in the Bhanage thesis shows that a mixed ligand species, presumably [HRh(CO)(PPh$_3$)(TPPTS)$_2$], should operate at the interface between the organic and the aqueous phases. The exchange phenomenon between PPh$_3$ and TPPTS maintains the catalyst at the interface, provided that a large excess of hydrosoluble ligand is present. After each run, all the rhodium complexes are recovered in the aqueous phase. Thus, the authors suppose that all the rhodium is maintained in the interfacial area by this exchange phenomenon.

However, the selectivity of 66% in linear aldehyde is characteristic of the behaviour of a triphenylphosphine containing rhodium complex working into the organic phase in the absence of PPh$_3$ extra ligand [16]. So, as a first hypothesis, the organic part of [HRh(CO)(PPh$_3$)(TPPTS)$_2$] works in the organic phase although the presence of some water in the interface should result in higher selectivities. As a second hypothesis, the active species is [HRh(CO)(PPh$_3$)$_3$] in the organic phase as in classical hydroformylation but the PPh$_3$/TPPTS exchange in the final step permits the recovery of rhodium in the aqueous phase due to the large TPPTS/PPh$_3$ ratio (around 40).

For our part, we have undertaken a study on the hydroformylation of R-(+)-limonene which gives a single C$_{11}$ aldehyde as shown in Eq. (1)).



(1)

The reaction was carried out in the absence of solvent at 80°C, under a CO/H$_2$ pressure of 15 bar, for 21 h. Due to the very low solubility of the substrate in water the complex in a pure biphasic system gave traces of aldehyde. We examined the effects of the addition of small amounts of PPh$_3$ on the rate of the reaction catalysed by [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(TPPTS)$_2$].

As soon as we introduced a few amounts of PPh$_3$ to [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(TPPTS)$_2$], the reaction rate increased significantly, as shown in Fig. 1, until a plateau was reached for exactly one equivalent of PPh$_3$ per rhodium atom. We confirmed by infrared and NMR spectroscopies that in the yellow organic phase we produced only [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(PPh$_3$)$_2$] and not the mixed species [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(TPPTS)(PPh$_3$)] which may be formed at the interface.

In independent experiments we observed by ^{1}H NMR the effects of addition of PPh$_3$ to the complex [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(TPPTS)$_2$] in the mixed CD$_3$OD/D$_2$O monophasic solvent (40/60 vol). The spectrum of a solution containing only the starting complex showed the two tert-butyl signals at 0.84 and

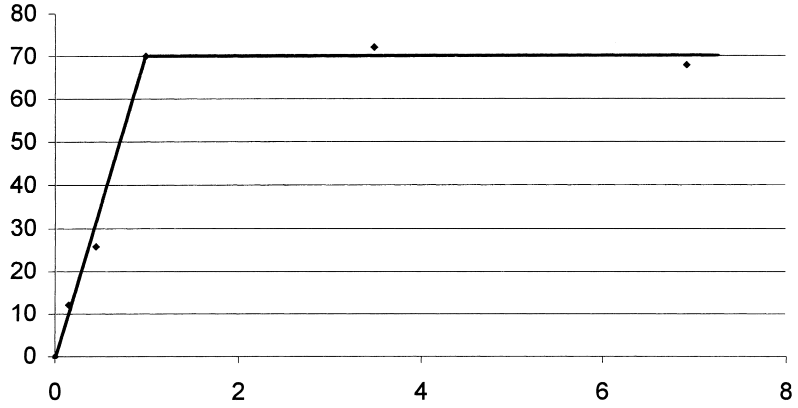


Fig. 1. Hydroformylation of (+)-limonene catalyzed by $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2\text{-}(TPPTS)_2]$ in the presence of variable amounts of PPh_3(P/Rh).

1.79 ppm. Addition of a significant excess of PPh_3 to $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ led to produce two other species characterized for the first one by two singlets at 0.73 and 1.54 and for the second by two singlets at 0.77 and 1.58 ppm. Finally, addition of an excess of PPh_3 and TPPTS, resulted in the presence of two couples of signals at 0.84; 1.79 and at 0.73; 1.54 ppm. Although the system is not yet in the equilibrium conditions, we assign these two latter signals to the mixed complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)(PPh_3)]$. Indeed, in the second experiment an excess of PPh_3 was exclusively introduced so that the third complex observed (0.77; 1.58 ppm) has the formula $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$; in the last experiment the excess of TPPTS shifts the equilibria towards the left suppressing the presence of the species containing the two PPh_3 ligands (Eq. (2)).

$$[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2] \underset{TPPTS}{\overset{PPh_3}{\rightleftharpoons}}$$
$$\times\ [Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)(PPh_3)] \underset{TPPTS}{\overset{PPh_3}{\rightleftharpoons}}$$
$$\times\ [Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2] \qquad (2)$$

We observed in addition that contacting a limonene phase containing $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$ with an aqueous phase containing TPPTS (ratio TPPTS/PPh_3 ranging from 10 to 20) did not restore the formation of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ even at 80°C. Thus, in the present case, the ligand exchange does not occur. Since the plateau of Fig. 1 begins at a rhodium to PPh_3 molar ratio of exactly 1 : 1, the catalytic precursor which is responsible for the catalytic activity is presumably $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$ in the bulk of the organic phase.

The major point for this dinuclear complex is that the rhodium complex cannot be fully immobilized in the aqueous phase, contrary to the initial goal.

4. Cyclodextrins

4.1. General presentation of cyclodextrins

Cyclodextrins (CD) are the products of the α-D-glucopyranose polycondensation. They are cyclic oligomers built up from α-D-glucopyranosyl unities linked 1–4′. They are divided in 3 main groups according to the number of glycopyranosyl unities: (see Table 1 and Fig. 2).

The rings have the shape of a truncated cone, the primary alcohol functions are on the small base and the secondary one on the large base. The internal cavity is essentially hydrophobic [17] being covered by the hydrogens linked to the carbons 3 and 5 and the glycosidic oxygens.

The diameters of the cavity are about 470–520 pm for the α-cyclodextrin, 600–640 pm for the β-cyclo-

Table 1

Cyclodextrin name	Number of sugars (*n*)
α-cyclodextrin (αCD)	6
β-cyclodextrin (βCD)	7
γ-cyclodextrin (γCD)	8

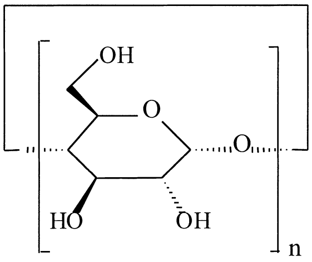


Fig. 2. General frame of a cyclodextrin.

Table 2

Cyclodextrin	Solubility
α-cyclodextrin	150 g/l
β-cyclodextrin	18.5 g/l
γ-cyclodextrin	220 g/l

dextrin and 750–830 pm for the γ-cyclodextrin [18,19]. We should stress the fact that βCD is of relatively low solubility in water (18.5 g/l), whereas αCD and γCD are respectively eight and 12 times more soluble [18] (see Table 2).

The most remarkable property of the cyclodextrins is their capacity to form inclusion complexes in aqueous solutions with various molecules [20], including alkenes. In a first approximation, we have to consider that this phenomenon does not depend on the chemical nature of the substrate [21]. In the solid state, the guest molecule stays inside the cavity and, although it is not demonstrated, it is generally admitted that the same phenomenon occurs in a liquid phase [19]. Determination of the CD-substrate dissociation constant compared to theoretical models show that the association which is occurring is more complex than a 1 : 1 model [17].

Thermodynamic studies [21] showed that the enthalpy variation ΔH is always negative (dissociation is favoured by increasing the temperature) but the entropy variation ΔS can be positive or negative according to the substrate because several forces are implicated in the complex formation [21]: (i) non specific Van der Waal's forces [19], (ii) hydrogen bonds [19], (iii) hydrophobic interactions [19] (estimated at 30% of the free energy [22]), (iv) forces created by the water inserted in the CD cavity ('activated water').

The compensation of ΔH by ΔS can be due to two molecular mechanisms: (i) compensation of the CD-substrate interaction enthalpy by the decrease in the degree of the substrate's motional freedom due to the interaction, (ii) compensation of the solvation enthalpy by the decrease of the degree of solvant molecules' motional freedom [23].

The formation of the complex is in fact the succession of several steps [21]: (i) approach of the substrate to the CD, (ii) elimination of the water molecules out of the CD cavity, (iii) assimilation of these water molecules to the bulk, (iv) interaction of the CD and the substrate, (v) rebuilding of the hydrated structure round the final complex.

Except in their use in the catalysis of cyclopentadiene and acrylonitrile cyclo-addition by the simultaneous inclusion of the two molecules [17], the CD's play the role of transfer agent due to their complexing properties. Therefore, the substrate must be non-soluble in the phase containing the catalyst. The easiest way is to use a water-insoluble substrate and a water-soluble catalyst. The substrate can also be included in the CD which, then, brings it into the aqueous phase where the contact with the catalyst is possible. After the reaction, the CD permits the substrate to leave the cavity and to return into the organic phase and, then, is again ready to play its role of a phase transfer agent.

4.2. *Hydroformylation reaction in the presence of a cyclodextrin*

After the preliminary studies of Jackson et al. in the hydroformylation of 1-hexene catalysed by $HRh(CO)(TPPMS)_3$ in the presence of αCD, (TPPMS being the di(phenyl)(meta-sulfonatophenyl)phosphine), Monflier and co-workers recently reported the use of modified cyclodextrins in catalytic biphasic reactions like the Wacker oxidation and the hydroformylation of water-insoluble olefins, without adding the organic solvent [24–27]. The runs of hydroformylation were made at 50 bar. They tested several cyclodextrins, functionalised or not, and they found that the best results are obtained for the dimethylated βCD (heptakis(2,6-di-O-methyl)-β-cyclodextrin or DMβCD) and that the activity is largely dependent on the degree of substitution of the cyclodextrin. To explain their results, they suggested the lower stability of the CD-aldehyde complex than those for the modified CD-aldehyde complex. The low *n*/*i* ratio (around 1.9) is thought to be due to the ability of the modified CD for a pre-orientation of the substrate in the cavity and the interactions between the CD and the catalyst.

4.3. Hydroformylation using a $Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$/ βCD system

Hydroformylation reactions were carried out on 1-octene under the same mild conditions as previously described for $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ [5]. As satisfactory results were obtained, the experiments were extended to 1-decene and limonene. The experimental conditions and the catalytic results are displayed in Table 3.

The first row shows that, in the absence of any cyclodextrin, the yield of aldehyde in 20 h is low, i.e. the turnover frequency is only 3.7 h^{-1}.

The runs 3–5 are recycling runs, done with the same catalytic solution as in run 2 except that a greater amount of βCD was added. The catalyst, in the presence of βCD, significantly improves the yields in nonanal. If we compare runs 2 and 3–5 it appears that adding three times more βCD results in an increase in the yield in the same proportions. Run 3 shows a higher level of activity than the two next ones because of a small loss of aqueous catalytic solution after each recycle.

These experiments show clearly that mass transfer is improved presumably because the βCD/octene inclusion complex is formed and the substrate is brought into the aqueous phase. Moreover, as the linearity decreases dramatically from 98% for run 1 without βCD to 70–76% for the runs with βCD, and as catalysis cannot occur either in the organic phase or at the interphase, it is clear that cyclodextrin has a predirecting effect of the substrate towards the hydrosoluble complex. Thus the turnover frequency increases from 4 h^{-1} (run 2) to 15 h^{-1} (run 3) when the concentration increases for [βCD] 8.8 to 28.5 mmol/l.

Octene present in the aqueous phase comes logically from the mass transfer of octene itself and from the transfer of octene brought by CD. The selectivity in the linear aldehyde is mainly due to the most rapid phenomenon, ie the transfer by CD, slightly corrected by the presence of free octene. Indeed, when octene is free in water, 98% of the linear aldehyde is produced, whereas when it is included in the CD, the organic environment induces a larger tendency for the alkene to give the branched aldehyde. The 70% linearity observed for runs 4 and 5 confirms that there is essentially an organic environment for the terminal C=C bond. The limiting step of the transfer is the solubility of the βCD (Table 2), so we used heptakis(2,6-di-O-methyl)-β-cyclodextrin (DMβCD), which is much more soluble in water (590 g/l). Unexpectedly, the results obtained were lower than with unmodified βCD. Due to the presence of ether functions on the βCD, the height of the cone is larger, and then, presumably, octene is totally included in the βCD, thus preventing the catalyst from approaching the alkene. To infer this assumption, the same catalytic

Table 3

Run number	[βCD] (mmol/l)	[DMβCD] (mmol/l)	Yield (%)	$\frac{n}{n+i}$	TOF (h^{-1})
1	0	0	11	98	3.7
2	8.8	0	13	93	4.3
3	28.5	0	48	76	15
4	28.5	0	41	70	12.9
5	28.5	0	39	68	12.3
6	0	25.3	9	92	3.0
7	0	25.3	16	92	4.9
8	0	25.3	16	88	5.0
9	0	25.3	18	87	5.6

H_2O: 40 ml.
Octene: 10 ml (64 mmol).
Catalyst: 0.2 g (0.12 mmol).
TPPTS: 0.7 g (1.14 mmol) 80°C, 15 bar.

Table 4

Run number	[DMβCD] (mmol/l)	Yield (%)	$\frac{n}{n+i}$	TOF (h^{-1})
10	0	5	98	2
11	20.2	74	87	27
12	20.2	65	81	23

H_2O: 40 ml.
Decene: 10 ml (53 mmol).
Catalyst: 0.2 g (0.12 mmol).
TPPTS: 0.7 g (1.14 mmol) 80°C, 15 bar, 20 h.

Table 5

Run number	[DMβCD] (mmol/l)	Yield (%)	P_t (bar)	TOF (h^{-1})
14	0	2	5	1
15	25	2	5	1
16	25	14	5	6
17	25	8	18	3

H_2O: 40 ml.
Limonene: 10 ml (61.7 mmol).
Catalyst: 0.2 g (0.12 mmol).
TPPTS: 1.4 g (1.14 mmol) 80°C, 20 h.

run was carried out with 1-decene, the results being reported in Table 4. In this case, the yields are better than those with octene because the double bond part of the alkene is outside the DMβCD and is thus more accessible to the coordination of the rhodium centre. The linearity of the aldehydes is a little bit higher (81 to 87%) than 1-octene with βCD (68 to 76%) because the hydrophobicity of the DMβCD cavity is lower. In the case of the βCD all the alcohol functions are linked together by hydrogen bonds and thus form a rigid cone, whereas, in the case of the DMβCD, these bonds are broken and the cone becomes less rigid, permitting a rearrangement of the DMβCD to include more water.

^{1}H, ^{13}C, ^{31}P, and ^{103}Rh NMR studies have been carried out in order to detect the interactions between DMβCD, i.e. the more soluble one, and the rhodium complex. At 400 MHz, and even recording the spectra at various temperatures, especially 5, 25, and 80°C, we did not observe any significant shift for any signal, so that we can conclude that the main role of the cyclodextrin vector is to include the alkene and to bring it into the aqueous phase.

Preliminary experiments on limonene were carried out. In the absence of transfer agent, no transformation of the substrate was observed. However, addition of DMβCD led to modest yields in the corresponding aldehyde. As usual, we noted that the first recycling (run 16) led to a large improvement of the catalytic activity. Similarly, increasing the pressure (run 17) resulted in a proportional increase in the yield (see Table 5).

Operating in the same area of supramolecular chemistry, we are focusing on the novel synthetic catalytic systems based on the principles of enzymes. We are investigating on the preparation of catalysts linked to macropolycyclic molecules, like crown ethers or calix[4]arenes to permit the encapsulation of substrates and to improve the reactivity of the hydrophobic molecules toward the water-soluble rhodium based catalysts.

5. Supported aqueous phase catalysis

Another way to increase the interfacial area between the organic and aqueous phases is to deposit a thin film of water on the hydrophilic surface of an inorganic support. This method, developed by Davis et al. [12] several years ago, presently known as SAPC, seems to contain a very powerful concept in order to transform a substrate of very low solubility in aqueous phase, without any detectable leaching of rhodium in the bulk [28]. Particularly useful are supports, generally silica, of great specific areas containing mainly meso (20 to 500 Å) and macropores (>500 Å). Most of the studies have been done with TPPTS which possesses high solubility in water (1100 g/l). At the present time, it is admitted that the reaction occurs at the interface of the aqueous film and the organic phase, more precisely the sulphonate groups are strongly solvated by water whereas the most organic part of the molecule is emerging in the organic phase [13]. As soon as a thin film of water is maintained on the solid, the catalyst can be recycled by a simple filtration after the run.

We have examined the catalytic activity of the $[Rh_2(\mu\text{-S}^tBu)_2(CO)_2(TPPTS)_2]$ complex in SAP catalysis. Two methods can be used to prepare the starting material: either to add in a Schlenk tube a water solution containing the complex to silica, the adsorption being rapid and giving a yellow hydrated solid, or to prepare in the autoclave the catalytic system by the successive introduction of silica, rhodium complex, TPPTS, toluene, water and octene. As these methods give rise to the same performances [29], it is more convenient to use the second one because the species introduced are slightly less sensitive to oxidation. Particularly, addition of adjusted quantities of water and/or TPPTS permit to obtain directly the aqueous film on the support containing all the reactive species of interest.

5.1. SAPC with the silica/$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] system

5.1.1. Optimized hydration degree

As already mentioned in the literature, for the studies carried out with [HRh(CO)$(TPPTS)_3$], we observed that this SAPC is very sensitive to the hydration level [12,28,30–32]. All our experiments used a Sipernat 22 silica, which is characterized by a mean granulometry of 100 µm and a BET surface area of 162 m^2/g. The percentages of water given in Table 6 takes into account the amounts of water contained by silica (determined by Thermo Gravimetric Analysis), by the [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$], by TPPTS (one molecule of water per Na atom). The experiments have been carried out under mild conditions (5 bar H_2/CO, 80°C, 15 h, TPPTS/Rh molar ratio=6.0, stirring rate: 1870 rpm). Table 6 shows the results near the optimum value. These results plotted in Fig. 3 show clearly that the reaction rate varies sharply on both sides of the maximum. The other parameters have then been optimized, but the hydration degree is the most determinant one, so we have examined it more deeply.

5.1.2. Analysis of the parameters

The scheme previously proposed by Horváth [13] for [HRh(CO)$(TPPTS)_3$] can be summarized as the immobilization of the sulphonate groups in the aqueous phase, the other part of the molecule emerging in the organic phase. In the present experiments, the selectivity stays around 82%, as we mentioned above, and this value is a strong indicator that the catalytic reaction takes place in the organic phase. After each run, the solid was recovered by the simple filtration and analysed by NMR spectroscopy. NMR in the solid state shows the presence of TPPTS, its oxide, and a weak signal which could correspond to the [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] complex. Further analyses have been carried out: addition of an excess of water allowed the extraction of all the catalytic system. ^{31}P NMR of this solution showed unambiguously the doublet due to [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] besides TPPTS and OTPPTS. No coloration of the organic phase was noted, and no rhodium was detected either by infrared or by ICP analyses. Thus, the Horváth model is valid concerning the selectivity of the reaction, but does not explain at all the variations in the reactivity. Indeed, for all the values of hydration of interest (12.4 to 12.9%) the calculations give amounts of water equivalent between one and two monolayers of a continuous film covering the silica surface. In our opinion, this film is not thick enough to retain strongly the catalyst on the surface and to avoid its leaching. The strong affinity of water towards TPPTS, coordinated or not, allows the proposition that this ligand is preferentially hydrated after silica has been hydrated by a monolayer of strongly bonded water [33], and thus mobilises the required amounts of water to complete its solvation sphere.

Focusing on the fact that, at the end of the run, the catalyst is not modified at all, the TPPTS and [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] are, during all the run, in the

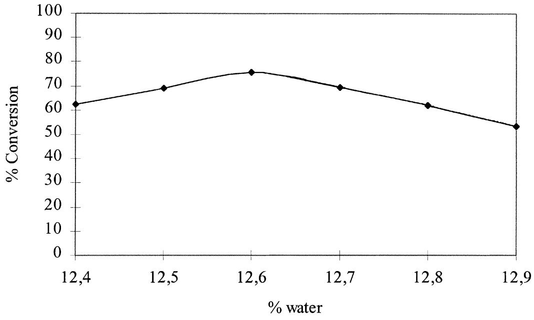


Fig. 3. Influence of the hydration percentage of silica on the rate of hydroformylation of 1-octene.

Table 6

% H_2O	% Conversion	% Linearity
12.4	62.5	82.2
12.5	69.0	82.5
12.6	75.5	82.6
12.7	69.5	82.6
12.8	61.8	82.4
12.9	53.4	82.3

same bulk of water, because if it were not the case, the pressure of CO would transform all the catalyst in $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$, which would leak into the organic phase. This would not be possible with a continuous film on the silica surface. Thus, in order to form this environment favourable to the vicinity of both complex and extra-ligand, we have to imagine that a small volume of water, more or less thick, is formed immediately after the introduction of the products and that this volume is large enough to contain at the same time the catalyst and TPPTS. When the quantity of water introduced is less than the optimum, hydration sphere is only just formed so that the mobility of the catalytic system components is dramatically reduced, among them concerning the exchange between free and coordinated TPPTS. Adding some more water improves this mobility and the optimum (12.6%) corresponds to all the $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ molecules emerging in the organic phase. When the activity begins to decrease, this corresponds to volumes of water so large that some molecules of the catalyst are completely included in the aqueous phase. From our preliminary calculations to modelise this SAPC system, when the silica is hydrated at 12.6% in mass, the form and thickness of the volume is just the compromise between a good contact area and a good mobility of the catalyst. Moreover, we introduced twice the quantity of silica, with the same 12.6% hydration, keeping the other parameters unchanged. We observed an important increase in the yield (from 75.5 to 93.4%). The water volume form appears more favourable to a good mass transfer than in the first case, through an appropriate rearrangement of the layers on the silica surface to provide to the volume a larger interfacial area.

In fact, the water volumes on silica behave as ‘interfacial microreactors’ so that we can consider that the SAPC acts through ‘interfacial microreactors’.

6. Conclusions

In the hydroformylation reaction, if we want to conjugate the catalytic functionalisation of heavy alkenes to the recovering of the catalyst, the use of cyclodextrins or the SAP catalysis allows to improve greatly the transfer phenomena between the organic phase and the aqueous phase where the catalyst is maintained. However, for these two approaches of catalysis, we need to understand even better the phenomena ruling the approach of the alkene towards the metallic centre, particularly to know how alkenes are included in the CD cavity and how $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ can be retained at the interface in an optimal way.

Acknowledgements

We thank Wacker Chimie S.A. for a generous gift of Cyclodextrins, Rhône-Poulenc Chimie for giving us TPPTS, Degussa for a gift of silica and Comptoir Lyon-Alemand-Louyot for a generous loan of rhodium salts.

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