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# Hydroformylation by rhodium catalysts supported on oligomeric arylamides

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**Abstract**

Hydroformylation of various unsaturated substrates has been carried out using an oligomeric complex obtained by adding $Rh(CO)_2(acac)$ to oligo-1,4-phenyleneterephthalamide (OPTA). The reaction, performed in autoclave at 80 °C and 80 atm ($CO/H_2 = 1{:}1$) using an innovative glass device, gave satisfactory results. The catalyst could be easily recycled and reused 8–9 times without significant loss of efficiency.
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## 1. Introduction

Hydroformylation of alkenes for the industrial production of aldehydes (ca. 7 million tonnes per year) and their derivatives is one of the most important reaction involving synthesis gas: a distinctive feature of this process is that rhodium carbonyl complexes, generally modified with ligands, such as phosphines and phosphites, are employed as catalysts to an increasing extent, because they allow high reaction rates to be achieved and to obtain the desired products with good selectivities [1].

However, the so-called oxo-process is still affected by some drawbacks, such as the technical difficulties associated with the separation of products from the solvent and the soluble, catalytically active metal complexes as well as the high cost of the required catalysts; indeed, the world production of rhodium does not exceed 2–3 tonnes per year and the cost of the metal is currently $32.15 [2] per gram, thus making rhodium derivatives very expensive. Ingenious methods have been devised which address both the problem of product recovery and effective recycling of the catalyst [3–5]. Some of these methods have now reached industrial maturity, i.e.: (i) employment of water-soluble rhodium carbonyl complexes containing hydrophilic ligands (mostly sodium salts of sulphonated mono- or di-phosphines), thus offering the considerable advantage of carrying out the process in an aqueous biphasic system [6,7]; (ii) use of rhodium carbonyl complexes with suitably fluorinated ligands (fluorous biphasic catalysis) which allow the reaction to occur in perfluorinated solvents, where the catalysts are soluble, in the presence of an immiscible organic phase where the oxo-products gradually migrate [8,9]; (iii) application of supercritical carbon dioxide as reaction medium which can be released as a gas at the end of the process [10–12]; (iv) use of ionic liquids as biphasic hydroformylation media [13–16]; (v) linking of the substrate to a polymeric matrix (solid–liquid hydroformylation) [17]; (vi) immobilisation of the catalytically active metal or metal derivative on an inorganic support [18–22] and (vii) co-ordination of the catalytic species to a polymeric matrix containing functional groups able to interact with the transition metal [23–27].

It has been shown that catalytic reactions carried out in the presence of transition elements (Pd, Pt, Rh, etc.) immobilised on a polymeric matrix offer a series of advantages over traditional homogeneously catalysed reactions [28,29]. In the growing field of heterogenised organometallic catalysis, oligomeric organic species having a number of different

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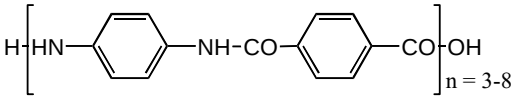



Fig. 1. OPTA.

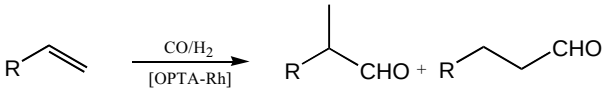
molecular structures may represent a valid option in the choice of the catalyst support [30,31]. Some of us have designed and synthesised, a range of oligomeric aromatic amides whose structures and functionalities make them "active", supports for heterogenised catalytic systems. The latter have been successfully applied in organic processes of industrial relevance, such as hydrogenation and oxidation [32–34]. One of the most representative terms of this class, namely, the oligo-1,4-phenyleneterephthalamide (OPTA, Fig. 1), is structurally similar to Kevlar®, although its lower average molecular mass ($\overline{MM}$ in the range 750–400 a.m.u.) implies a significant higher relative amount of end groups (–$NH_2$ and –COOH), capable of binding many catalytically active elements [35].

OPTA is very stable towards chemical, thermal and mechanical stresses, although its insolubility in most organic solvents (a property which, on the other hand, makes it an ideal candidate for a support) renders its complete characterisation which is rather a difficult task [36,37]. Its synthesis is versatile, since, by a proper choice of reaction conditions, it is possible to modify the structural features of this oligomeric species especially in terms of MM and distribution of functional groups [38].

Since several years, some of us are involved in the investigation of the rhodium-catalysed hydroformylation and of related methods to improve the separation of the catalyst from the reaction products [17,39–41]. As part of our ongoing interest in rhodium-catalysed hydroformylation and in methods to improve catalyst confinement and recovery, we have prepared catalytic systems made up of OPTA and different relative amounts of $Rh(CO)_2(acac)$. Notably, heterogenisation of the catalyst precursor is achieved without any preliminary modification of the molecular structure of the organic support. To the best of our knowledge, this is the first example of an OPTA-Rh catalytic system (Scheme 1).

Hydroformylation of various substrates with OPTA-Rh has been carried out in a solid–liquid biphasic system with two main goals, i.e.:

- the study of the properties of the new support metal system in view of its application as catalyst precursor for the oxo-process and
- the set-up and optimisation of the hydroformylation experiment in order to obtain high yields and reproducible results.




Scheme 1. Hydroformylation reaction with OPTA-Rh as a catalyst.

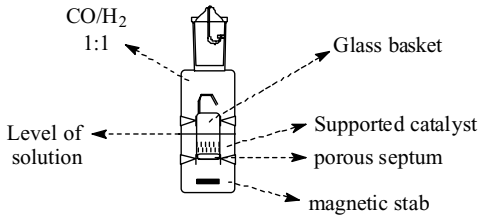



Fig. 2. Glass device used in the hydroformylation reactions.

## 2. Experimental

### 2.1. Materials and methods

The catalyst precursors $Rh(CO)_2(acac)$ (acacH: acetylacetone) was purchased from Fluka and was used without further purification. The OPTA was prepared, as described previously [32]. Solvents were purified following standard procedures. $^1$H NMR spectra were recorded in $CDCl_3$ solution on a Varian Mercury Plus spectrometer operating at 400 MHz, chemical shifts ($\delta$) given in ppm relative to TMS and IR spectra were measured on KBr discs or Nujol dispersions with an FT-IR Perkin–Elmer model 1720 spectrophotometer; gas-chromatographic analyses were performed with a Perkin–Elmer model 8500 instrument. Mass spectra were recorded by means of a Hewlett-Packard model GCD GC–MS, using the appropriate columns and conditions. Thermogravimetric analysis (TGA) was done on a Perkin–Elmer model DSC-1 Thermal Analysis System. The glass device used in the hydroformylation experiments is depicted in Fig. 2.

### 2.2. Preparation of the OPTA-Rh catalytic system

The OPTA-Rh [3% (w/w) as $Rh(CO)_2(acac)$] catalytic system was prepared by adding 250 mg of the solid OPTA to a solution of $Rh(CO)_2(acac)$ (7.5 mg, 0.029 mmol) in 100 ml of distilled water/glacial acetic acid (9:1 (v/v)). The suspension was stirred for 6–8 h at 25 °C, filtered and the powdered material collected, washed several times with water, dried under a vacuum for 12 h and used as such for the catalysis experiments. The catalytic systems containing different relative amounts of Rh (1 and 10% (w/w)) were prepared following the same procedure.

The catalytic systems were characterised by TGA and infrared spectrophotometry. The different percentages of rhodium in the OPTA supporting material resulted from TGA. Samples of the catalyst (2–4 mg) were weighed in a Perkin–Elmer model TGA-2 thermobalance and heated in air at a rate of 20 °C $min^{-1}$ in the temperature range 323–1073 K. The OPTA volatilises completely before reaching 973 K without leaving any residue; the final weight is thus exclusively due to the metal [42]. It should be noted that 3% (w/w) of $Rh(CO)_2(acac)$ corresponds to 1.2% (w/w) of Rh metal. The IR spectra show significant peaks at 3321, 1646, 1543, 1515, 1018 and 865 $cm^{-1}$.

### 2.3. Activation of the complex OPTA-Rh

OPTA-Rh system (100 mg) was placed in a small glass basket provided with a sintered glass bottom and the basket was then partially dipped into a glass vessel containing 20 ml of toluene (Fig. 2). All operations were carried out under a nitrogen purge. The vessel was transferred into a 150 ml stainless steel reactor which was then charged with syngas to a pressure of 80 atm and heated at 80 °C for 24 h. After cooling at room temperature, the residual gases were released, the glass basket was taken out of the glass vessel and the yellowish OPTA-Rh catalyst dried under a vacuum. This activated catalyst was used without any further treatment.

### 2.4. Hydroformylation reactions catalysed by the OPTA-Rh system

The reactions were carried out in a 150 ml stainless steel autoclave equipped with a glass vial properly modified to hold a glass basket inside (Fig. 2). The glass basket is provided with a porous sintered glass bottom. In a typical run, the insoluble solid catalytic system OPTA-Rh (38.5 mg) is placed in the glass basket and the latter hung into the vial, so as to partially dip into a solution of the substrate (0.048 mol) in 20 ml of toluene. Efficient stirring is provided by a magnetic stirring bar at the bottom of the vial: this arrangement, while assuring an intimate contact between the reagents and the catalyst, prevents mechanical stress of the latter and allows for easy re-use of the catalyst for several reaction cycles.

The vessel is transferred into a 150 ml stainless steel reactor which is charged with syngas to the required pressure and heated at 40–80 °C, for 24 h (Tables 1 and 2). After cooling at room temperature, the residual gases are released and the solvent evaporated. The crude reaction products were analysed by GC. If necessary, the mixtures of *iso*- and *n*-aldehyde were separated by flash chromatography using a 2:8 mixture of diethyl ether/*n*-hexane as eluent. The aldehydes were characterised by GC–MS and $^1$H NMR.

Table 2
Hydroformylation reactions of some substituted alkenes with OPTA-Rh catalyst

| Run | Substrate | Conversion (%) | Starting product (%) | Aldehydes yield (%) |
|---|---|---|---|---|
| 1 | 1-Octene | 100 | – | 100[a] |
| 2 | *trans*-2-Octene | 100 | – | 100[b] |
| 3 | *trans*-3-Octene | 60 | 40[c] | 20[c] |
| 4 | 2-Methyl-1- hexene | 13 | 87 | 100[d] |
| 5 | Cyclohexene | 100 | – | 100[e] |
| 6 | Limonene | 60 | 40 | 60[f] |
| 7 | α-Methylstyrene | 13 | 87 | 100[g] |

Reaction conditions: substrate: 0.048 mol, 3% OPTA-Rh catalyst: 38.5 mg, Rh/substrate molar ratio: 1:11,000, solvent toluene, temperature: 80 °C, pressure: 80 atm ($CO/H_2 = 1$), reaction time: 24 h.

[a] 2-Methyloctanal: 40% and nonanal: 60%.

[b] Isomerisation of the substrate occurs; composition of the mixture of isomeric aldehydes: nonanal 17%, 2-methyloctanal: 48%, 2-ethylheptanal: 26%, 2-propylhexanal: 9%.

[c] Isomerisation of the substrate occurs; isomeric composition of residual alkenes: 1-octene: 5%, 2-octene: 28%, 3-octene: 40%, 4-octene: 7%; composition of the mixture of isomeric aldehydes: nonanal: 9%, 2-methyloctanal: 5%, 2-ethylheptanal: 4%, 2-propylhexanal: 2%.

[d] 3-Methylheptanal: 13%.

[e] Cyclohexanecarbaldehyde: 100%.

[f] 3-(4-Methylcyclohex-3-enyl)butanal: 60%.

[g] 3-Phenylbutanal: 13%.

## 3. Results and discussion

The supporting matrix for the preparation of the catalytic system is the oligomeric arylamide OPTA [32,33], whose structure contains a significant number of end groups and is capable to co-ordinatively interact with the rhodium derivatives. The preparation of the catalytic system is relatively simple, but the resulting catalyst, as obtained, following the procedure is described in Section 2, does not give rise to an appreciable reaction rate when used for the first time. Accordingly, in a hydroformylation experiment carried out with styrene using a 1:11,000 catalyst/substrate molar ratio, after stirring for 24 h at 80 °C and 80 atm ($CO/H_2 = 1:1$), the yield of aldehydes was only 56% (branched/linear isomers ratio = 85:15). This result indicates that a preliminary

Table 1
Hydroformylation reaction of styrene with OPTA-Rh catalyst

| Run | Temperature (°C) | Catalytic precursor[a] | Rh/substrate | Conversion (%) | Styrene (%) | Yield (%) | Branched aldehyde (%) | Linear aldehyde (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 40 | 10% OPTA-Rh | 1:3300 | 15 | 85 | 15 | >99 | – |
| 2 | 60 | 10% OPTA-Rh | 1:3300 | 100 | 0 | 88[b] | 85 | 15 |
| 3 | 40 | 3% OPTA-Rh | 1:11000 | – | 100 | – | – | – |
| 4 | 60 | 3% OPTA-Rh | 1:11000 | 84 | 16 | 84 | 75 | 25 |
| 5 | 80 | 3% OPTA-Rh | 1:11000 | 100 | 0 | 100 | 75 | 25 |
| 6 | 60 | 1% OPTA-Rh | 1:33000 | 10 | 90 | 10 | >99 | – |
| 7 | 80 | 1% OPTA-Rh | 1:33000 | 15 | 85 | 15 | >99 | – |
| 8 | 80 | $Rh(CO)_2(acac)$ | 1:10000 | 92 | 8 | 92 | 98 | 2 |

Reaction conditions: substrate 0.048 mol, catalyst 38.5 mg, solvent toluene, pressure 80 atm ($CO/H_2 = 1$), reaction time 24 h.

[a] Weight percentage of $Rh(CO)_2(acac)$ added to OPTA.

[b] 2-Phenylpropanol 5.2%, 3-phenylpropanol 1.8% and ethylbenzene 5%.

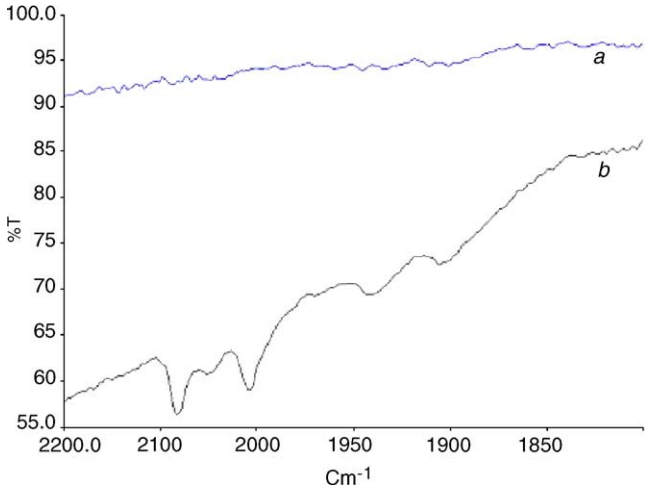



Fig. 3. FTIR spectrum of the 3% OPTA-Rh before (curve a) and after the activation procedure (curve b) in the diagnostic region of metal-carbonyl CO stretching frequencies.

activation step is needed, after which the catalytic system becomes much more efficient (Table 1). The activation step can be accomplished better by submitting the catalyst precursor to the same conditions of a hydroformylation process, without introducing the reagent alkene in the autoclave. The IR spectrum of the activated complex (Fig. 3) provides a sound evidence of the structural change following the activation step. Actually, two well-defined absorption bands appear in the M–CO carbonyl region at 2083 and 2008 $cm^{-1}$ which are lacking in the spectrum of the OPTA-Rh catalytic system before the activating procedure. It has been reported [43] that these two bands are typical for a rhodium dicarbonyl moiety in similar complexes with nitrogen ligand groups.

Table 1 summarises the results obtained in the hydroformylation of styrene catalysed by the OPTA-Rh catalytic system containing variable relative amounts of Rh. The complexes have been prepared according to the procedure described in the experimental section, i.e. by adding 250 mg of OPTA to a solution having the appropriate concentration (% (w/w)) of $Rh(CO)_2(acac)$ in distilled water/glacial acetic acid (9:1 (v/v)).

The first runs were carried out using an activated OPTA-Rh system containing 10% Rh as rhodium dicarbonyl (Table 1). At 40 °C (run 1), a complete chemo- and regio-selectivity to 2-phenylpropanal was obtained, although the conversion of styrene was low (only15%). On increasing the temperature to 60 °C (run 2), complete conversion of the substrate was achieved but some hydrogenation of the starting styrene to ethylbenzene and of the products aldehydes to 2- and 3-phenylpropanol was also observed. Besides, the regio-selectivity of the hydroformylation reaction changed giving 85% of the branched aldehyde. The catalyst system was recycled six times with no decrease in activity i.e the same solid catalyst was re-used under the reaction conditions of run 2 and comparable results were obtained. By reducing the amount of rhodium to 3% and the ratio Rh/substrate to 1:11000 no aldehydes were detected when the hydroformylation was run at 40 °C (run 3). The conversion of styrene rose to 85% when the reaction was performed at 60 °C (run 4) and the chemo-selectivity to the aldehydes was complete with a branched/linear ratio of 75:25. A further increase of the temperature to 80 °C brought about a complete conversion of the substrate with unchanged regio-selectivity (run 5). The catalyst was effectively recycled for six times under the conditions of run 5 giving similar results; it is important to point out that even if the rhodium loading is reduced, both yields and selectivities remain the same in all catalytic cycles. The remarkable activity shown by the catalyst system with 3% Rh loading suggested a further reduction of the relative amount of rhodium supported by the polymeric support to 1% but the results in the hydroformylation of styrene were unsatisfactory both at 60 °C (run 6) and 80 °C (run 7).

It is worth noting that in this hydroformylation process the regio-selectivity appears to be different as compared with that obtained under homogeneous catalysis conditions, i.e. by using $Rh(CO)_2(acac)$ as catalytic precursors (run 8). Actually, using rhodium dicarbonyl acetylacetonate in a 10,000:1 substrate/catalyst molar ratio at 80 °C for 24 h a 92% conversion was obtained and the percentage of 2-phenylpropanal was 98%. Using the catalytic system OPTA-Rh, the regio-selectivity is quite different: the amount of 3-phenylpropanal seems to depend on the conversion of the styrene. Indeed, at low conversion, the regio-selectivity is practically complete towards the more branched oxo-isomer (2-phenylpropanal), whereas at high conversion of the substrate the regio-selectivity ranged between 85:15 and 75:25. We cannot easily explain this behaviour. Concerning run 1, a possible rationale could be found in the greater stability of the isomeric alkylrhodium intermediate, which is directly transformed into the acyl species leading to the isomeric aldehyde [1]. As far as runs 6 and 7 are concerned, it is possible to assume that traces of non-co-ordinated rhodium carbonyls are released in the reaction mixture and, thus act as the only catalyst of the hydroformylation. Support for this hypothesis comes from the fact that the second experiment carried out using the same catalyst batch did not give any oxo-products.

Having found the best experimental conditions for the hydroformylation of styrene with the OPTA-Rh catalyst system—3% OPTA-Rh, 80 °C, $CO/H_2$ = 1:1, 80 bars and reaction time 24 h, we applied the same conditions to the hydroformylation of other substrates. The results relative to several alkyl-substituted alkenes are reported in Table 2.

Hydroformylation of 1-octene (run 1) showed complete conversion and selectivity to the aldehydes, although with unsatisfactory regio-selectivity because the *n*- and *iso*-isomers were obtained in comparable amounts. Hydroformylation of *trans*-2-octene (run 2) and *trans*-3-octene (run 3) produced, in each case, a mixture of aldehydes due to competing isomerisation of the starting alkene. In the case of *trans*-3-octene (run 3), reactivity of all isomeric alkenes

Table 3
Hydroformylation reactions of some oxygen-functionalised alkenes with OPTA-Rh catalyst

| Run | Substrate | Conversion (%) | Starting product (%) | Yield (%) | Branched aldehyde (%) | Linear aldehyde (%) |
|---|---|---|---|---|---|---|
| 1 | 1,2-Epoxy-9-decene | 100 | 0 | 94[a] | 63 | 37 |
| 2 | 5-Hexen-1-ol | 33 | 67 | 33 | 37 | 63 |
| 3 | Vinyl acetate | 46 | 54 | 46 | 76 | 24 |

Reaction conditions: substrate: 0.048 mol, 3% OPTA-Rh catalyst: 38.5 mg, Rh/substrate molar ratio: 1:11,000, solvent toluene, temperature: 80 °C, pressure: 80 atm ($CO/H_2 = 1$), reaction time: 24 h.

[a] 6% of a mixture of isomeric unsaturated compounds.

formed in the hydroformylation mixture (Table 2, footnote c) was found to be unsatisfactory; indeed, the yield in aldehydes is only 20%, the rest being a mixture of the starting olefin (40%) and its isomers (40%). Hydroformylation of 2-methyl-5-hexene (run 4) was completely regio-selective leading only to the linear aldehyde, 3-methylheptanal, although conversion after 24 h was low. Complete conversion to cyclohexanecarbaldehyde as the sole product was obtained in the hydroformylation of cyclohexene (run 5). Notably, hydroformylation of limonene (run 6) under the chosen reaction conditions occurred only at the vinylidenic double bond, giving 3-(4-methylcyclohex-3-enyl)butanal in 60% yield. Finally, unsatisfactory results were obtained in the hydroformylation of α-methylstyrene (run 7), since, after 24 h, only 13% of the substrate was converted to 3-phenylbutanal, the latter being, however, the sole reaction product. This result can be compared with that obtained in the hydroformylation of 2-methyl-5-hexene, as the same conversion and regio-selectivity were obtained: in the hydroformylation of 1,1-disubstituted alkenes, using the described catalytic system which provides excellent chemo- and regio-selectivity although at the expense of activity. In view of the appreciable results obtained with alkyl-substituted alkenes, the new catalytic system was further tested in the hydroformylation of some functionalised alkenes, besides, this might give the opportunity to investigate the interaction of any oxygenated functional group present in the olefin with the catalyst system.

Hydroformylation of the substrates shown in Table 3 was highly chemo-selective, always giving a mixture of isomeric aldehydes; no product of hydrogenation was detected. 6% of 1,2-epoxy-9-decene (run 1) isomerised to other unsaturated products which however were not converted to aldehydes. Similar results are obtained when hydroformylation of 1,2-epoxy-9-decene is carried out using other rhodium catalyst precursors in homogeneous phase [44]. 5-Hexen-1-ol (run 2) and vinyl acetate (run 3) were not very reactive under the hydroformylation condition used. As far as the hydroformylation of vinyl acetate is concerned, the regio-selectivity towards the branched aldehyde is lower than that obtained using $Rh(CO)_2(acac)$ (in an experiment carried out under the same conditions described above, using rhodium dicarbonyl acetylacetonate as catalytic precursor with a substrate/catalyst 10,000:1 molar ratio, the yields in aldehydes were comparable, whereas the regio-selectivity toward branched aldehyde was 93%) and/or using a Rh(I) complex with phosphorus ligands [45,46].

Recycling of the catalyst system at the end of each cycle is very simple: the glass basket containing the solid OPTA-Rh is removed from the glass vial and is then placed in another vial charged with a fresh feed of substrate.

After the activation step, there is a high leach (almost 50%) of rhodium from the support during the first run. TGA shows some, although not significant, loss of rhodium in the following runs. After four runs, the active complex still contains 30% of the initial amount of Rh. Despite this leaching, the catalyst systems retains most of its initial activity for 8–9 runs, after which it can no longer be considered efficient.

In order to rule out the possibility that leached rhodium catalyses the reaction, fresh styrene was added to the solution recovered from a previous experiment and subjected to hydroformylation conditions: no aldehydes were detected, thus confirming that OPTA-Rh is the actual catalyst. The solution coming from the activation procedure, instead does catalyse the hydroformylation of styrene: after 24 h at 80 °C under 80 bar of syngas, 95% of 2-phenylpropanal and 5% of 3-phenylpropanal were obtained, which suggests that the active species is the $Rh(CO)_2(acac)$ extracted from the crude OPTA-Rh.

## 4. Conclusions

A simple catalytic system for heterogenous hydroformylation has been devised: the catalyst support is an oligomeric aromatic amide which is easily prepared from commercially available starting materials; the catalyst precursor is obtained by direct interaction of the OPTA support with a soluble rhodium carbonyl derivative without any previous functionalisation and modification of the organic matrix.

The catalyst system has been tested in the hydroformylation of a range of olefins. Various hydroformylation experiments of styrene allowed us to find the optimal reaction conditions. The system is extremely active and high conversions are achieved with a substrate/Rh ratio up to 11,000. It also provides complete chemo-selectivity to the oxo-products, with acceptable regio-selectivity. A “special” reactor has been designed to simplify the recycling of the catalyst which could be re-used for several runs without appreciable loss of activity.

We have reported the first application of the OPTA-Rh system to hydroformylation: studies are currently being carried in our laboratories to further and better characterise this new organometallic species. Our goal is to exploit the potential of this catalytic system in the synthesis of biological relevant compounds.

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