Hydroformylation of functionalized olefins catalyzed by SiO$_2$-tethered rhodium complexes

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Abstract

SiO$_2$-tethered rhodium complexes deriving from Rh(CO)$_2$acac and the commercially available 3-(mercapto)propyl- and 3-(1-thioureido)propyl-functionalyzed silica gel, respectively, have been used as catalysts in the hydroformylation of some functionalized olefins directed to the preparation of intermediates for valuable biologically active compounds. The oxo-reaction, catalyzed by these systems, showed a good activity, with conversion, chemo- and regioselectivity values comparable with those obtained with the well-known homogeneous rhodium catalysts. These SiO$_2$-tethered catalytic systems showed a quite good resistance to rhodium leaching which occurred in a quite small extent.
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1. Introduction

Hydroformylation of alkenes for the industrial production of aldehydes (ca. 7 millions t/year) and derivatives is one of the most important reactions involving homogeneous cobalt and rhodium complexes [1]; in particular, rhodium compounds, generally modified with ligands such as phosphines and phosphites, give rise to high reaction rates and good selectivities to the desired products [2].

The *oxo*-process however 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 and the high cost of precious catalysts – the world production of rhodium does not exceed 2–3 t/year and the cost of the metal is currently 32.15$/g, thus making rhodium derivatives very expensive. With the aim to combine the high activity and selectivity of homogeneous catalysts and the easy separation of hetero-

geneous ones, in the last years immobilized homogeneous hydroformylation catalysts have been widely studied [3–6]. The most common method to heterogenize homogeneous catalysts is to tether metal complexes to either organic polymers and inorganic matrixes modified with donor ligands [7–19]; inorganic oxides are often preferred because of their rigid structure and tolerance to various reaction conditions. Silica is one of the most commonly employed support as transition metal complexes can be easily tethered to it through a ligand present or in the complex or on the SiO$_2$ surface. Typical donor ligands used to anchor rhodium complexes to the silica support are phosphines, amines and thiols and some functionalized SiO$_2$-tethered rhodium compounds have been recently studied demonstrating the presence of a linkage between the rhodium atom and the thiol ligand and/or the rhodium atom and nitrogen [20]; these catalysts have been employed in the hydroformylation of some conventional olefins [20–22].

In this last decade we have widely studied the hydroformylation of olefins containing different functionalities directed to the preparation of valuable biologically active compounds [23–31]. Despite of their usefulness, the hydroformylation

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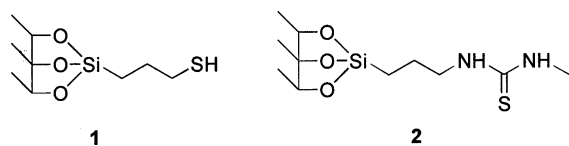*E-mail address:* spag@unive.it (S. Paganelli).

Fig. 1. Functionalyzed silica gel.

of functionalized olefins has very poorly been studied in heterogeneous phase [14]; in this view we decided to evaluate the catalytic activity of functionalized SiO_2-tethered rhodium complexes in the hydroformylation of some olefinic substrates to prepare valuable intermediates for the synthesis of different biologically active compounds. In the perspective of a possible scale-up of this reaction, we chose as supporting materials two not expensive commercially available functionalized silica gel: 3-(mercapto)propyl-functionalyzed silica gel (**1**) and 3-(1-thioureido)propyl-functionalyzed silica gel (**2**) (see Fig. 1). These commercial supports contain sulfur and nitrogen ligands, which can strongly bind the rhodium atom and, in principle, prevent metal leaching during the reaction [22].

2. Experimental

2.1. Materials and methods

The catalytic precursor $Rh(CO)_2(acac)$ (acacH = acetylacetone), 3-(mercapto)propyl-functionalyzed silica gel (**1**), 3-(1-thioureido)propyl-functionalyzed silica gel (**2**), styrene (**3**), 1,1-diphenylethene (**4**), *m*-diisopropenyl benzene (**5**), limonene (**6**), and vinyl acetate (**9**) were Aldrich products. ^{1}H-NMR spectra were recorded in solution ($CDCl_3$) on a Varian Mercury Plus spectrometer operating at 400 MHz. Gas-chromatograms were obtained on a Perkin-Elmer instrument mod. 8500. Mass spectra were recorded by means of a Hewlett Packard GC-MS mod. GCD, using the appropriate columns and conditions. ICP-MS measurements were carried out using a Perkin-Elmer-SCIEX mod. ELAN 5000 ICP-MS.

All the hydroformylation experiments were carried out in a 150 ml stainless steel autoclave and in order to avoid the catalyst deterioration due to the friction effect of stirring, we used a modified glass vial as shown in Fig. 2.
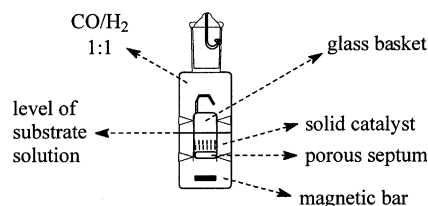

Fig. 2. Special glass vial to be introduced into the high-pressure reactor for solid–liquid biphasic hydroformylation experiments.

The new glass device consists of a vial modified to be able to hold a glass basket having a porous septum as the bottom (porous size = $100 \, \mu m$); the anchored catalyst is positioned in the basket, which is partially immersed in the substrate solution, whereas the magnetic stirring bar is on the bottom of the vial. This method allows to have an efficient stirring without any mechanical stress of the catalyst. The recycle of the catalyst, at the end of the reaction, can be easily performed by transferring the glass basket in a vial containing a fresh substrate solution.

2.2. Preparation of 3-(mercapto)propyl silica gel–Rh complex (Rh-**1**)

3-(Mercapto)propyl-functionalyzed silica gel (**1**) (150 mg) was impregnated with a CH_2Cl_2 (15 ml) solution of $Rh(CO)_2(acac)$ (52.5 mg, 0.2 mmol) under N_2 and stirred at room temperature overnight. The resulting powder was filtered off, washed several times with CH_2Cl_2 and dried under vacuum. ICP-MS determination showed an actual rhodium loading of 1.25 mmol/g silica.

2.3. Preparation of 3-(1-thioureido)propyl silica gel–Rh complex (Rh-**2**)

3-(1-Thioureido)propyl-functionalyzed silica gel (**2**) (100 mg) was impregnated with a CH_2Cl_2 (15 ml) solution of $Rh(CO)_2(acac)$ (35.0 mg, 0.14 mmol) under N_2 and stirred at room temperature overnight. The resulting powder was filtered off, washed several times with CH_2Cl_2 and dried under vacuum. ICP-MS determination showed an actual rhodium loading of 0.72 mmol/g silica.

2.4. Olefin preparation

2.4.1. Preparation of 2-tosyloxystyrene (**7a**)
The olefin was prepared by $NaBH_4$ reduction of 2-tosyloxyacetophenon to (2-tosyloxy)-1-phenylethanol, followed by dehydration of the obtained carbinol in the presence of *p*-toluensulfonic acid in benzene at reflux, as previously described [31].

2.4.2. Preparation of 2-benzyloxystyrene (**7b**)
The olefin was prepared by Wittig reaction on 2-benzyloxybenzaldehyde using a mixture of methyltriphenylphosphonium bromide and sodium amide in anhydrous diethyl ether as previously described [31].

2.4.3. Preparation of 1-[(2-hydroxy-5-methyl)phenyl]-1-phenylethene (**8**)
The olefin was prepared by *p*-cresol *ortho* alkenylation with phenyl acetylene catalyzed by alumina activated by calcination at 773 K for 5 h as previously described [30].

2.5. Hydroformylation reactions catalyzed by SiO$_2$-tethered rhodium complexes

The reactions were carried out using a stainless steel autoclave equipped with the glass device depicted in Fig. 2. The apparatus described above makes possible the use of the same catalyst for many reaction recycles.

In a typical run, the basket containing the catalytic complex was introduced, under a nitrogen purge, in the glass vessel containing the substrate in toluene (see Tables and plots). The vessel was transferred into a 150 ml stainless steel reactor, which was pressurized with syngas at the due pressure and heated at 40–80 °C, for the required time (see Tables and plots). After cooling at room temperature, the residual gases were released and the reaction products were characterized as described elsewhere [30,31,33,35,37,45].

2.6. Leaching evaluation procedure

The organic solution (10 ml) recovered from a styrene hydroformylation experiment, and freshly distilled styrene (0.96 mmol) were placed, under a nitrogen purge, in a 150 ml autoclave. The vessel was charged with 80 atm syngas at 80 °C and stirred for 24 h. The reaction mixture, analysed by GC, showed a 20% conversion into oxo-products.

3. Results and discussion

The hydroformylation of functionalized olefins represents a powerful tool for the preparation of valuable intermediates for the synthesis of important biologically active compounds. Therefore, we chose the olefins depicted in Fig. 3 as the
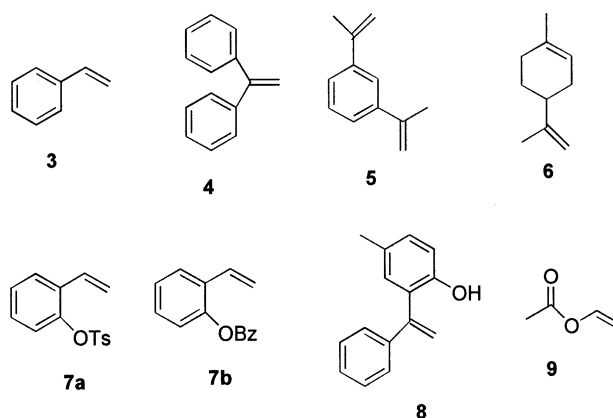
Fig. 3. Functionalyzed olefins hydroformylated in the presence of the catalytic systems Rh-**1** and Rh-**2**.

substrates to be hydroformylated with our silica anchored rhodium complexes.

3.1. Styrene hydroformylation

A first set of oxo-experiments was performed on styrene as this aromatic olefin is a widespread studied model substrate for functionalized olefins [2]. The hydroformylation reactions were carried out in the presence of the catalytic system Rh-**1** at 80 atm of syngas (CO/H$_2$ = 1) and 80 °C for 24 h with a substrate to rhodium catalyst molar ratio = 400. The recovered solid catalyst was furtherly reused in eight experiments and the data obtained are reported in Fig. 4.

The catalytic system was very active showing a complete conversion and a very high chemoselectivity: the only byproduct was ethylbenzene, not exceeding 2%. The regioselectivity towards the branched aldehyde, 2-phenylpropanal,
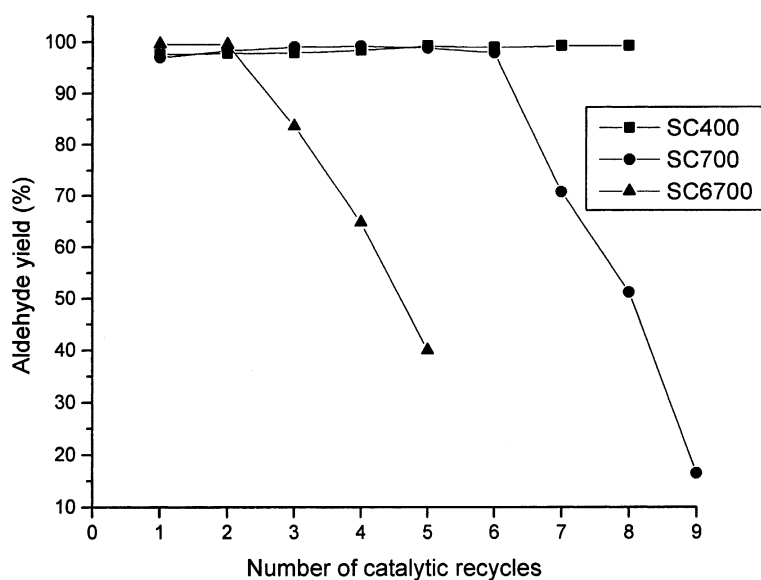
Fig. 4. Dependence of the catalytic activity of 3-(mercapto)propyl silca gel-Rh (Rh-**1**) on the number of styrene hydroformylation recycles at different substrate to catalyst molar ratio (SC400: substrate/catalyst molar ratio = 400; SC700: substrate/catalyst molar ratio = 700; SC6700: substrate/catalyst molar ratio = 6700).

even if lower than that exerted by homogeneous modified rhodium carbonyl complexes, was quite good, ranging from 75 to about 84%. The catalyst activity remained practically unchanged even after eight recycles and both chemo- and regioselectivity did not show any significative differences. The activity of this catalytic system is very high and after 1 h the substrate conversion is practically complete. Owing to this good catalytic activity we decreased the catalyst to substrate molar ratio from 1/400 to 1/700 and 1/6700, respectively (see Fig. 4). We can observe that:

(i) using a molar ratio catalyst to substrate = 1/700 the activity remains practically unchanged for six catalytic cycles but it significatively decreases up to a 16.5% conversion at the ninth catalytic recycle.

(ii) by strongly decreasing the molar ratio between the catalyst and the substrate (1/6700) the catalytic activity dramatically decreases. This is probably due to the small rhodium content in the catalytic system, which can be partially deactivated by impurities and oxygen traces that can be present in the reaction medium and/or by a small leaching degree.

(iii) in all cases a small quantity of rhodium complex is leached from the functionalized silica gel. To evaluate any leaching of the active phase during the reaction we adopted the procedure suggested by Sheldon et al. [32]. In particular the organic solution separated by the solid catalyst was added with freshly distilled styrene and hydroformylated under standard conditions. Some styrene conversion into oxo-products (20%) was detected indicating a leaching degree (see Section 2).

The hydroformylation of styrene by using the catalytic system Rh-**2** has shown the same trend previously observed with the Rh-**1** catalyst, even if the Rh-**2** activity is quite lower than that showed by Rh-**1**. In fact, after 1 h at 80 °C and 80 atm of syngas the conversion was only 46%; in all cases, the chemo- and regioselectivity were rather good. Also this catalytic system underwent a deactivation depending on the number of catalytic recycles and the substrate to catalyst molar ratio (see Fig. 5).

3.2. 1,1-Diphenylethene (**4**) hydroformylation

The hydroformylation of the commercially available 1,1-diphenylethene (**4**) is a powerful tool for the preparation of 3,3-diphenylpropanal, a valuable intermediate for the synthesis of pharmacologically active compounds as, for instance, the spasmolitic *Fenpiprane* and the choleretic *Diisopromine* [33]. Since the interest of the pharmaceutical manufacture for these key intermediates in the preparation of new drugs [34] we decided to test the performance of the tethered rhodium catalysts Rh-**1** and -**2** in the hydroformylation of 1,1-diphenylethene (**4**) (Scheme 1). The results obtained are reported in Table 1.

The activity of both these catalytic systems is rather low and it dramatically decreases in few catalytic recycles: in fact, the substrate conversion is only about 6% after four runs. Moreover, also the chemoselectivity is not very good due the hydrogenation of the olefinic double bond. It is known that the oxo-reaction of this olefin suffers the drawback of the substrate hydrogenation [33] and these catalytic systems seems not to be able to improve the chemoselectivity of the
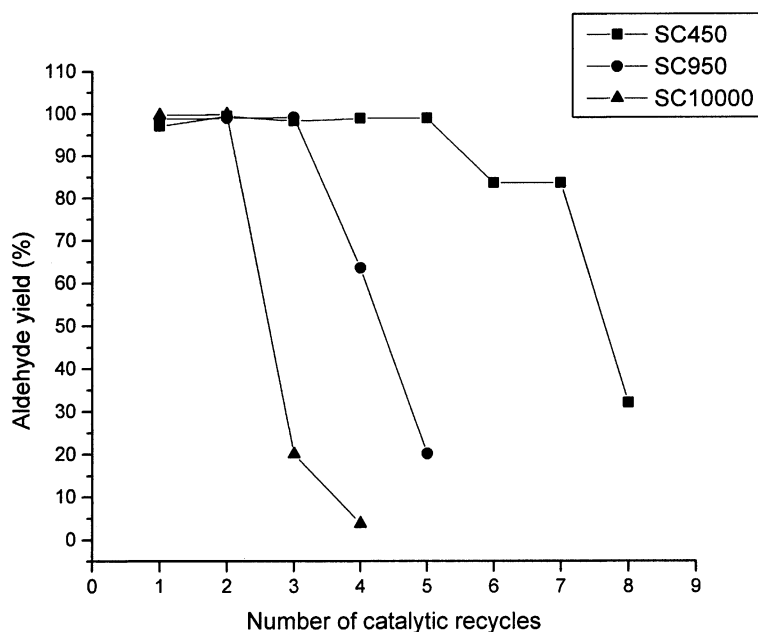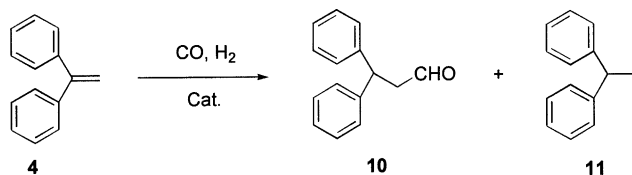

Fig. 5. Dependence of the catalytic activity of l-(3-thioureido)propyl silica gel-Rh (Rh-**2**) on the number of styrene hydroformylation recycles at different substrate to catalyst molar ratio (SC450: substrate/catalyst molar ratio = 450; SC950: substrate/catalyst molar ratio = 950; SCI0000: substrate/catalyst molar ratio = 10,000).

Scheme 1. 1,1-Diphenylethene hydroformylation.

Table 1
Hydroformylation of 1,1-diphenylethene (**4**) catalyzed by Rh-**1** and -**2**

Run	Catalyst	Conv. (%)	Aldehyde **10** yield (%)	Hydrog. prod. **11** (%)
1	Rh-**1**	49.0	39.7	9.3
2[a]	Rh-**1**	23.5	15.9	7.6
3[a]	Rh-**1**	12.8	6.0	6.8
4[a]	Rh-**1**	6.2	3.0	3.2
5	Rh-**2**	48.8	41.2	7.6
6[a]	Rh-**2**	21.5	15.3	6.2
7[a]	Rh-**2**	10.3	4.0	6.3
8[a]	Rh-**2**	5.3	2.0	3.3

Reaction conditions: substrate = 5.5 mmol; sub./cat. (molar ratio) = 250/1; toluene = 10 ml; temp. = 80 °C; t = 48 h; p(CO) = p(H$_2$) = 50 atm.
[a] Reaction carried out by using the catalyst recovered from the previous experiment.

reaction. On the contrary, the regioselectivity towards the formation of the normal aldehyde **10** is complete.

3.3. m-Diisopropenylbenzene (**5**) hydroformylation

m-Diisopropenylbenzene (**5**) is a diene having two equivalent vinylidenic double bonds. The interest for this substrate hydroformylation is depending on the selectivity towards the monoaldehyde **12** formation because this product is a valuable intermediate for the preparation of Florhydral®, a synthetic odorant commercialised by Givaudan [35,36]. We carried out some hydroformylation experiments by using both the catalytic systems Rh-**1** and Rh-**2** and the results are depicted in Table 2. These anchored catalysts

Table 2
Hydroformylation of *m*-diisopropenylbenzene (**5**) catalyzed by Rh-**1** and -**2**

Run	Catalyst	Conv. (%)	Aldehyde **12** yield (%)	Dialdehyde **13** (%)
1	Rh-**1**	95.0	35.1	59.9
2[a]	Rh-**1**	92.3	40.8	51.5
3[a]	Rh-**1**	78.2	50.3	27.9
4[a]	Rh-**1**	18.8	17.3	1.5
5	Rh-**2**	83.3	49.4	33.9
6[a]	Rh-**2**	66.9	49.5	17.4
7[a]	Rh-**2**	48.3	40.8	7.5
8[a]	Rh-**2**	15.2	14.0	1.2

Reaction conditions: substrate = 6.3 mmol; sub./cat. (molar ratio) = 800/1; toluene = 10 ml; temp. = 80 °C; t = 24 h; p(CO) = p(H$_2$) = 35 atm.
[a] Reaction carried out by using the catalyst recovered from the previous experiment.

Table 3
Hydroformylation of *m*-diisopropenylbenzene (**5**) catalyzed by Rh-**1** and -**2** at 40 °C

Run	Catalyst	Conv. (%)	Aldehyde **12** yield (%)	Dialdehyde **13** (%)
1	Rh-**1**	36.9	33.1	3.8
2[a]	Rh-**1**	20.1	19.0	1.1
3	Rh-**2**	21.8	20.6	1.2
4[a]	Rh-**2**	3.7	3.7	–

Reaction conditions: substrate = 6.3 mmol; sub./cat. (molar ratio) = 800/1; toluene =10 ml; temp. = 40 °C; t = 72 h; p(CO) = p(H$_2$) = 35 atm.
[a] Reaction carried out by using the catalyst recovered from the previous experiment.

showed a good activity for two catalytic recycles with good conversions at 80 °C for 24 h. Analogously to the reported data [35] the selectivity towards the monoaldehyde strongly depends on the substrate conversion degree; in fact, when the catalytic efficiency gets lower and the conversion does not exceed 20%, almost only monoaldehyde is obtained in the oxo-reaction. With the aim to improve this selectivity we performed some hydroformylation experiments at low temperature (40 °C) (see Table 3). As expected the conversion was rather low (up to about 37%), even after 72 h reaction: the selectivity towards the monoaldehyde, also in this case, showed to be strongly dependent on the substrate conversion and not on the reaction temperature. In fact, for a conversion of 3.7% (run 4 of Table 3) the desired aldehyde **12** is the only reaction product (Scheme 2).

3.4. Limonene (**6**) hydroformylation

Naturally occurring monoterpenes represent a useful source of inexpensive olefins and the functionalization of these olefins can provide aldehyde derivatives, important building blocks for the preparation of perfumes, flavours and pharmaceuticals. Among these olefins, in these last years, limonene attracted the interest of some researchers and it was hydroformylated in homogeneous phase using rhodium [37] and platinum catalytic precursors [38,39]. On the basis of the interesting reported results, we decided to perform some hydroformylation reactions with both the catalytic systems Rh-**1** and -**2.** The results are showed in the Table 4 (Scheme 3).

Both the catalytic systems showed a good activity for two catalytic recycles: the conversion of the substrate was very good after 6 h of reaction (75–88%) at 80 °C, affording only the *oxo*-aldehyde **14**. The activity of both catalytic systems
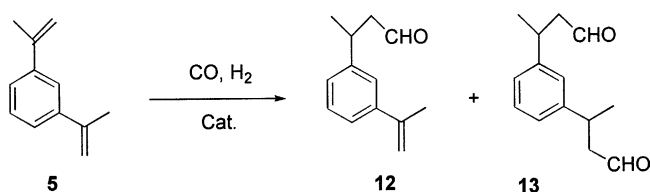

Scheme 2. *m*-Diisopropenyl benzene hydroformylation.

Table 4
Hydroformylation of limonene (**6**) catalyzed by Rh-**1** and -**2**

Run	Catalyst	Conv. (%)	Aldehyde **14** yield (%)
1	Rh-**1**	88.0	88.0
2[a]	Rh-**1**	84.3	84.3
3[a]	Rh-**1**	75.2	75.2
4[a]	Rh-**1**	42.1	42.1
5	Rh-**2**	84.7	84.7
6[a]	Rh-**2**	61.0	61.0
7[a]	Rh-**2**	44.9	44.9
8[a]	Rh-**2**	35.6	35.6

Reaction conditions: substrate = 5.0 mmol; sub./cat. (molar ratio) = 500/1; toluene = 10 ml; temp. = 80 °C; t = 6 h; p(CO) = p(H$_2$) = 40 atm.

[a] Reaction carried out by using the catalyst recovered from the previous experiment.
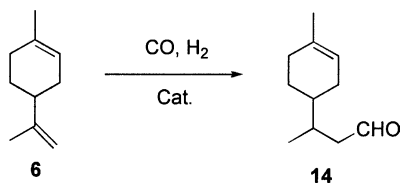
Scheme 3. Limonene hydroformylation.

decreases after three catalytic recycles, but the chemo- and the regioselectivity remain always excellent (see Table 4).

3.5. Hydroformylation of 2-tosyloxystyrene (*7a*) and 2-benzyloxystyrene (*7b*)

2-Chromanol is an interesting precursor of several therapeutically active molecules as the antispycotic Sarizotan [40], the neuroprotectant Repinotan [41] and many others [42,43]. In principle, the hydroformylation of 2-hydroxystyrene could represent a convenient route to 2-chromanol, if the linear aldehyde 3-(2-hydroxyphenyl)propanal is regioselectively produced. To avoid all the problems connected with the instability of 2-hydroxystyrene under reaction conditions, we carried out some hydroformylation experiments on the two derivatives 2-tosyloxy-and 2-benzyloxystyrene, prepared according to a literature procedure [31]. As shown in Tables 5 and 6, the activity of the anchored catalysts Rh-**1**

Table 5
Hydroformylation of 2-tosyloxystyrene (**7a**) catalyzed by Rh-**1** and -**2**

Run	Catalyst	Conv. (%)	Aldehyde yield (%)	*n*-Aldehyde **15a** (%)	Hydrog. prod. **17a** (%)
1	Rh-**1**	100	99.9	13.7	0.1
2[a]	Rh-**1**	100	99.2	14.2	0.8
3[a]	Rh-**1**	99.3	98.7	17.7	0.6
4[a]	Rh-**1**	99.1	98.1	15.3	1.0
5	Rh-**2**	99.4	98.8	15.7	1.2
6[a]	Rh-**2**	100	99.2	14.4	0.8
7[a]	Rh-**2**	99.5	98.9	14.3	0.6
8[a]	Rh-**2**	99.3	98.6	15.0	0.7

Reaction conditions: substrate = 1.09 mmol; sub./cat. (molar ratio) = 400/1; toluene = 10 ml; temp. = 80 °C; t = 24 h; p(CO) = p(H$_2$) = 40 atm.

[a] Reaction carried out by using the catalyst recovered from the previous experiment.

Table 6
Hydroformylation of 2-benzyloxystyrene (**7b**) catalyzed by Rh-**1** and -**2**

Run	Catalyst	Conv. (%)	Aldehyde yield (%)	*n*-Aldehyde **15b** (%)	Hydrog. prod. **17b** (%)
1	Rh-**1**	100	98.2	18.9	1.8
2[a]	Rh-**1**	100	98.3	18.7	1.7
3[a]	Rh-**1**	100	98.8	19.2	1.2
4[a]	Rh-**1**	100	98.7	19.8	1.3
5	Rh-**2**	99.7	97.9	20.4	1.8
6[a]	Rh-**2**	100	98.2	20.1	1.8
7[a]	Rh-**2**	100	98.5	20.2	1.5
8[a]	Rh-**2**	99.5	97.5	19.8	2.0

Reaction conditions: substrate = 1.09 mmol; sub./cat. (molar ratio) = 400/1; toluene = 10 ml; temp. = 80 °C; t = 24 h; p(CO) = p(H$_2$) = 40 atm.

[a] Reaction carried out by using the catalyst recovered from the previous experiment.

a) R = Ts
b) R = Bz
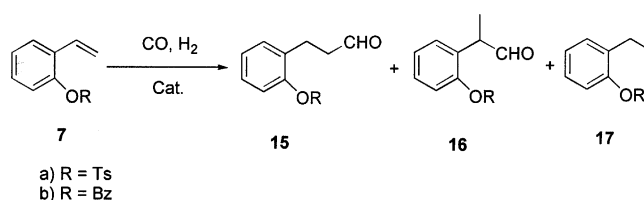
Scheme 4. 2-Tosyloxy- and 2-benzyloxystyrene hydroformylation.

and -**2** is very high remaining practically unchanged after three catalytic recycles. Also the chemoselectivity is very good and only a small amount of double bond hydrogenation product was detected in the reaction mixture. Unfortunately, both these catalytic systems did not give the desired regioselectivity, the *n*-aldehyde **15** not exceeding 21% (Scheme 4).

3.6. Hydroformylation of 1-[(2-hydroxy-5-methyl) phenyl]-1-phenylethene (*8*)

In a previous paper we regioselectively hydroformylated olefin **8** to obtain the corresponding linear aldehyde, isolated as the hemiacetal **18**, that can be easily transformed in to *Tolterodine*, an important urological drug [30]. This reaction, when performed in homogeneous phase, is affected by the undesired olefinic double bond hydrogenation; only in the aqueous biphasic system the chemoselectivity of the reaction was complete [30]. In the view of these results we decided to carry out the oxo-process in a solid–liquid biphasic system, by using the SiO$_2$-tethered rhodium complexes Rh-**1** and -**2**. The results are reported in Table 7.

The activity of both catalytic systems is not very satisfactory and they undergo a fast deactivation with a halving of the conversion already in the first catalytic recycle. On the contrary, the chemoselectivity was excellent, being the hemiacetal **18** the only reaction product. Encouraged by this outstanding result, we prolonged the reaction time up to 96 h under the same reaction conditions and in the presence of the catalytic system Rh-**1**: the conversion reached 95% affording only the desired hemiacetal **18** (Scheme 5).

Table 7
Hydroformylation of l-[(2-hydroxy-5-methyl)phenyl]-l-phenylethene (**8**) catalyzed by Rh-**1** and -**2**

Run	Catalyst	Conv. (%)	Hemiacetal **18** (%)
1	Rh-**1**	42.5	42.5
2[a]	Rh-**1**	23.1	23.1
3[a]	Rh-**1**	14.2	14.2
4[a]	Rh-**1**	8.1	8.1
5	Rh-**2**	41.9	41.9
6[a]	Rh-**2**	20.8	20.8
7[a]	Rh-**2**	11.7	11.7
8[a]	Rh-**2**	5.2	5.2

Reaction conditions: substrate = 2.4 mmol; sub./cat. (molar ratio) = 500/1; toluene = 10 ml; temp. = 100 °C; t = 24 h; p(CO) = p(H$_2$) = 40 atm.

[a] Reaction carried out by using the catalyst recovered from the previous experiment.
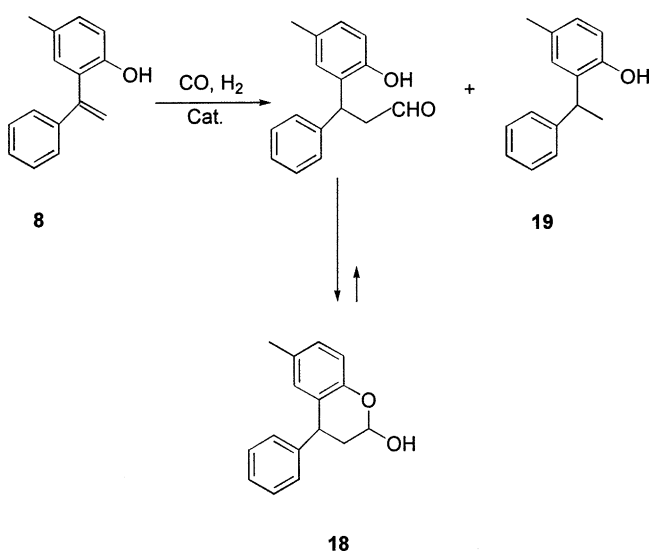
Scheme 5. l-[(2-hydroxy-5-methyl)phenyl]-l-Phenylethene hydroformylation.

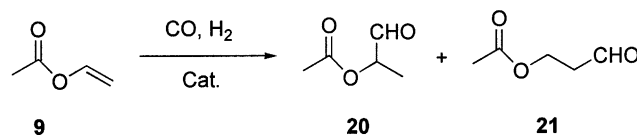## 3.7. Hydroformylation of vinylacetate (**9**)

The hydroformylation of vinylacetate (**9**) catalyzed by homogeneous rhodium based catalytic precursors, affords the branched oxo-aldehyde 2-acetoxypropanal (**20**) in good yield; this aldehyde is an important intermediate for a large number of biologically active molecules such as steroids, antibiotics and peptides [44]. Analogously to the well-known homogeneous catalysts, also Rh-**1** and -**2** catalytic systems showed a good activity towards the hydroformylation of substrate **9** giving high aldehyde yields under mild reaction conditions and in relatively short reaction times (see Table 8). The regioselectivity, even if lower than that observed in homogeneous phase [45], is quite good, the *iso*-aldehyde **20** being, in any case, not minor than 75%. The deactivation of both catalysts Rh-**1** and -**2**, in this case, is quite slow and after three catalytic recycles the activity remains high, the substrate conversion being about 80% (Scheme 6).

Table 8
Hydroformylation of vinylacetate (**9**) catalyzed by Rh-**1** and -**2**

Run	Catalyst	Conv. (%)	Aldehyde yield (%)	*iso*-Aldehyde **20** (%)
1	Rh-**1**	93.2	93.2	76.3
2[a]	Rh-**1**	88.4	88.4	77.2
3[a]	Rh-**1**	80.3	80.3	77.9
4[a]	Rh-**1**	78.5	78.5	75.1
5	Rh-**2**	90.4	90.4	80.7
6[a]	Rh-**2**	91.0	91.0	78.4
7[a]	Rh-**2**	91.2	91.2	80.3
8[a]	Rh-**2**	71.6	71.6	79.0

Reaction conditions: substrate = 5.0 mmol; sub./cat. (molar ratio) = 500/1; toluene = 10 ml; temp. = 80 °C; t = 12 h; p(CO) = p(H$_2$) = 40 atm.

[a] Reaction carried out by using the catalyst recovered from the previous experiment.

Scheme 6. Vinyl acetate hydroformylation.

3.8. Dependence of the activity of the catalytic systems Rh-**1** and -**2** on the nature of the substrates

From the results obtained in the hydroformylation experiments, it is clear that the activity of both catalytic systems Rh-**1** and -**2** is strongly dependent on the nature of the substrate. In order better to visualize this behaviour, we have reported in Figs. 6 and 7 the relationship between conversion and catalytic recycles, for all the hydroformylated substrate **4**–**9**. We can see that in some cases the catalytic activity is high and prolonged in the time; for instance, for substrates **7a** and **7b** the behaviour of the catalysts is very close to that observed in styrene hydroformylation while when more steric hindered substrates, such as olefins **4** and **8**, are subjected to
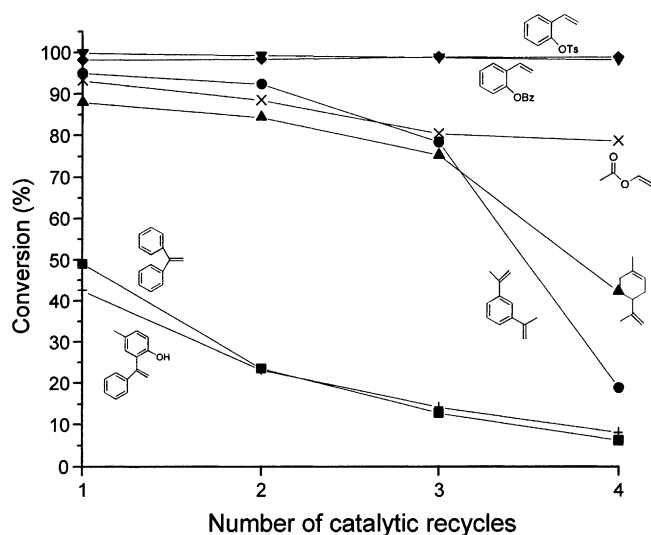

Fig. 6. Relationship between number of catalytic recycles and substrate conversion for Rh-**1** catalyzed hydroformylations carried out on substrates **4**–**9** at the reaction conditions depicted in Tables 1–8.
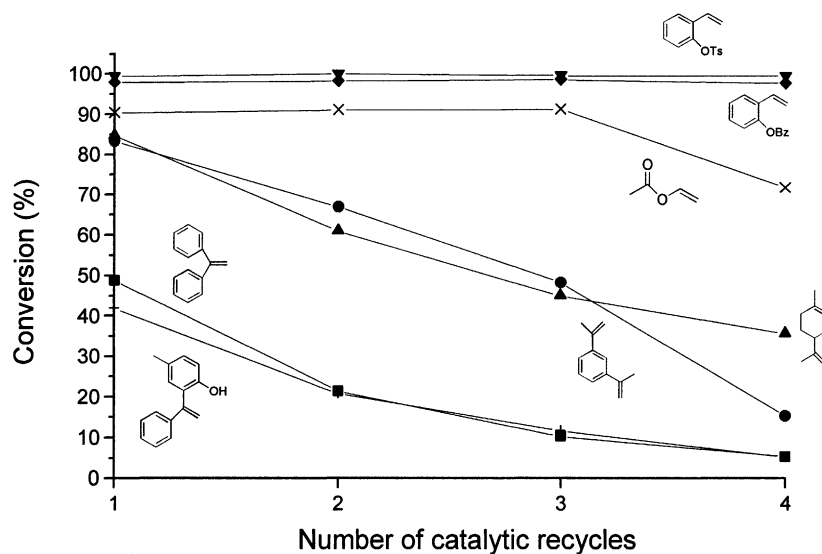
Fig. 7. Relationship between number of catalytic recycles and substrate conversion for Rh-**2** catalyzed hydroformylations carried out on substrates **4–9** at the reaction conditions depicted in Tables 1–8.

the oxo-process, the activity of both catalytic systems Rh-**1** and -**2** is low even in the first hydroformylation experiment; this is probably due to the hindered steric structure of the molecules that could make more difficult the approach to the transition metal tethered to the functionalized silica support. In general, the activity of these catalytic systems, when in the presence of substrates containing a vinylidenic double bond, is markedly lower than that displayed in the hydroformylation of vinylic olefins, as 1,1-disubstituted substrates are more sensitive to the steric hindrance.

On the whole, the reactivity of the two catalytic systems is quite similar but the Rh-**2** catalyst is a little less active than Rh-**1**, probably due to a lower coordinative power of the donor ligands present on the funtionalized silica.

4. Conclusions

It is possible to conclude that the functionalized silica gel tethered rhodium catalysts Rh-**1** and -**2** showed a good activity in the hydroformylation of various functionalyzed olefins. The reaction occurs with conversion, chemo- and regioselectivity values comparable with those of the well-known homogeneous rhodium catalysts. It is to point out that the catalytic activity is strongly dependent on the nature of the substrates. In the presence of steric hindered substrates the reaction rate is slower than that obtained in homogeneous phase, but both chemo- and regioselectivity are always good and in some cases even better than those obtained with homogeneous catalytic systems. For instance, in the case of 1-[(2-hydroxy-5-methyl)phenyl]-1-phenylethene (**8**), the substrate hydrogenation side reaction is completely absent. As the most of the heterogenized catalysts, also these catalytic systems suffer the leaching phenomenon, even if in a quite small extent.

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