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Highly Selective Hydroformylation of Vinylarenes to Branched Aldehydes by $[Rh(cod)Cl]_2$ Entrapped in Ionic Liquid Modified Silica Sol-Gel

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A co-entrapped mixture of $[Rh(cod)Cl]_2$ and $Na[Ph_2P\text{-}3\text{-}(C_6H_4SO_3)]$ within a silica sol-gel matrix modified with ca. 5 % of 1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride catalyzes, in *n*-heptane, the hydroformylation of a variety of vinylarenes. At 50 °C and under 6.9 bar each of H_2 and CO the reaction is high-yielding and highly selective. Non-hindered substrates give >95 % of branched aldehydes and only <5 % of the linear isomers. The ceramic catalyst is leach-proof and recyclable. It does not lose its high catalytic activity and selectivity for at least four runs. The selectivity depends on the pressure of the gases, the temperature and the solvent. The electronic nature has no influence on the selectivity, but the latter is diminished by steric effects. Upon omission of the sol-gel component, the catalyst deteriorates and practically loses its activity after the first half-life of the reaction. In the absence of the ionic liquid, the catalyst undergoes substantial leaching.

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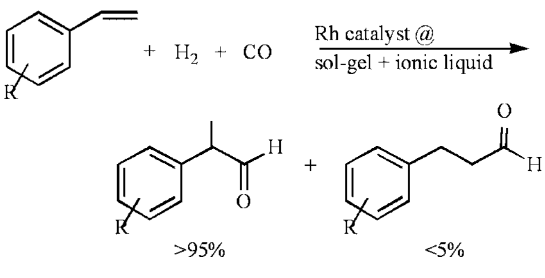
Introduction

Hydroformylation of terminal olefins is a very useful reaction in the chemical industry.[1] Since this process yields usual two kinds of products, linear aldehydes (or alcohols), and the corresponding branched isomers, much work has been performed in order to make this process a more selective one. However, most of the studies were directed to the selective preparation of the linear regioisomers, which are starting materials for a variety of polymers, detergents, cosmetics and other widespread products. The investigation of selective hydroformylation to yield branched products deserved much less interest despite the fact that branched aldehydes are starting compounds for the asymmetric synthesis of many pharmaceuticals.[2] In fact, the number of studies that lead to substantial selectivity in favor of branched products is very limited. Good results were obtained mainly with terminal olefins bearing electron-withdrawing substituents[2,3] or with substrates capable of chelating to the catalysts[4] such as vinyl acetate, butenylphenylphosphane and some *N*-allylamides. Selective hydroformylations towards branched products in which neutral or electron-rich alkenes have been used are even rarer.[5] In this study, aimed at the improvement of the selectivity towards branched products, we have combined two domains of modern catalysis: the use of sol-gel technology that enables facile recovery and recycling of the expensive rhodium catalyst,[6] and the application of an ionic liquid that frequently enhances catalytic processes,[7] and that in our case, promotes also the highly selective hydroformylation to yield branched products. In this research we concentrated on the transformation of vinylarenes by a mixture of $[Rh(cod)Cl]_2$ and $Na[Ph_2P\text{-}3\text{-}(C_6H_4SO_3)]$ entrapped within a sol-gel matrix confined with ca. 5 mol-% of silica-bound imidazolium-based ionic liquid. The ceramic catalyst, so formed, promotes the transformation of a series of styrene derivatives to branched aldehydes in >95% selectivity (Scheme 1).



Scheme 1.

Results and Discussion

In a series of experiments we have hydroformylated styrene in the presence of a variety of rhodium complexes and tertiary phosphanes co-entrapped in a sol-gel matrix (from tetramethoxysilane) modified with a silyloxylated imid-

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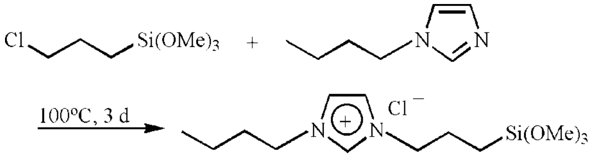
azolium ionic liquid (cf., e.g., ref.[8]). The best results, in terms of yield and selectivity were obtained when the molar ratio ion liquid/tetramethoxysilane was between 1:20 and 1:30. A particularly efficient catalyst was obtained by mixing 0.0608 mmol of $[Rh(cod)Cl]_2$, 0.1207 mmol of $Na[Ph_2P\text{-}3\text{-}(C_6H_4SO_3)]$, 32 mmol of prehydrolyzed $Si(OMe)_4$ and 1.13 mmol of 1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride (prepared as shown in Scheme 2) in THF for 6 h followed by aging at room temperature for 12 h and drying at 13–130 Pa at 80 °C. No loss of rhodium or phosphorus was observed during the immobilization process. The average surface area of several samples of the heterogenized catalyst was shown by N_2/BET measurements to be 292 m^2/g, the pore diameter being 27 Å. When one-half of this catalyst was mixed with 1 mmol of freshly distilled styrene in 15 mL of *n*-heptane and heated at 50 °C under 6.9 bar H_2 and 6.9 bar CO for 12 h, GC analysis of the resulting mixture indicated the formation of 97.13% of 2-phenylpropanal and 2.85% of the 3-phenyl isomer. An experiment with a fivefold amount of the reactants gave a mixture of the two aldehydes that were isolated on a preparative 5% Apiezon L/Chromosorb W column followed by immediate transformation into the corresponding 2,4-dinitrophenylhydrazones. In this experiment, 88% of branched and 2% of linear aldehydes were isolated. Upon completion of the hydroformylation, the ceramic material was washed with *n*-heptane followed by sonication with dichloromethane and drying under reduced pressure. This operation did not remove any rhodium or phosphorus from the matrix and allowed the reuse of the catalyst system for further hydroformylation of styrene without loss of the catalytic activity or of its selectivity for four consecutive runs. In the fifth run, however, some deterioration of the catalyst started to take place. These results are summarized in Table 1. Similar hydroformylation reactions (including catalyst recycling experiments) were conducted with several substituted styrenes, as well as with 2-vinylnaphthalene. The results are listed in Table 2. Many examples reported in the literature indicate the pronounced electronic effect on the selectivity in hydroformylation (see, for example, ref.[2]). The results listed in Table 2 show, however, that in our system the electronic effect is negligible. Substrates with electron-donating and those with electron-attracting groups showed similar conversions with a similar selectivity of branched product, indifferently whether these groups are located at the *meta* or *para* position to the vinyl function. On the other hand, the steric effect associated with an *ortho* substitution, as in 2-chlorostyrene, causes a reduction in both the rate and the selectivity (cf. Entries 5, 6 and 7 in Table 2). The relatively low yield in the hydroformylation of 3-bromostyrene (Entry 4) and of 2-vinylnaphthalene (Entry 9) may result from the bulkiness of the substrates. The small pore size of the matrix (vide supra) may prevent the substrate from fast penetrating through the sol-gel backbone to reach the metal catalyst.[9] The selectivity, however, seems not to be affected by this bulkiness. The reaction conditions employed in Table 2 were selected after running model experiments with styrene in several solvents, under different hydrogen and carbon monoxide pressures at a temperature range between 25 and 100 °C. These experiments are summarized in Tables 3, 4, and 5.



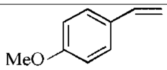
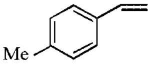
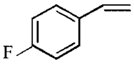
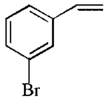
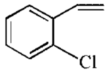
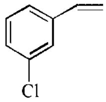
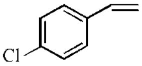
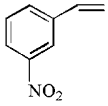
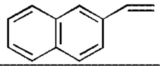
Scheme 2.

Table 1. Hydroformylation of styrene by $[Rh(cod)Cl]_2$ and $Na[Ph_2P\text{-}3\text{-}(C_6H_4SO_3)]$ to give $C_6H_5CH(CH_3)CHO$ (*b* = branched) and $C_6H_5(CH_2)_2CHO$ (*l* = linear).[a]

Run no.	Total yield of aldehydes (%)	Yield of branched aldehydes (%)	Yield of linear aldehyde (%)	Ratio *b*/*l*
1	100	97.1	2.9	34:1
2	99.5	96.7	2.8	35:1
3	99.5	96.8	2.7	36:1
4	99.5	96.8	3.0	32:1
5	80	77.0	3.0	26:1

[a] Reaction conditions: 1 mmol of substrate, 15 mL of *n*-heptane, 1.2 g of ceramic catalyst prepared from 16.45 mmol of prehydrolyzed $Si(OMe)_4$ and 0.56 mmol of 1-butyl-3-[3-(trimethoxysilyl)-propyl]imidiazolium chloride that contained 0.0304 mmol of $[Rh(cod)Cl]_2$ and 0.0603 mmol of $Na[Ph_2P\text{-}3\text{-}(C_6H_4SO_3)]$; 6.9 bar of H_2, 6.9 bar of CO; 50 °C; 12 h.

Table 2. Hydroformylation of some vinylarenes under comparable conditions (*b* = branched; *l* = linear).[a]

Entry	Substrate	Conversion (%)[b]	Yield of *b* (%)[b]	Yield of *l* (%)[b]	Ratio *b*/*l*[b]
1		100	96.9	3.1	31:1
2		99	95.5	3.5	28:1
3		99.5	95.3	4.2	23:1
4		74	71.3	2.7	31:1
5		84	76.4	7.6	10:1
6		98.5	96.5	2.0	50:1
7		98.5	95.3	3.2	30:1
8		100	100	–	–
9		85	82.5	2.5	34:1

[a] Reaction conditions as in Table 1. [b] In the first run. The yields are determined by GC and are the average of at least two experiments that did not differ by more than 3%.

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Table 3 indicates that the hydroformylation of styrene proceeds well with high selectivity in producing branched products both in aliphatic and in aromatic hydrocarbons. However, in THF substantial hydrogenation of both the starting vinylarene, as well as the aldehydes was found to take place. In 1,2-dichloroethane the reaction became completely non-selective.

Table 3. Effect of several solvents on the hydroformylation of styrene by a mixture of $[Rh(cod)Cl]_2$ and $Na[Ph_2P\text{-}3\text{-}(C_6H_4SO_3)]$ encaged in ionic liquid modified silica sol-gel (*b* = branched; *l* = linear).[a]

Entry	Solvent	Total yield of aldehydes (%)	Yield of *b* (%)	Yield of *l* (%)	Ratio *b*/*l*
1	*n*-heptane	100	97.1	2.9	34:1
2	*n*-hexane	99	95.9	3.1	31:1
3	*n*-pentane	98.8	95.5	3.3	29:1
4	toluene	98.5	94.7	3.8	25:1
5	THF	55[b]	53.7	1.3	42:1
6	1,2-dichloroethane	99.3	55.3	44.0	1.3:1

[a] Reaction conditions as in Table 2, except that the solvent was different. [b] The conversion was 95%. Side products (40%) consisted mainly of ethylbenzene, 2- and 3-phenylpropanol, and polymeric material.

Changes in the pressure were found to hardly effect the reaction rate. In all experiments listed in Table 4 the total yield was >96%. The selectivity, however, increased slightly parallel to the increase in the pressure of the gases. Thus, under a total pressure of 6.9 bar, styrene gave only 89.5% of the branched 2-phenylpropanal, whereas under 55.2 bar the yield rose to 97.8%.

Table 4. Effect of the pressure on the hydroformylation of styrene by a mixture of $[Rh(cod)Cl]_2$ and $Na[Ph_2P\text{-}3\text{-}(C_6H_4SO_3)]$ encaged in ionic liquid modified silica sol-gel (*b* = branched; *l* = linear).[a]

Entry	Initial H_2 pressure (bar)	Initial CO pressure (bar)	Ratio *b*/*l*[b]
1	3.45	3.45	8.5:1
2	6.9	6.9	29:1
3	13.8	13.8	31:1
4	27.6	27.6	45:1

[a] Reaction conditions: 1 mmol of styrene, 15 mL of *n*-pentane, 1.25 g of ceramic catalyst containing 0.0304 mmol of $[Rh(cod)Cl]_2$, 0.0603 mmol of $Na[Ph_2P\ (3\text{-}C_6H_4SO_3)]$ and the sol-gel-ionic liquid combination described in the Experimental Section; 50 °C; 12 h. [b] In the first run.

The influence of the temperature is more pronounced (see Table 5). While the total yield increased along with the elevation of the temperature, a reverse correlation was found between the temperature and the selectivity for branched products. A temperature of 50 °C was therefore selected as optimal for our experiments.

It is noteworthy, that all four components of the catalyst system, the rhodium complex, the sulfonated phosphane, the modified ionic liquid and the silica sol-gel matrix, proved essential for the selective hydroformylation to yield branched products. In principal, the hydroformylation of styrene takes place also under homogeneous conditions (in the absence of the sol-gel material). However, the non-immobilized catalyst deteriorates at 50 °C within less than 2 h and forms an inactive deposit (mirror) of metallic rhodium. In a typical experiment, the hydroformylation stopped after 68% of the styrene had reacted. By comparison of the profiles of the reactions by the non-entrapped and by the entrapped catalyst (Figure 1) one can realize that both reactions start at a similar rate of styrene consumption that follows a first-order rate law but only the immobilized catalyst leads the reaction to completion. The selectivity for branched products also decreases to some extent when the heterogenized catalyst is replaced by the homogeneous one [the branched (*b*)/linear (*l*) ratio becomes 19:1 as compared with 34:1 in the reaction with the entrapped rhodium complex]. Of course the catalyst cannot be reused under homogeneous conditions. Under such conditions, the addition of the ionic liquid component causes a solubility problem and leads to a further decrease in the yield (40% with a selectivity of 21:1). In the absence of the tertiary phosphane hardly any hydroformylation takes place. Substitution of the salt of the sulfonated phosphane by PPh_3 causes substantial metal leaching. We assume that sodium 3-(diphenylphosphanyl)-benzenesulfonate may undergo ion exchange with the ionic liquid forming an immobilized rhodium complex with a carbene-like ligand. The latter may be responsible for the

Table 5. Effect of the temperature on the hydroformylation of styrene and 4-chlorostyrene (*b* = branched; *l* = linear).[a]

Entry	Substrate	Reaction temp. (°C)	Total yield of aldehydes (%)	Ratio *b*/*l*[b]
1	$C_6H_5CH{=}CH_2$	20	16	40:1
2	$C_6H_5CH{=}CH_2$	50	100	34:1
3	$C_6H_5CH{=}CH_2$	75	99	14:1
4	$C_6H_5CH{=}CH_2$	100	99	10:1
5	$4\text{-}ClC_6H_4CH{=}CH_2$	50	96	31:1
6	$4\text{-}ClC_6H_4CH{=}CH_2$	75	99	12:1
7	$4\text{-}ClC_6H_4CH{=}CH_2$	100	99.5	6:1

[a] Reaction conditions as in Table 2, except that the hydroformylation was run at different temperatures. [b] In the first run.

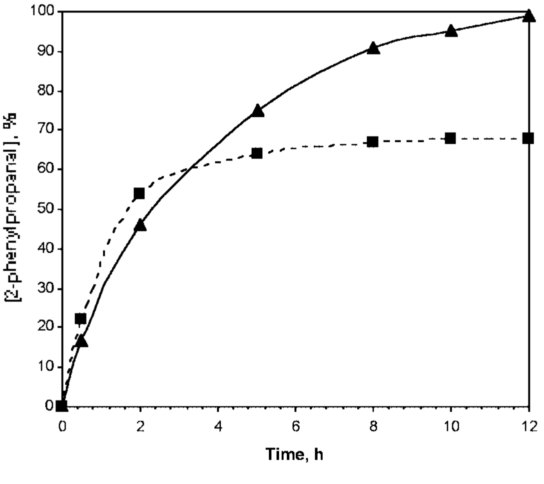

Figure 1. Concentration/time profiles for the formation of 2-phenylpropanal from styrene by the sol-gel entrapped $[Rh(cod)Cl]_2$/ $Na[Ph_2P(3\text{-}C_6H_4SO_3)]$/ionic liquid catalyst (---▲---) and by the non-entrapped (sol-gel-free) catalyst (---■---).

high conversion and *b*/*l* selectivity.[5d] In this respect we recall the observation that various transition metal compounds are able to coordinate with imidazolium nitrogen atoms forming useful catalyst (see, for example, ref.[10]).

Conclusions

In this study we have shown that the co-entrapment of a rhodium complex, a sulfonated tertiary phosphane and an ionic liquid within silica sol-gel, forms a stable and recyclable hydroformylation catalyst. The ceramic catalyst promotes the transformation of vinylarenes under mild conditions to predominantly branched aldehydes with high selectivity. The study is in line with the recent attempts to develop sol-gel encapsulated ionic liquids that may show a unique catalytic activity in a highly selective fashion.[11]

Experimental Section

General: The various styrene derivatives, 1-vinylnaphthalene and 1-butylimidazole were purchased from Sigma–Aldrich. The vinylarenes were distilled prior to the application. (3-Chloropropyl)trimethoxysilane and tetramethoxysilane were obtained from Gelest Silanes & Silicones and used without further purifications. Di-μ-chlorobis[(1,2,5,6-η)-1,5-cyclooctadiene]dirhodium[12] and sodium 3-(diphenylphosphanyl)benzenesulfonate[13] were prepared according to literature procedures. The following analytical instruments were used: Bruker Vector 22 FTIR spectrometer, Bruker AMX-300 NMR instrument, Hewlett Packard model Agilent 4890D gas chromatograph, Hewlett Packard model 4989A mass spectrometer equipped with an HP gas chomatograph model 5890 series II, an Optima 3000 instrument was used for inductively coupled plasma (ICP) measurements, a Perkin–Elmer spectrophotometer model 403 equipped with a Juniper rhodium cathode lamp was used for leaching analysis, and a Micrometrics ASAP 2020 instrument was used for N_2/BET surface area and pore diameter measurements of the sol-gel matrices.

1-Butyl-3-[3-(trimethoxysilyl)propyl]imidazolium Chloride: A solution of (3-chloropropyl)trimethoxysilane (19.85 g, 0.1 mol) and 1-butylimidazole (12.52 g, 0.1 mol) was stirred at 100 °C for 3 d. The resulting orange-brown viscous oil was left under 130 Pa at 80 °C for 12 h and proved to be analytically pure. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50 (m, 2 H), 0.89 (t, J = 7.2 Hz, 3 H), 1.31 (m, 2 H), 1.82 (m, 2 H), 1.95 (m, 2 H), 3.48 (s, 9 H), 4.27 (t, J = 7.2 Hz, 2 H), 4.32 (t, J = 7.4 Hz, 2 H), 7.45 (br. s, 1 H), 7.64 (br. s, 1 H), 10.68 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.26, 12.77, 18.77, 23.50, 31.50, 49.00, 50.01, 50.96, 121.51, 121.92, 136.63 ppm. $C_{13}H_{27}ClN_2O_3S$ (322.909): calcd. C 48.36, H 8.43, Cl 10.98, N 8.68; found C 48.33, H 8.67, Cl 10.60, N 8.51.

Preparation of the Immobilized Rhodium Catalyst: Typically, to a mixture of tetramethoxysilane (5 mL, 32 mmol), which had been prehydrolyzed with water (4 mL, 222 mmol) for 15 min, was added a solution of 1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride (365 mg, 1.13 mmol) in 2 mL of MeOH, and a mixture of di-μ-chlorobis[(1,2,5,6-η)-1,5-cyclooctadiene]dirhodium[12] (30 mg, 6.08×10^{-2} mmol), sodium 3-(diphenylphosphanyl)benzenesulfonate dihydrate[13] (44 mg, 0.1207 mmol) and 2.5 mL of THF. The mixture was stirred at room temperature until gelation was completed (ca. 6 h). The gel was left for 12 h and dried at 130 Pa at 80 °C for 12 h. The material was sonicated twice with CH_2Cl_2 (10 mL) for 15 min and dried again at 130 Pa to constant weight (3.5 h). Ca. 2.5 g of an orange ceramic material was obtained. The combined washings were subjected to atomic absorption analysis and were found to be rhodium-free (sensitivity limit 1 ppm).

Catalytic Hydroformylation: A 100 mL miniautoclave equipped with a mechanical stirrer and a sampling device was charged at 50 °C with the heterogenized catalyst (containing 3.04×10^{-2} mmol of the dirhodium complex and 0.0603 mmol of the tertiary phosphane), the substrate (1 mmol) and an appropriate solvent (15 mL). The autoclave was sealed and purged with hydrogen and then pressurized with H_2 (usually to 6.9 bar) and with the same pressure of CO. The stirred reaction mixture was then heated (usually at 50 °C) for 12 h. After cooling to 0 °C, the excess gases were released and the remaining mixture filtered and the solid washed with heptane (2×30 mL). The filtrate was concentrated and analyzed by GC, MS and NMR and compared with authentic samples. The filtered ceramic catalyst was refluxed for 20 min in heptane (20 mL) and sonicated for 15 min with CH_2Cl_2 (20 mL). The combined washings were concentrated and subjected either to ICP or atomic absorption analysis for metal leaching analysis. The filtered solid was dried at 130 Pa at 80 °C for 5 h prior to its use as catalyst for a further run of hydroformylation.

Acknowledgments

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