



Regioselective hydroformylation of vinylarenes in aqueous media by a sol–gel entrapped rhodium catalyst

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ABSTRACT

Two methods for selective hydroformylation of vinylarenes in aqueous media are described. One method relies on the application of $[\text{Rh}(\text{cod})\text{Cl}]_2$ and a tertiary phosphane entrapped within an ionic liquid-confined silica sol–gel support. The second method utilizes the same rhodium compound, engaged within ionic-liquid-free hydrophobicized sol–gel. Both methods are best carried out at 50 °C in aqueous emulsions or microemulsions that consist of the substrate, a surfactant, a co-surfactant and >89% water. The optimal H_2/CO ratio is between 1 and 1.1. Both methods allow the reuse of the heterogenized catalyst for several runs. While the regioselectivity and the yield are hardly affected by the electronic nature of the substrates, they are significantly dependent on the reaction temperature, on the surfactant employed, and on the hydrophobicity of the support of the catalyst. Despite the use of H_2 in the reactions, no transformation of the organometallic catalyst into metallic nanoparticles could be detected.

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1. Introduction

Hydroformylation of terminal olefins is a frequently applied reaction in the chemical industry [1–4]. Usually this reaction leads to the production of either two isomeric compounds, linear (*l*) and branched (*b*) aldehydes, or the corresponding alcohols. Consequently, many efforts have been directed to make the process more selective [5–7]. In particular, methods have been studied for preferential formation of the linear regioisomers used for the production of polymers, detergents, cosmetics and other widespread products. Previously [8,9], we reported a significant increase in the selectivity towards the production of branched aldehydes from vinylarenes by using a mixture of $[\text{Rh}(\text{cod})\text{Cl}]_2$ and $\text{Na}[\text{Ph}_2\text{P}(\text{C}_6\text{H}_4-3-\text{SO}_3)]$ entrapped within an ionic liquid (IL)-confined silica sol–gel (SG) matrix. The use of the ceramic support enables recycling of the catalyst and the ability to perform one-pot multi-step reactions in conventional organic solvents [9]. With the attempt to replace the environmentally disfavored harmful organic solvents by benign and inexpensive media, major industries, e.g., the Ruhrchemie/Rhône-Pulenc plants (RRP) have already found ways to perform hydroformylations in water. These methods require the modification of some of the reaction components with hydrophilic auxiliaries. The RRP process is also usually limited to short olefins and is often not

applicable to highly water-insoluble substrates [10,11]. Among the various ways to overcome the insolubility problems associated with the hydroformylation process in water, is the use of microemulsions [12–15]. However, this method does not address the selectivity problem or manage to recover the catalyst by conventional processes. Thus, in the course of our studies on catalysis in aqueous media by recyclable catalysts, we developed a three-phase emulsion/sol–gel transport system (EST) where water-insoluble substrates can be solubilized by micelle producing surfactants and promoted by sol–gel entrapped reusable catalysts [16,17]. This system consists of up to ~90% water and has already proven to be applicable to catalytic hydrogenations [16,17], to C–C coupling reactions [18,19], double bond isomerization [20] and disproportionation of dihydroarenes [21]. By using a sulfur-bridged dirhodium catalyst we were also able to carry out hydroformylation in aqueous microemulsions, albeit in low regioselectivity [22]. In order to increase the selectivity we investigated the possibility of using the immobilized $[\text{Rh}(\text{cod})\text{Cl}]_2$ -tertiary phosphane-ionic liquid system also in the aqueous microemulsions. Although the results were positive, experiments conducted for the recycling of the catalyst revealed in some cases a gradual decrease in the conversions. Therefore, we found it imperative to seek further experimental conditions that may overcome this shortcoming and provide better reuse of the catalyst.

Consequently, two methods for selective hydroformylation of vinylarenes by an immobilized rhodium complex in aqueous microemulsion were developed.

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2. Experimental

2.1. Instruments

^1H and ^{13}C NMR spectra were recorded with either Bruker DRX-400 or Bruker Avance II-500 instrument. Infrared spectra were recorded with a Perkin-Elmer 65 FTIR spectrometer. Mass spectral measurements were performed with a Q-TOF-II spectrometer. ICP-MS analyses were obtained with a Perkin-Elmer model ELAN DRC-II instrument. Gas chromatographic analyses were carried out with a Hewlett-Packard model Agilent 4890D equipped with either a 30 m long column packed with Carbowax 20 M-poly(ethylene glycol) in fused silica (Supelco 25301-U) or with a 15 m long column packed with bonded crosslinked (5% phenyl) methyl polysiloxane [HP-5]. Transmission electron microscopy was done with a scanning transmission electron microscope (STEM) Tecnai G²F20 (FET company) operated at 200 kV and equipped with EDAX-EDS for identification of elemental compositions.

2.2. Chemicals

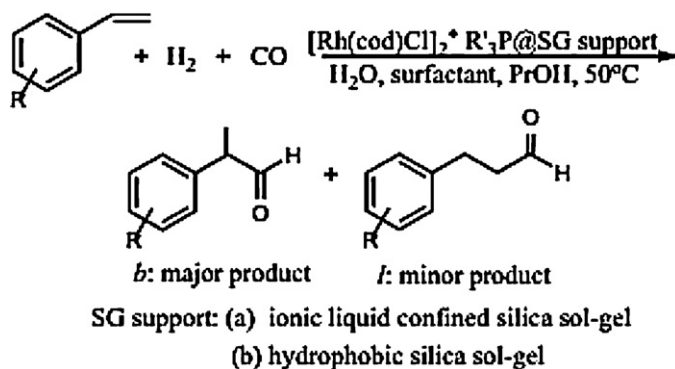
Most vinylarenes, cationic surfactants, reference and starting compounds and rhodium trichloride trihydrate were purchased from the Sigma-Aldrich Chemical Company. Tetramethoxysilane (TMOS), phenyl- and propyltrimethoxysilane were obtained from ABCR-Glest Inc. Octyltriethoxysilane (OTEOS) was purchased from Alfa Aesar. Sodium dodecyl sulfate was obtained from Ridel de Haën, Marlipal 24/70 was purchased from Sasol Co. 1-Butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride [8], Sodium (diphenylphosphanyl)benzene 3-sulfonate [23] and di- μ -chlorobis[(1,2,5,6- η)-1,5-cyclooctadiene]dirhodium [24] were prepared according to literature procedures.

2.3. Emulsification of the substrates

A mixture of the vinylic starting compounds (1 mmol, 0.5–0.8 wt.% of the desired emulsion), triply distilled water (TDW, 89.3 wt.%), a suitable surfactant (3.3 wt.%) and the co-surfactant (usually 1-propanol, 6.6 wt.%) and 5–7 mg of 2,5-di-*tert*-butyl hydroquinone was agitated at room temperature for 20 min. The mixture was then degassed by bubbling N_2 through it for 20 min and mixed with the heterogenized catalyst.

2.4. Preparation of the immobilized catalyst

(a) The entrapment of $[\text{Rh}(\text{cod})\text{Cl}]_2$ together with $\text{Na}[\text{Ph}_2\text{P}(\text{C}_6\text{H}_4-3-\text{SO}_3)]$ within silica sol-gel confined with 1-butyl-3-[(3-trimethoxysilyl)propyl]imidazolium chloride was performed as previously described [8]. In a series of experiments the sulfonated triphenylphosphane was replaced by tri-1-butylphosphane which led to practically the same yields of aldehydes (*vide infra*). (b) Entrapment of $[\text{Rh}(\text{cod})\text{Cl}]_2$ within hydrophobic silica sol-gel was carried out as follows: octyltriethoxysilane (2 ml, 6.68 mmol) (or the corresponding propyl- or phenyltrimethoxysilane) was hydrolyzed with TDW (0.5 ml) and EtOH (5.6 ml) by stirring at room temperature for 24 h. Separately a mixture of TMOS (3.6 ml, 24.2 mmol) was treated with H_2O (2.4 ml) and MeOH (2.0 ml) together with sodium (diphenylphosphanyl)benzene 3-sulfonate (45 mg, 0.124 mmol) by stirring at room temperature for 10 min. The two hydrolyzed silanes were combined and a solution of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (30 mg, 0.06 mmol) in THF (2.5 ml) was added. Stirring was continued as long as possible (48–96 h) and the resulting gel was aged for two days, dried at 100 °C and 0.1 Torr for 24 h. The ceramic material was washed and sonicated with CH_2Cl_2 (2×20 ml) to ensure the removal of any metallic compound that was not entrapped



Scheme 1.

within the sol-gel matrix, and redried at 100 °C and 0.1 Torr to give a constant weight. The organic solvent used to wash the sol-gel was evaporated and the immobilized rhodium complex was subjected to ICP-MS analysis. The exact rhodium content of the sol-gel matrix was calculated from the analyses of the washing solutions and from the recovered support after the catalytic process.

2.5. Catalytic hydroformylation

The emulsion or microemulsion of the substrate (usually 15–20 ml) was placed in a glass-lined autoclave equipped with a mechanical stirrer together with the immobilized rhodium catalyst. The autoclave was sealed and purged three times with hydrogen and then pressurized to the desired pressure of H_2 and CO. The reaction mixture was heated at the desired temperature for the required length of time. The reaction vessel was cooled to room temperature, the gases were released and the remaining mixture was filtered. The filtrate was treated with NaCl (1 g), which caused the mixture to separate into two phases. The sol-gel material, as well as the aqueous layer, were extracted with CH_2Cl_2 (2×10 ml) to ensure complete removal of the products. The combined organic solutions were dried (MgSO_4), concentrated and analyzed both by GC and ^1H NMR. The heterogenized catalyst was dried at 100 °C and 0.1 Torr for 5 h in order to be ready for use in the next run.

3. Results and discussion

Although styrene does not undergo hydroformylation in pure water at 50 °C by the $[\text{Rh}(\text{cod})\text{Cl}]_2$ -tertiary phosphane catalyst system, the reaction takes place upon addition of a suitable surfactant that solubilizes the substrate. Heterogenization of the catalyst by its entrapment within a silica sol-gel matrix confined with an ionic liquid such as 1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride, causes the reaction to form the branched 2-phenylpropanal at 50 °C, in a highly regioselective fashion. The results were in fact similar to those observed in unwanted organic solvents. For example, the hydroformylation of styrene demonstrated TON of 1666 (TOF after 16 h was 104 h^{-1}). The engagement of the catalyst within the ceramic support enables recycling it several times (*vide infra*). The process shown in Scheme 1 takes place also with other vinylarenes (see Table 1).

For practical reasons we applied in the aqueous medium the same sulfonated phosphane as in the organic solutions [8] although one can use sulfonate-free phosphanes such as tri-1-butylphosphane, that leads to the same yields and selectivities. The latter phosphane requires however, exclusion of air throughout the entire workup. We do not recommend the use of triphenylphosphane since this phosphane leads, for unknown reasons,

Table 1Hydroformylation of representative vinylarenes in the presence of an ionic liquid in aqueous microemulsions under comparable conditions.^a

Entry	Substrate	<i>b/l</i> ^{b,c}	Conversion(%) ^b	Yield of 2-propanal ^b (%) ^{b,c}	Yield of 3-propanal ^b (%) ^{b,c}	Ratio
1	Styrene		100	99	1	99.0:1
2	4-Methylstyrene		98	94	4	23.5:1
3	4-Fluorostyrene		100	96	4	24.0:1
4	4-Chlorostyrene		98	93	5	18.6:1
5	1-Vinylnaphthalene		99	94	5	18.8:1
6	2-Vinylnaphthalene		98	85	13	6.5:1

^a Reaction conditions: vinylarene (1 mmol, 0.5–0.8 wt.%), cetyltrimethylammonium bromide (CTAB, 3.3 wt.%), 1-ProH (6.6 wt.%), triply distilled water (TDW, 89.0–89.3%), heterogenized catalyst prepared from [Rh(cod)Cl]₂ (30 mg, 0.06 mmol), Na[Ph₂P-3-C₆H₄SO₃] (45 mg, 0.124 mmol), tetramethoxysilane (TMOS, 5.1 g, 33.6 mmol), 1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride (0.4 g, 1.24 mmol); H₂ (6.9 bar), CO (7.6 bar); 50 °C; 16 h; stirring rate 300 rpm.

^b The conversions and yields were determined both by GC and by ¹H NMR.

^c The data in the table are the average of at least two experiments that did not differ by more than ±3%.

to substantial metal leaching. Any system in which the leaching per catalytic run exceeded 0.059% was discarded.

In some cases the presence of IL caused a gradual decrease in rate already after 2–4 runs. The regioselectivity, however, was hardly affected. Typical results of such a case in which the rate, but not the selectivity, dropped substantially are those of the hydroformylation of 4-methylstyrene summarized in Table 2. A similar behavior was observed in the reactions of 4-fluoro-, 4-chloro- and 4-cyanostyrene.

In search for an alternative recyclable system that can be applied in water, we found that the [Rh(cod)Cl]₂-phosphane system acts as a selective catalyst also in the absence of the IL, provided the sol-gel support had been hydrophobized beforehand. Some typical examples of selective hydroformylation by [Rh(cod)Cl]₂ within IL-free octylated sol-gel are summarized in Table 3. In this system, the recycling is more efficient than in the previous one. The yields hardly change in the first five runs (see e.g., the examples given in Table 8). The experiments shown in this table and in similar ones carried out for shorter periods (e.g. 4 h) revealed that the electronic nature of the substrates has no significant influence either on the yields or on the selectivity. However, both proved to depend on the nature of the surfactant. For example, the hydroformylations of 4-methylstyrene shown in Table 4 indicate that the selectivity in the presence of cationic surfactants is higher than those observed in the presence of non-ionic or anionic additives. This observation can be rationalized by the fact that cationic surfactants are more suitable to be adhered onto the partially negatively charged silica sol-gel matrix [25–27]. Among the cationic alkylammonium bromides, the C₁₆-derivative gave the best results.

Another factor that influences the hydroformylation is the hydrophobicity of the ceramic support of the catalyst. The introduction of phenyl, octyl or propyl moieties into the ceramic support has been compared. ICP analyses indicated that the entrapment of the rhodium complex within non-hydrophobized sol-gel (i.e., prepared from TMOS alone) leaches readily into the microemulsion. A similar phenomenon was observed in rhodium and in palladium catalyzed disproportionation of vicinal dihydroarenes in aqueous microemulsions [21] and to a certain extent also in the rhodium catalyzed double bond isomerization of allylarenes under the EST

conditions [20]. The undesired leaching process could be reduced to 0.011–0.059% per catalytic cycle (or even eliminated completely) when carefully hydrophobized sol-gel matrices were employed. There are, however, differences in the rate and in the selectivity among the different hydrophobic ceramic supports studied. The results obtained with the aforementioned supports, summarized in Table 5, indicate that the catalyst within octylated sol-gel (i.e., prepared from 78 mol% of tetramethoxysilane and 22 mol% of octyltriethoxysilane) leads both to high conversions and high selectivity. The phenylated ceramic support gives likewise high yields but with lower selectivity. The catalyst within the propylated sol-gel reacts at a similar selectivity as in the phenylated support but at a lower rate.

In this respect, we wish to draw our attention to the fact that the preparation of sol-gel supports by the conventional protocols [27] is affected by a variety of factors (including the quality of the alkoxysilanes). This may cause variations in the structural features of the sol-gel that may consequently influence the catalytic hydroformylations. Therefore, a good quality of the alkoxysilanes (>95%) is essential.

The most influential factor that affects the selectivity is the reaction temperature. In a series of experiments at different temperatures between 30 and 90 °C we found dramatic changes of the *b/l* ratios. Some representative results summarized in Table 6 indicate that although at low temperatures the hydroformylation is slow, under such conditions the selectivity is the highest. We chose 50 °C as our standard temperature for high selectivity and reasonable reaction rates and yields.

As long as the ratio between the pressure of the H₂ and the CO is close to unity the aldehydes are neither contaminated with carbinols nor with ethylarene derivatives. Between 13.8 and 69 bars changes of the pressure do not influence significantly the rate and the selectivity. The influence of the ratio between the pressures of H₂ and CO on the hydroformylation at 50 °C is shown in Table 7.

As already indicated, in the ionic liquid-deficient aqueous system the catalyst is reusable at least 4–5 times with little changes in the yields of aldehydes. However, while at low temperature (50 °C) the recycled catalyst leads to the formation of branched aldehydes in high selectivity, at higher temperatures (e.g., 90 °C) the reaction

Table 2Examples of catalyst recycling in the hydroformylation of 4-methylstyrene by heterogenized [Rh(cod)Cl]₂ and a tertiary phosphane in an aqueous medium in the presence of an ionic liquid.^a

Run No.	Conversion (%) ^b	Yield of <i>b</i> (%) ^b	Yield of <i>l</i> (%) ^b	Ratio <i>b/l</i>
1	98	94	4	23.5:1
2	97	93	4	23.2:1
3	78	74	4	18.5:1
4	61	58	3	19.3:1

^a Reaction conditions as in Table 1.

^b The data are the average of at least two experiments that did not differ by more than ±3%.

Table 3Hydroformylation of some vinylarenes by [Rh(cod)Cl]₂ and a tertiary phosphane in an aqueous medium in the absence of the ionic liquid.^a

Entry	Substrate	Conversion (%) ^b	Yield of <i>b</i> (%) ^b	Yield of <i>l</i> (%) ^b	Ratio <i>b</i> / <i>l</i> ^b
1	Styrene	100	98	2.0	49.0:1
2	4-Methylstyrene	96	90	6	15.0:1
3	4-Fluorostyrene	95	90	5	18.0:1
4	4-Chlorostyrene	94	89	5	17.8:1
5	4-Cyanostyrene	94	88	6	14.7:1
6	1-Vinylnaphthlene	80	76	4	18.5:1
7	2-Vinylnaphthalene	87	80	7	11.4:1
8	4-Vinylbiphenyl	100	98	2	49.0:1
9	Vinyl benzoate ^c	91	81	10	8.1:1

^a Reaction conditions: vinylarene (1.0 mmol, 0.5–0.8 wt.% of the microemulsion), CTAB (3.3 wt.%), 1-PrOH (6.6 wt.%), TDW (89.0–89.3%) together with heterogenized rhodium catalyst prepared from [Rh(cod)Cl]₂ (30 mg, 0.06 mmol), Na[Ph₂P(C₆H₄-3-SO₃)] (45 mg, 0.124 mmol), TMOS (3.6 ml, 24.2 mmol) and OTEOS (2 ml, 6.68 mmol); unless noted otherwise H₂ (6.9 bar), CO (7.6 bar); stirring rate 300 rpm; 50 °C, 16 h.

^b The percentages were determined both by GC and by ¹H NMR, and are the average of at least two experiments that did not differ by more than ±3%.

^c Initial H₂ pressure 34.5 bar and initial CO pressure 35.9 bar.

Table 4Effect of the nature of the surfactant on the hydroformylation of 4-methylstyrene in aqueous media.^a

Entry	Surfactant ^b	Conversion (%) ^c	Yield of <i>b</i> (%) ^c	Yield of <i>l</i> (%) ^c	Ratio <i>b</i> / <i>l</i>
1	DTAB	81	73	8	9.1:1
2	TDAB	88	79	9	8.8:1
3	CTAB	96	90	6	15.0:1
4	ODTAB	94	83	11	7.5:1
5	Marlipal 24/70	82	69	13	5.3:1
6	SDS	98	78	20	3.9:1

^a Reaction conditions as shown in Table 3 except that a variety of surfactants were used.

^b DTAB = dodecyltrimethylammonium bromide; TDAB = tetradecyltrimethylammonium bromide; CTAB = cetyltrimethylammonium bromides (or hexadecyltrimethylammonium bromide); OTTAB = octadecyltrimethylammonium bromide; Marlipal 24/70 = C₁₂–C₁₄ alcohols polyoxyethyleneglycol ethers; SDS = sodium dodecyl sulfate.

^c The data are average of at least two experiments that did not differ by more than ±3%.

Table 5Hydroformylation of 4-methylstyrene in aqueous microemulsion by [Rh(cod)Cl]₂ entrapped within differently hydrophobicized sol-gel.^a

Entry	Hydrophobic moiety	Conversion	Yield of <i>b</i> (%) ^b	Yield of <i>l</i> (%) ^b	Ratio <i>b</i> / <i>l</i>
1	Propyl	50	43	7	6:1
2	Octyl	96	90	6	15:1
3	Phenyl	99	83	16	5:1

^a Reaction conditions as in Table 3 except for entries 2 and 3 where 6.68 mmol of *n*-propyltriethoxysilane and phenyltrimethoxysilane, respectively were applied instead of the octylated precursor.

^b The data are average of at least two experiments that did not differ by more than ±3%.

Table 6Dependence of the yield and of the regioselectivity of the hydroformylation of 4-methylstyrene on the reaction temperature.^a

Entry	Reaction temp. (°C)	Reaction time (h)	Conversion (%) ^b	Yield of <i>b</i> (%) ^b	Yield of <i>l</i> (%) ^b	Ratio <i>b</i> / <i>l</i>
1	30	16	15	14	1	14:1
2	50	16	96	90	6	15:1
3	70	12	100	77	23	3.3:1
4	90	4	99	61	38	1.6:1

^a Reaction conditions as given in Table 3 except the temperature and the time.

^b The data are average of at least two experiments that did not differ by more than ±3%.

is of very low selectivity. The selectivity in this system decreases gradually also at 50 °C upon recycling. Examples of catalyst recycling in the hydroformylation of 4-methylstyrene at 50 and 90 °C are summarized in Table 8.

Finally, it is notable that although many organometallic catalysts are converted in the presence of dihydrogen or hydrogen donors into metallic nanoparticles [28,29] particularly when an aqueous medium is employed [20,21], we were unable to

Table 7Effect of the relative H₂ and CO pressure in the hydroformylation of 4-methylstyrene and on the regioselectivity on the yield at 50 °C.^a

Entry	H ₂ (bar)	CO (bar)	Conversion (%) ^b	Yield of <i>b</i> (%) ^b	Yield of <i>l</i> (%) ^b	Ratio <i>b</i> / <i>l</i>
1	6.9	6.9	96	90	6	15:1
2	20.7	20.7	100	94	6	16:1
3	34.5	34.5	100	94	6	16:1
4	6.9	13.8	76	68	8	8.5:1
5	6.9	20.7	63	56	7	8:1
6	6.9	34.5	56	50	6	8:1

^a Reaction conditions as in Table 3 except that the gas pressure varied.

^b The data are average of at least two experiments which did not differ by more than ±3%.

Table 8Effect of catalyst recycling in the hydroformylation of 4-methylstyrene on the yield and on the regioselectivity in an aqueous medium at 50 and at 90 °C.^a

Run No.	Reaction temp. (°C)	Conversion (%)	Yield of <i>b</i> (%) ^b	Yield of <i>l</i> (%) ^b	Ratio <i>b</i> / <i>l</i> ^b
1	50	96	90	6	15:1
2	50	94	87	7	12:1
3	50	93	85	8	11:1
4	50	92	80.5	11.5	7:1
5	50	95	83	12	7:1
1	90	99	61	38	1.6:1
2	90	96	54	42	1.3:1
3	90	94	54	40	1.3:1
4	90	92	56	36	1.5:1
5	90	81	49	32	1.5:1

^a Reaction conditions as in Table 3 except that the recycled catalyst was used either at 50 or at 90 °C.^b The average of at least two experiments that did not differ by more than ±3%.

detect Rh(0) species after the hydroformylation processes by TEM-EDAX-EDS analyses. Surprisingly, the FTIR spectra of the heterogenized rhodium catalysts before and after the hydroformylations did not reveal any real visible changes. The spectra contained the characteristic signals of [Rh(cod)Cl]₂, of rhodium bound phosphane and those of the catalyst-free silica sol–gel [30].

4. Conclusions

Hydroformylation of vinylarenes in a highly regioselective manner can be performed at 50 °C by two methods in aqueous microemulsions. Both methods apply immobilized [Rh(cod)Cl]₂ together with a tertiary phosphane as their catalyst. In one method the catalyst is encaged in non-hydrophobicized ionic-liquid-confined sol–gel formed by polycondensation of TMOS and 1-butyl-3-[3-trimethoxysilyl]propyl]imidazolium chloride. In the second method the presence of the ionic liquid is not required, but the sol–gel matrix has to be hydrophobicized with alkyl or aryl groups. Octylated sol–gel gives the best results. The heterogenized catalysts in both methods can be recycled. In the method that involves ionic-liquid the reaction yield (but not the selectivity) diminishes gradually upon the recycling. When the hydroformylation is performed by the catalyst within hydrophobic sol–gel the yield is hardly affected in the first 4–5 runs but the ratio of the *b*/*l* isomeric products decreases somewhat upon recycling. The efficiency and selectivity of hydroformylation by both methods depend (i) on the reaction temperature, (ii) on the electronic nature of the surfactant, (iii) on the hydrophobicity and quality of the sol–gel support, and (iv) on the H₂/CO ratio.

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