

1-Heptene hydroformylation over phosphinated silica-anchored rhodium thiolate complexes

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Abstract

The rhodium (I) pentafluorophenylthiolate complexes $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ and $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{CO})_2]_2$ were anchored on phosphinated silica. These catalysts were tested in the hydroformylation reaction of 1-heptene in toluene at 343–393 K using a gas feed ratio of $\text{CO}:\text{H}_2 = 1$ mole. The conversion of 1-heptene versus the reaction time followed S-shaped curves in which the induction period depended on the catalyst precursor and number of cycles in the reaction. Selectivity towards linear aldehyde was high, although the extent of isomerisation to internal olefins was found to be important. The addition of free PPh_3 to the reaction medium markedly increased the yield to linear aldehyde but the rate of the reaction appeared to be retarded. The results are compared with those obtained on using these complexes in homogeneous phase under similar conditions. The effects of temperature, pressure and the phosphine/Rh mole ratio on the reaction rate and selectivity are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hydroformylation of olefins catalysed by Rh complexes still remains of great interest not only from a mechanistic point of view but also due to the requirement of suitable reaction conditions, which determine the yields of the appropriate aldehyde [1–6]. The original process was conducted exclusively in homogeneous media, although alternative ways are being developed to avoid the difficulties inherent to the need to separate the catalyst from the reaction products. Modulation of the properties of the catalyst by varying the nature of the ligands is possible

but catalyst-product separation and catalyst recycling have become an aspect of maximum interest as regards economical and environmental demands and requirements.

Several approaches or alternatives have been developed in order to solve the problem: (1) performing the reaction in a biphasic medium — typically a water/organic solvent mixture — by using water-soluble complexes with ligands such as sulfonated phosphines, or taking advantage of the amphiphilic properties of some ligands [7–15]; (2) another approach is based on the limited solubility of fluorinated compounds in non-fluorinated ones. The catalytic reaction can be performed under mild conditions in a fluorous biphasic system (FBS), consisting of a fluorous phase containing the catalyst and an organic phase containing the reagents. At high temperature, both phases are mis-

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cible and can be separated by lowering the temperature [16,17]; (3) immobilising the complexes in a matrix (polymer, inorganic oxide), attempting to preserve the structure of the precursor in order to maintain the selectivity of the homogeneous analogue, or by the precipitation of metals that can readily be modified in situ by tertiary phosphines, which significantly enhance selectivity towards linear aldehydes [18–21]; (4) using sulfonated phosphine complexes anchored on porous carriers, such as silica, alumina and porous glass [22–25].

Considerable attention has been devoted to the synthesis and characterisation of thiolate-containing rhodium complexes due to the relative ease with which they are able to stabilise monomers or di- and poly-nuclear complexes and due to their intrinsic property of producing unsaturated metal sites via intramolecular M–SR interactions [26,27]. The use of the dinuclear Rh thiolate complexes $[\text{Rh}(\mu\text{-SR})(\text{COD})]_2$, $[\text{Rh}(\mu\text{-SR})(\text{CO})_2]_2$ and their related phosphine derivatives as catalysts in the hydroformylation reaction of olefins has also been explored. Correlation of their activity and selectivity versus the reaction conditions and nature of SR and phosphine has also been discussed [28–34].

However, there are few references to immobilised thiolate complexes studied as catalysts in this reaction. In three cases, the complexes were anchored by a condensation reaction of the silica hydroxyls and (alkoxy)₃ silyl groups from the thiolate or phosphine ligands [35–37]. Another two are based on a polymer matrix: either a phosphinated cross-linked polystyrene [38] or a cationic exchange resin [39]. Within this context, this work reports the synthesis and catalytic performance in 1-heptene hydroformylation of Rh-containing perfluorothiolate ligands attached chemically to phosphinated silica. Their characterisation and catalytic behaviour are compared to those of similar species employed under homogeneous conditions [34].

2. Experimental

All manipulations were carried out under a dry oxygen free nitrogen atmosphere using standard Schlenk techniques. The rhodium content on the silica-supported catalysts was measured by atomic ab-

sorption spectroscopy in a Perkin-Elmer 3030 Atomic Absorption Spectrophotometer.

2.1. Precursors

$[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ [40] and $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{CO})_2]_2$ [41] were prepared according to published methods. Silica Grace 951 ($S_{\text{BET}} = 627 \text{ m}^2 \text{ g}^{-1}$) was purchased from Grace Davison, US.

3-Triethoxysilylethyldiphenylphosphine was prepared by a procedure described in [42]. The phosphinated silica was prepared from silica (5 g) previously degassed at 473 K and 3-triethoxysilylethyldiphenylphosphine (2 ml) in toluene under reflux for 24 h, filtered out, washed with toluene and dried in vacuo [43]. The phosphorus content was 2.7 wt.%. All other reagents were commercial samples and were used as purchased.

2.2. Preparation of catalysts

Catalysts were prepared according to the following method: a solution of the rhodium thiolate complexes $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ or $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{CO})_2]_2$ in toluene was added to the phosphinated SiO_2 , previously degassed under vacuum at 323 K for 12 h. The mixture was refluxed for 24 h, after which it was cooled to room temperature and filtered off. After extraction with toluene in a Soxhlet for 3 h, it was dried under vacuum for one day at room temperature and kept under nitrogen.

Hereafter, the catalysts used in the present work will be referred to as: **1** — prepared following the above procedure using 0.2925 g of $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ and 0.7274 g of phosphinated silica (Rh content: 3 wt.%, P/Rh mole ratio: 3); **2** — from 0.1670 g of $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{CO})_2]_2$ and 0.500 g of phosphinated silica (Rh content: 3 wt.%, P/Rh mole ratio: 3); **3** — using 0.2200 g of $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ complex and 1.681 g of phosphinated silica (Rh content: 2 wt.%, P/Rh mole ratio: 4).

2.3. Characterisation

2.3.1. Specific surface area determination

N_2 adsorption–desorption isotherms of supports and catalysts were recorded at the temperature of liquid N_2 with a Micromeritics ASAP 2000 apparatus. Samples were previously degassed at 413 K for 6 h.

2.3.2. X-ray photoelectron spectroscopy (XPS)

Photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer fitted with a Mg K α ($h\nu = 1253.6$ eV, 1 eV = 1.6302×10^{-19} J) 120 watt X-ray source and a hemispherical electron analyser. A DEC PDP 11/53 computer was used for collecting and processing the spectra. The powdered samples were pressed into small stainless steel cylinders and then mounted on a sample rod, placed in a pretreatment chamber and degassed at 298 K and 10^{-5} Torr for 5 h prior to being transferred to the analysis chamber. The residual pressure during data acquisition was maintained below 3×10^{-9} Torr (1 Torr = 133.33 N m $^{-2}$). The 20 eV energy regions of the photoelectrons of interest were scanned a number of times in order to obtain acceptable signal-to-noise ratios. Intensities were estimated by calculating the integral of each peak, after smoothing, subtraction of the S-shaped background, and fitting the experimental curve to a combination of Lorentzian and Gaussian lines of variable proportions. Accurate binding energies (± 0.2 eV) could be determined by referencing to the C 1s peak at 284.9 eV.

2.3.3. Infrared spectroscopy

Catalytic precursors were characterised by infrared spectroscopy over the 4000–400 cm $^{-1}$ range as self-supported pellets. The wafers were prepared by pressing about 10 mg of sample between two mica disks for 5 min under 5 tonnes cm $^{-2}$. The equipment used was a Nicolet ZDX Fourier transform IR spectrophotometer working at a resolution of 4 cm $^{-1}$. An all-glass cell equipped with greaseless stopcocks and KBr windows was used for the thermal and gas treatments.

2.4. Catalytic activity

Catalytic activity measurements were carried out in a 300 cm 3 stainless steel autoclave (Magnedrive Autoclave Engineers). The appropriate amount of catalyst to achieve the final Rh concentration used previously under homogeneous conditions (2×10^{-3} M) was introduced in the reactor and after pumping out, 1-heptene (2.5 ml) in toluene (50 ml) were added by suction. Carbon monoxide was then introduced (5 bar) and the mixture was warmed to the final reaction temperature. Subsequently, the CO pressure was raised to 15 bar and H $_2$ was added up to 30 bar. Dur-

ing the experiment, an equimolar mixture of CO:H $_2$ was fed to the reactor keeping the total pressure constant. The reaction mixture was stirred magnetically at 750 rpm. Analysis of the products in the liquid samples, removed periodically from the reactor, was accomplished using gas–liquid chromatography, with a 20 m column of 16% Carbowax 20M on a Chromosorb WAW-DMCS 80/100 support, in the case of aldehydes, and 20% β , β' -oxypropionitrile on Chromosorb P 80/100 for the isomerised olefins. Konik KNK300-HRGC and Shimadzu GC-RIA chromatographs were used. After each experiment, the reaction mixture was filtered out using a cannula system under nitrogen and the solid catalyst was washed with toluene. The reactor was then closed, maintaining a nitrogen atmosphere, dried under vacuum and used for hydroformylation in a new cycle using the same procedure.

3. Results and discussion

3.1. Catalytic activity

Dimeric thiolate rhodium complexes have been widely studied as hydroformylation catalysts [28–34]. In a previous work [34], we reported a detailed study of 1-heptene hydroformylation with [Rh(μ -SC $_6$ F $_5$)(COD)] $_2$ and [Rh(μ -SC $_6$ F $_5$)(CO)] $_2$ as homogeneous catalysts in toluene and the effect of the addition of PPh $_3$ on activity and selectivity. The reaction of these complexes with varying amounts of PPh $_3$ was also discussed.

Here, we undertook the study of the performance of these complexes anchored on phosphinated silica in this reaction and under the same conditions used in the homogeneous process to make accurate comparisons. Fig. 1 shows the kinetic curves for the hydroformylation of 1-heptene at 343 K and a total pressure of 30 bar, using catalysts **1** and **2**, which differ only in the precursor used for the preparation, for the first three cycles. As can be observed, in both cases the kinetic curves are S-shaped, and the induction period increases with the number of the cycle. Although the reaction rate decreases progressively with successive cycles, catalytic activity was still observed during the sixth cycle for both catalysts. Catalyst **2** is more active although the induction periods are longer than for

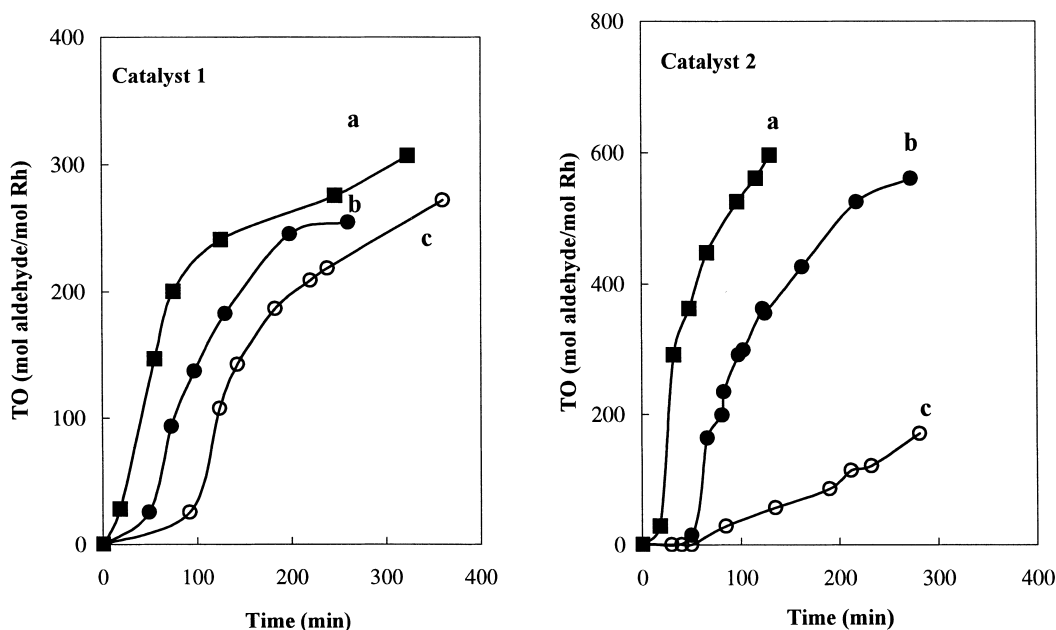


Fig. 1. Kinetic curves for the hydroformylation of 1-heptene by catalyst 1: $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ supported on phosphinated silica and catalyst 2: $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{CO})_2]_2$ on phosphinated silica: (a) first cycle; (b) second cycle; (c) third cycle (2 PPh_3/Rh added to catalyst 2). For reaction conditions see Table 1.

catalyst 1. The addition of 2 mol of external PPh_3 to catalyst 2 in the third cycle (Fig. 1c, catalyst 2) elicits a decrease in the reaction rate and an increase in the selectivity towards linear aldehyde. Selected data of the catalytic performance are depicted in Table 1.

The reaction rate, conversion and selectivity to *n*-octanal depend on the rhodium thiolate complex used as precursor, both active even without the addition of external PPh_3 . The highest hydroformylation rate ($\text{TOF} = 9.09 \text{ min}^{-1}$) was achieved with catalyst 2 in the first cycle, which is also more selective than catalyst 1 to linear aldehyde, and the yield of isomerisation products (2- and 3-heptene) is lower. Changes in activity and selectivity were observed, depending on the cycle number. The reaction becomes slower at higher cycle numbers for both catalysts and more selective to *n*-octanal. As expected, the addition of external PPh_3 , slows down the reaction, but at the same time makes it more selective to *n*-octanal (Figs. 2 and 3). During the reaction, temperature was kept constant at 343 K and the total pressure was 30 bar.

A comparison of these results and those of the homogeneous systems at total conversion of 1-heptene

was made. In the first cycle, catalyst 1 shows a ratio of $A_1/\Sigma A_i = 60$ and 59, 49% in the second and third cycle, respectively (A_1 represents terminal aldehyde and ΣA_i represents all aldehydes). This ratio increases up to 78% during the fourth cycle after the addition of two moles of PPh_3/Rh while the $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ complex in homogeneous conditions gave a ratio of $A_1/\Sigma A_i = 40\%$ without PPh_3 and 53 and 75% when one and two moles of PPh_3/Rh were added. Catalyst 2 shows a ratio $A_1/\Sigma A_i = 63, 71$ in the first and second cycles, respectively, and 77% in the third one after the addition of 2 mol of PPh_3 while under homogeneous conditions $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{CO})_2]_2$ gave a ratio of $A_1/\Sigma A_i = 44, 50$ and 52% with $\text{PPh}_3/\text{Rh} = 0, 1$ and 2, respectively. Obviously, heterogeneous processes are slower than their homogeneous analogues, but they are more selective to linear aldehyde. These results allow the proposal of similar active species under both conditions. The selectivities are comparable and rate, as expected, is much slower under heterogeneous conditions but these species do show activity after seven consecutive cycles.

Table 1
Hydroformylation of 1-heptene^a

Catalyst	Cycle	<i>T</i> (K)	<i>P</i> (bar)	P/Rh ^b	Time (min)	TOF (min ⁻¹) ^c	TO ^d	Conv. (%) ^e	<i>A</i> ₁ /Σ <i>A</i> _{<i>i</i>} (%) ^f	Isom. (%) ^g
1	1	343	30	0	55	2.66	146	99	53	48
1	2	343	30	0	97	1.41	137	99	59	48
1	3	343	30	0	183	1.02	187	97	62	43
1	4	343	30	2	1372	0.25	342	99	78	1
2	1	343	30	0	32	9.09	291	99	63	48
2	2	343	30	0	98	2.97	291	100	71	59
2	3	343	30	2	281	0.61	170	23	77	1
2	4	393	30	2	45	5.52	248	63	74	41
2	5	368	30	2	1285	0.52	674	100	76	4
2	6	368	38	2	2644	0.26	681	100	75	3
3	1	393	38	2	44	7.93	277	100	71	36
3	2	393	38	0	58	3.46	97	100	44	90
3	3	393	38	2	61	6.40	339	100	73	25
3	4	393	38	2	30	9.39	282	93	74	26
3	5	393	30	2	80	3.14	251	83	73	28
3	6	393	38	2	55	3.36	185	94	73	44
3	7	393	38	2	160	1.62	260	97	74	32

^a Reaction conditions: CO:H₂ = 1; 2.5 ml of 1-heptene, 50 ml of toluene. Catalyst **1**: [Rh(μ-SC₆F₅)(COD)]₂ on phosphinated silica (0.1840 g); catalyst **2**: [Rh(μ-SC₆F₅)(CO)₂]₂ on phosphinated silica (0.0902 g); catalyst **3**: [Rh(μ-SC₆F₅)(COD)]₂ on phosphinated silica (0.1850 g).

^b PPh₃/Rh ratio.

^c Maximum turnover frequency, defined as moles of aldehyde formed per mol of rhodium per minute.

^d Turnover (moles of aldehyde formed per mol of rhodium) corresponding to the reaction time.

^e Conversion of 1-heptene corresponding to the reaction time.

^f *n*-Octanal selectivity, total yield of moles of *n*-octanal per total moles of aldehydes.

^g Yield of isomerization by-products (2- and 3-heptene) corresponding to the reaction time.

With the aim of optimising the experimental conditions, in order to increase the reaction rate, and maintaining the selectivity levels, the influence of temperature and total pressure was studied. Fig. 4 shows the 1-heptene and *n*-octanal concentrations in percentage at 343 (a), and 393 K (b) for the third and fourth cycles, respectively, for catalyst **2**. Increasing temperature rendered the process faster but, by contrast, selectivity decreased although the global effect was the result of two opposing aspects: increasing cycle number (which increases selectivity and decreases rate) and increasing temperature (which increases rate and decreases selectivity).

The effect of the total reaction pressure is depicted in Fig. 5, in which the *n*-octanal concentration and 1-heptene conversion are plotted versus the reaction time with catalyst **3** at 393 K. As discussed above, the decreasing rate in consecutive cycles can be observed (fourth cycle, 38 bar (a) and sixth cycle 38 bar

(c)), while the *A*₁/Σ*A*_{*i*} ratio remains constant, although heptene isomerization increases.

The effect of pressure can mainly be seen on comparing Fig. 5b and c, the reaction being faster in the sixth (c) cycle at 38 bar than in the fifth cycle (b) at 30 bar. Catalyst **3** is remarkably more stable than catalyst **2**, which is exhausted in the sixth cycle.

4. Characterisation

4.1. Specific surface area and pore volume

The *S*_{BET} decreases from 627 to 409 m² g⁻¹ when the silica is phosphinated. Anchoring the complexes produces a further decrease in the surface area to values of 321, 295, 344 m² g⁻¹ in catalysts **1**, **2** and **3**, respectively. The hysteresis loops of the N₂ adsorption–desorption isotherms of silica, phosphinated silica and Rh complexes anchored to the latter

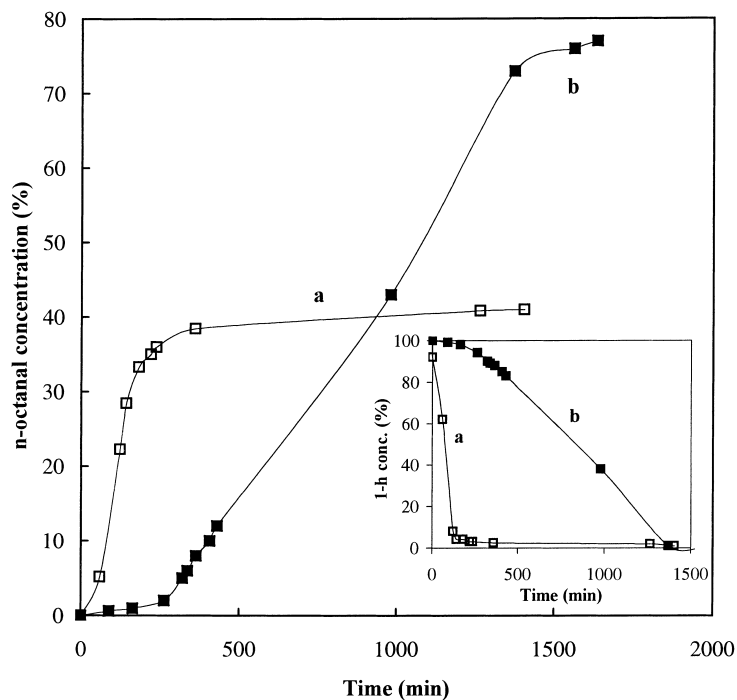


Fig. 2. Effect of PPh_3/Rh mole ratio on the hydroformylation reaction of 1-heptene (1h) on catalyst **1**: $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ supported on phosphinated silica: (a) $\text{PPh}_3/\text{Rh} = 0$, third cycle; (b) $\text{PPh}_3/\text{Rh} = 2$, fourth cycle. For reaction conditions see Table 1.

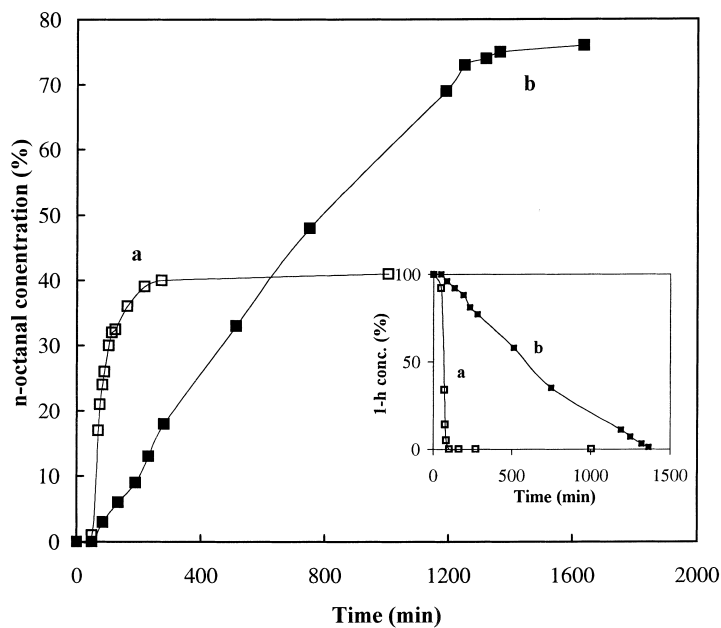


Fig. 3. Effect of PPh_3/Rh mole ratio on the hydroformylation reaction of 1-heptene on catalyst **2**: $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{CO})_2]_2$ supported on phosphinated silica (a) $\text{PPh}_3/\text{Rh} = 0$, second cycle; (b) $\text{PPh}_3/\text{Rh} = 2$, third cycle. For reaction conditions see Table 1.

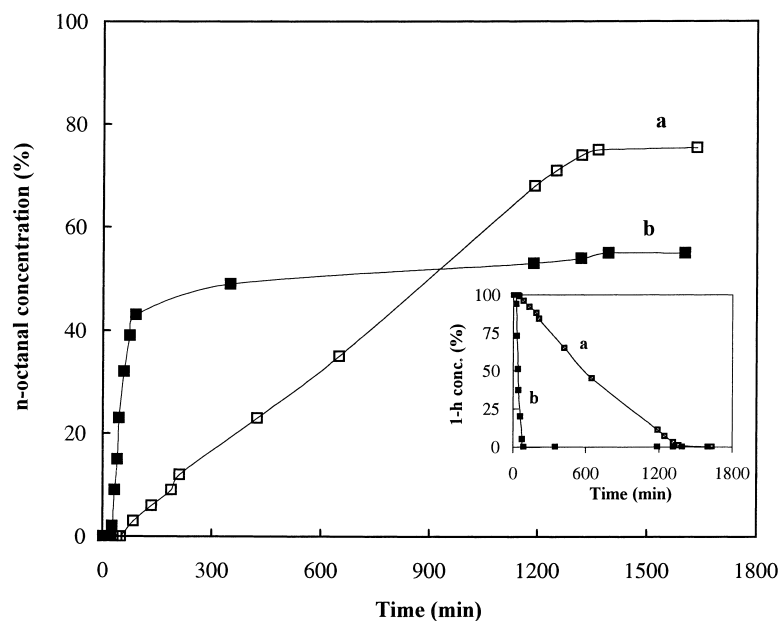


Fig. 4. Effect of temperature on hydroformylation reaction of 1-heptene on catalyst 2: $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{CO})_2]_2$ supported on phosphinated silica. Mole ratio $\text{PPh}_3/\text{Rh} = 2$: (a) $T = 343$ K, fourth cycle; (b) catalyst 3, $T = 393$ K, fourth cycle. See Table 1 for remaining experimental conditions.

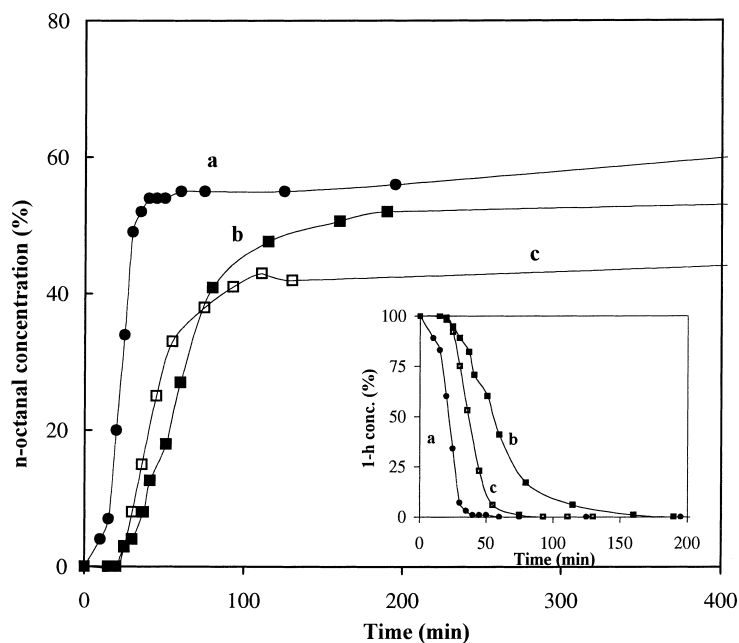


Fig. 5. Effect of total pressure on hydroformylation reaction of 1-heptene on $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ supported on phosphinated silica. Catalyst 3: $T = 393$ K. Mole ratio $\text{PPh}_3/\text{Rh} = 2$: (a) $P_T = 38$ bar, fourth cycle; (b) $P_T = 30$ bar, fifth cycle; (c) $P_T = 38$ bar, sixth cycle. See Table 1 for remaining experimental conditions.

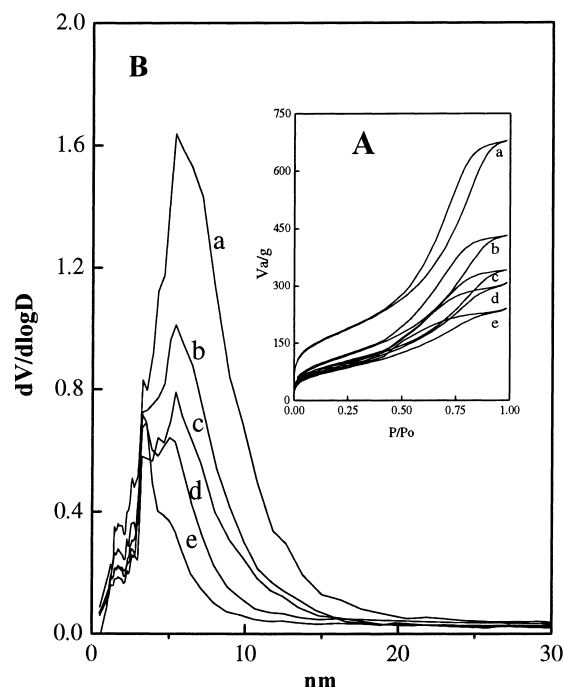


Fig. 6. (A) N₂ adsorption-desorption isotherms of (a) silica; (b) phosphinated silica; (c) catalyst 2; (d) catalyst 1; (e) catalyst 3. (B) Pore size distribution curves of (a) silica; (b) phosphinated silica; (c) catalyst 2; (d) catalyst 1; (e) catalyst 3.

are of type E of the de Boer classification, as shown in Fig. 6A. Fig. 6B shows the pore size distribution calculated using the BJH method [44], which in silica is broader, with a contribution by microporosity of 11%, and a micro plus mesopore volume of 1.05 cm³ g⁻¹. This value decreases to 0.66 cm³ g⁻¹ in phosphinated silica and to 0.47, 0.37 and 0.53 cm³ g⁻¹, respectively, for the Rh-containing samples 1, 2 and 3.

4.2. Infrared spectroscopy

Catalyst 2, which is the result of anchoring [Rh(μ-SC₆F₅)(CO)₂]₂ in phosphinated silica, shows a complex spectrum, with peaks centred at 2061 (deconvoluted in peaks at 2084, 2076, 2061, 2051 and 2043 cm⁻¹) 2008, 1990 and 1977 cm⁻¹. Although the P(silica)/Rh mole ratio is 3, it seems that the most abundant species consist of dimer compounds [Rh(μ-SC₆F₅)(CO)(P)]₂ with a small contribution of

monomers [Rh(SC₆F₅)(CO)_{2-n}P_n] (n = 1, 2) [37,34] Fig. 7(b).

Catalyst 1, resulting from anchoring [Rh(μ-SC₆F₅)(COD)]₂, was susceptible to study by FTIR as a self-supporting wafer subjected to thermal and gas treatments. The experimental protocol was as follows: degassing at 298 K for 16 h, at 353 K, for 1 h and cooling to room temperature. Then, the spectrum was recorded and taken as a subtracting reference for all the ensuing experiments to remove the support background. The sample was subjected to 30 Torr of CO at 298 K. Deconvolution of spectrum (a) discloses peaks attributable to bridged (1876 cm⁻¹), and linear (2051 cm⁻¹) Rh⁰CO species, as well as “Rh⁺CO” (1982 cm⁻¹) and “gem-Rh⁺(CO)₂” (2085, 2019 cm⁻¹) [36] due to the carbonylation of the original anchored complex (Fig. 7(a)). The presence of bridged carbonyl species is probably due to the thermal pretreatment and subsequent carbonylation (Figs. 7a and 8a). Upon subsequent outgassing at

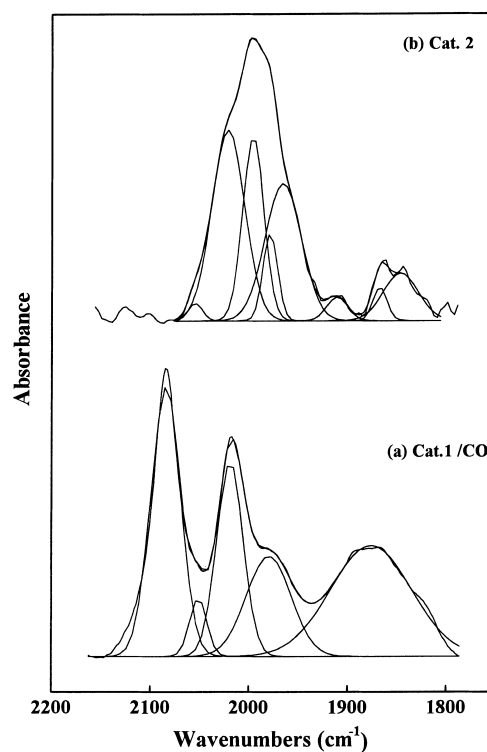


Fig. 7. Infrared spectra of catalyst 1 after CO adsorption (a) and catalyst 2; (b) in the carbonyl region.

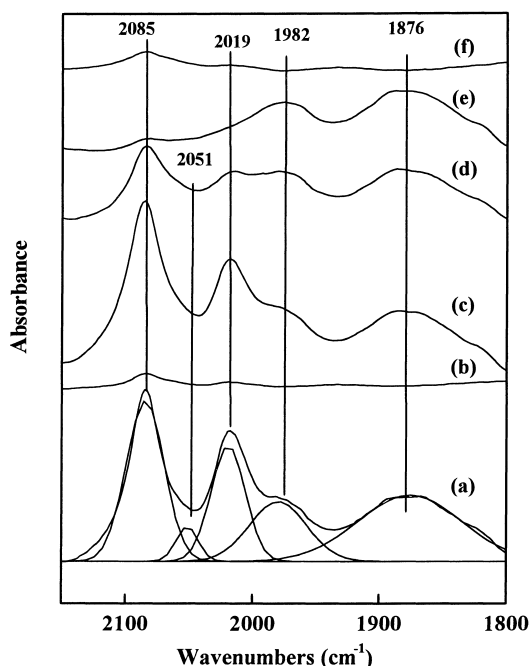


Fig. 8. Some selected spectra of catalyst **1** subjected to (a) 30 Torr CO; (b) outgassing at 353 K for 1 h; (c) 60 Torr CO; (d) outgassing at 298 K; (e) H₂ flow (40 ml/min) at 403 K for 1 h; (f) outgassing at 353 K for 1 h.

353 K, spectrum (b) shows very weak CO bands above 2000 cm⁻¹. The sample subjected to a pulse of CO (60 Torr) produces a reversible recarbonylation (c). Outgassing at 298 K decreases the intensity of the peaks (d) and the position remains constant during the treatment. The sample was then reduced under H₂ (30 Torr at 403 K), showing bands due to linear and bridged carbonyl species on reduced Rh⁰ (e). After outgassing at 353 K for 1 h, a weak peak at 2084 can be seen (f). The spectra are shown in Fig. 8.

4.3. XPS analysis

The binding energy values for the Si 2p, P 2p and Rh 3d peaks are summarised in Table 2. The BE values of the P 2p peak, with very poor resolution, do not show any significant differences and are in agreement with the results reported for other phosphine Rh complexes [45]. In phosphinated silica, the Si 2p peak has a value of 103.4 eV. In samples **1**, **2** and **3**, free and co-ordinated phosphine groups (two peaks for P 2p)

Table 2

Some selected BE (eV) values of support and catalysts

	BE (eV)		
	Si 2p	P 2p	Rh 3d
SiO ₂ -PPh ₂	103.4	132.9	
1	103.4	132.7	308.6, 313.4
2	103.3	132.8	308.9, 313.6
3	103.2	132.7	308.6, 313.1

may be present in the spectra but it was not possible to observe such effects. There are no remarkable differences in the BEs of the Rh 3d peaks assignable to Rh⁺¹ species in the supported Rh complexes, although catalyst **2**, prepared from [Rh(μ-SC₆F₅)(CO)₂]₂, had the highest value, probably due to the formation of a “Rh(CO)(SR)(phosphine)” entity, in which the back-donation Rh→CO diminishes the electronic density on Rh, increasing the BE value.

5. Conclusions

These perfluorothiolate compounds supported in phosphinated silica present strong catalytic activity in the hydroformylation reaction of 1-heptene after immobilisation on phosphinated silica. In this way, such catalysts are suitable for reuse during several reaction cycles. The addition of external PPh₃ increases the A₁/ΣA_i ratio, as in homogeneous conditions. Considering the BET and mean pore size values, no restrictions to internal diffusion are expected.

The reaction rate is lower than that observed for the homogeneous counterparts. However, activity is maintained for several cycles. No Rh-carbonyl species were detected in the liquid phase along the FTIR experiment. However, the contribution of a homogeneously catalysed reaction, cannot be completely ruled out.

An increase in temperature and pressure accelerates the reaction rate, although an increase in heptene isomerisation is observed at higher temperatures. Despite this, an increase in the total reaction pressure does not modify selectivity. The FTIR spectra show that both rhodium + 1 species (of dimeric and monomeric nature) and reduced rhodium, arising from the former under an H₂ atmosphere, could be present within the reaction conditions, although accurate assignment of

the role of the different species in the reaction is not possible. The enhanced selectivity in the hydroformylation reaction towards linear aldehyde can be correlated with the minimum electronic density in Rh and the highest density in the phosphorus, favouring the formation of the terminal versus secondary alkyl intermediate. From the results of the XPS analyses, no large differences using catalysts, **1**, **2** and **3** would be expected on varying the precursor, although the COD derivative renders the anchored catalysts more stable.

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