Three-Phase Microemulsion/Sol-Gel System for Aqueous Catalytic Hydroformylation of Hydrophobic Alkenes

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Dedicated to Professor Herbert Schumann on the occasion of his 70th birthday

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We extended the three-phase transport methodology to the catalytic hydroformylation of alkenes. The method enables to carry out an all-hydrophobic reaction – substrate, product and catalyst – in water. The alkene is microemulsified in the aqueous medium and the solubilized substrate is assumed to be carried to an organometallic rhodium catalyst entrapped within a partially hydrophobicized silica sol-gel matrix. The substrate is then spilled into the porous heterogenized catalyst in which the hydroformylation takes place. The products formed are desorbed from the ceramic material and microemulsified by the same surfactant. Upon breaking of the microemulsion the products are separated. The heterogenized catalyst can be easily separated from the reaction mixture by filtration and be recycled. The hydroformylation process was carried out on various alkenes with reaction yields from ca. 62 to 99 %.

Introduction

Recently, we have reported a general method for performing an all-hydrophobic reaction – hydrophobic substrates, products and catalysts – in water.[1,2] The method relies on a heterogeneous three-phase system, composed of an emulsion of the substrate and products in water (two phases) and a sol-gel entrapped catalyst (the third phase). The steps of the emulsion/sol-gel transport (EST) systems are: First, the substrate is emulsified with a suitable surfactant; second, the emulsion droplets are adsorbed on the surface of a porous, partially hydrophobic silica sol-gel material within which the catalyst is entrapped; third, the surfactant molecules which solubilized the substrate are adsorbed reversibly on the surface of the solid, and in doing so, spill the substrate into the pores where the catalyst resides;[3] fourth, the catalytic reaction takes place within the pores, and a (hydrophobic) product is formed; fifth, the product diffuses out and is emulsified spontaneously by the same surfactant; and finally, the emulsion is broken and the product separated. We have tried both, emulsions[1] and microemulsions,[2] and found that the latter are by far superior in versatility and scope. Reactions we have carried out, so far, by the EST approach were catalytic hydrogenation of various subsrates, including alkenes, alkynes, aromatic C=C bonds, nitro and cyano groups.[2] In $[CH_3(C_8H_{17})_3N]^+$-$[RhCl_4]^-$@silica sol-gel catalyzed hydrogenation of chalcone and *cis*-stilbene[1] we have also shown that one can control the type of products by altering the chain length of the hydrophobically modified sol-gel matrix.

We have now extended the methodology in its microemulsion version to include yet another important family of catalytic reactions, namely the hydrofomylation of alkenes. Because of economical and environmental reasons attempts have already been made to perform this industrially important process in biphasic and aqueous media, including microemulsions[4] using as catalysts either water-soluble complexes or water-insoluble compounds modified with hydrophilic ligands.[5] The present system permits not only the utilization of hydrophobic substrates, but also of hydrophobic catalysts that can be reused in consecutive runs.

Results and Discussion

Several rhodium complexes entrapped in hydrophobicized silica sol-gel matrices were investigated as potential catalysts for the hydroformylation of alkenes under micro-EST conditions. The best results were obtained by employing bis[1,2,5,6-η-(1,5-cyclooctadiene)]bis{μ-[3-(trimethoxysilyl)propanethiolato-(*S,S′*)]}dirhodium $\{Rh(cod)[\mu\text{-}S(CH_2)_3Si(OMe)_3]\}_2$, prepared from di-μ-chlorobis[(1,2,5,6-η)-1,5-cyclooctadiene]dirhodium, $[Rh(cod)(\mu\text{-}Cl)]_2$, and sodium 3-(trimethoxysilyl)-1-propanethiolate, $[(MeO)_3Si(CH_2)_3S]^-Na^+$, to which 5 equiv. of PPh_3 had been added

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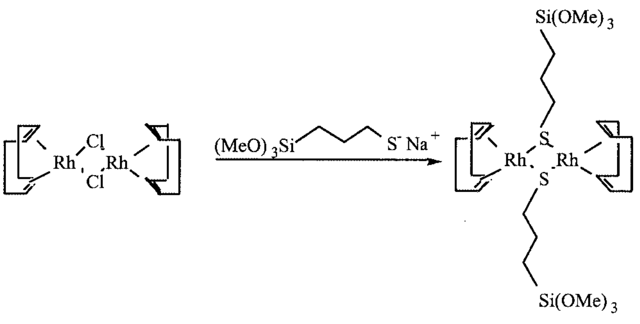
Table 1. Hydroformylation of representative alkenes under heterogeneous microemulsion conditions.[a]

Entry	Substrate	Microemulsion composition[% w/w][b]				H_2 + CO	t	Yield	Aldehydes	Minor products
		I	II	III	IV	[bar]	[h]	[% (*l*/*b*)][c]	[%][c]	[%][c]
1	cylopentene	6.7	9.7	6.3	77.3	13.8	15	98.5	c-C_5H_9CHO (98.5)	c-C_5H_{10} (1.5)
2	4-vinylcyclohex-1-ene	9.9	8.7	11.4	70.0	13.8	6	62.0 (6.46)	c-$C_6H_9(CH_2)_2CHO$ (53.7), c-$C_6H_9CH(Me)CHO$ (8.3)	c-$C_6H_{11}Et$ (0.7)
3	styrene[d]	9.6	8.5[e]	11.4	70.5	27.6	10	89.5 (0.22)	$Ph(CH_2)_2CHO$ (16.4),[f] PhCH()MeCHO (73.1)	PhEt (0.4)
4	4-bromostyrene	14.6	9.4	14.8	61.2	13.8	6	67.5 (0.32)	4-$BrC_6H_4(CH_2)_2CHO$ (16.5), 4-$BrC_6H_4CH(Me)CHO$ (51)	4-BrC_6H_4Et (1.3)
5	1-hexene	6.9	8.3	15.7	69.1	27.6	14	79.7 (1.38)	$Me(CH_2)_5CHO$ (52.0), $Me(CH_2)_3CH(Me)CHO$ (23.9), $Me(CH_2)_2CH(Et)CHO$ (3.8)	$Me(CH_2)_4Me$ (0.6), isomeric hexenes (0.7)
6	1-octene[g]	9.6	8.1[h]	15.2	67.1	13.8	4	79.1 (1.53)	$Me(CH_2)_7CHO$ (60.4), $Me(CH_2)_5CH(Me)CHO$ (18.7)	$Me(CH_2)_6Me$ (1.8), isomeric octenes (11.1)
7	allylbenzene	10.2	8.4	14.2	67.2	13.8	6	92.8 (2.03)	$Ph(CH_2)_3CHO$ (62.8), $PhCH_2CH(Me)CHO$ (30)	PhPr (1.5), (*E*)-PhCH=CHMe (5), (*Z*)-PhCH=CHMe (0.7)
8	4-allylanisole	12.1	10.3	15.2	62.4	13.8	6	91.2 (2.33)	4-$MeOC_6H_4(CH_2)_3CHO$ (63.8), 4-$MeOC_6H_4CH_2CH(Me)CHO$ (27.4)	4-$MeOC_6H_4Pr$ (1.4), (*E*)-4-$MeOC_6H_4CH$=CHMe (6.7), (*Z*)-4-$MeOC_6H_4CH$=CHMe (0.7)

[a] Reaction conditions as specified in the Exp. Sect. at 80 °C and under the H_2 and CO pressure given in this Table. [b] I = substrate; II = quaternary ammonium salt; III = *n*-butanol; IV = H_2O. [c] The yields are the average of at least two experiments. *l*/*b* is the linear/branched ratio. [d] When the hydrophobicity of the matrix was changed from octyl to phenyl, a mixture of $Ph(CH_2)_2CHO$ (14.5%), PhCH(Me)CHO (81%), and PhEt (0.8%) was obtained. [e] When the ammonium bromide was replaced by SDS, the yields of the two aldehydes and ethylbenzene were 4.9, 38.9 and 0.8%, respectively. [f] In further five runs [(ii)–(vi)] the yields of the linear and branched aldehydes were: (ii) 16.4, 71.0%; (iii) 16.0, 72.3%; (iv) 17.0, 73.5%; (v) 16.8, 72.6%; (vi) 15.8, 71.1%. [g] When the catalysts were PPh_3-free, after 14 h, a mixture of $Me(CH_2)_7CHO$ (27.0%), $Me(CH_2)_5CH(Me)CHO$ (19.3%), $Me(CH_2)_4CH(Et)CHO$ (3.3%), $Me(CH_2)_3CH(Pr)$-CHO (1.6%), $Me(CH_2)_6Me$ (22.0%) and isomeric 2- and 3-octene (23.7%) was obtained. [h] In the presence of SDS the yields of the two aldehydes, octane and isomeric octenes were 8.5, 12, 3, and 12%, respectively.

prior to its entrapment within a hydrophobically modified (with octyl groups) silica sol-gel matrix [Equation (1)]. The (trimethoxysilyl)propanethiolato ligand has already been shown to efficiently tether rhodium complexes to silica surfaces.[6] The added phosphane stabilizes the immobilized combined catalyst to form a long-lived leach-proof material, enhancing the reaction of hydroformylation and reducing, or completely eliminating, undesired isomerization and hydrogenation processes (see Table 1).



(1)

The surfactant of choice for the preparation of the microemulsions was *N*-dodecyl-*N*-(2-hydroxyethyl)-*N*,*N*-dimethylammonium bromide,[7] although anionic sodium dodecyl sulfate (SDS) could also be applied, although with somewhat lower efficiency. The microemulsion was typically formed by addition of the substrate to a solution of the surfactant in distilled water, followed by titration with *n*-butanol until the mixture became clear. Thus, in all experiments water was the major component (61–77%) of the reaction mixture (Table 1).

The catalytic hydroformylation was performed in a microautoclave charged with the sol-gel-entrapped catalyst and with the substrate-containing microemulsion, and then pressurized with H_2 and CO. Upon completion of the reaction, the solid catalyst was filtered off and the microemulsion broken with sodium chloride. The organic layer was separated and analyzed. The recovered catalyst was washed and reused in a second run. Usually we recycled it 3–6 times without observing any loss in catalytic activity. The results of representative hydroformylations are summarized in Table 1.

In the absence of *n*-butanol no microemulsions are formed and the hydroformylations take place at a lower rate (vide infra). Cycloalkenes (e.g., cyclopentene; Entry 1) are transformed almost exclusively into the respective cyclic aldehydes. However, if the cycloalkene has an exocyclic double bond, the latter undergoes hydroformylation in preference to the endocyclic bond. Thus, 4-vinylcyclohex-1-ene (Entry 2) yields, as long as the hydroformylation of the exocyclic function has not been completed, only 2- and 3-cyclohexylpropionaldehyde. Styrene (Entry 3) and its 4-bromo derivative (Entry 4) form mainly carboxaldehydes in which the carbonyl group is attached to the benzylic carbon atom, leaving the linear aldehydes as the minor products (*l*/*b* = 0.22–0.32). In the absence of *n*-butanol (i.e., under regular rather than microemulsion conditions) the hydroformylation of styrene furnished only up to 15% of $Ph(CH_2)_2$-CHO and 46% of PhCH(Me)CHO. Unlike the styrenes, aliphatic terminal olefins (1-hexene, 1-octene; Entries 5 and 6) yield preferentially the linear products (l/b = 1.38–1.58), so do the two allylarenes (Entries 7 and 8; l/b = 2.03 and 2.33) despite the fact that the latter substrates undergo catalytic double bond isomerization along the hydroformylation process. This phenomenon can be rationalized by the fact that at 80 °C, in the presence of the added PPh_3, under 13.8–27.6 bar H_2, a reverse double bond migration to the terminal olefins prevails.

Conclusions

Hydroformylation of hydrophobic alkenes can be performed in an aqueous medium under micro-EST conditions using a suitably selected surfactant and a cyclooctadienerhodium catalyst, chemically entrapped within a hydrophobicized silica sol-gel matrix. The successful hydroformylation in a highly selective manner requires the addition of triphenylphosphane to the catalyst. Recycling of the immobilized catalyst is possible. Since we have already demonstrated the utility of the EST system for the catalytic hydrogenation of hydrophobic substrates in water,[1,2] we believe that this technology is of general applicability to a wide range of reactions of hydrophobic substrates in aqueous media.

Experimental Section

Chemicals: Di-μ-chlorobis[(1,2,5,6-η)-1,5-cyclooctadiene]dirhodium[8] and *N*-dodecyl-*N*-(2-hydroxyethyl)-*N*,*N*-dimethylammonium bromide[7] were synthesized according to published procedures. All other chemicals except for the catalyst were obtained from commercial sources.

Preparation of Bis[1,2,5,6-η-(1,5-cyclooctadiene)]bis{μ-[3-(trimethoxysilyl)propanethiolato-(*S,S′*)]}dirhodium {Rh(cod)[S(CH$_2$)$_3$-Si(OMe)$_3$]}$_2$: To a solution of $(CH_3O)_3Si(CH_2)_3SH$ (0.38 mL) in dry THF (100 mL) was added under exclusion of air oil-free sodium hydride (0.06 g). The mixture was stirred at room temperature for 60 min. A solution of $[Rh(cod)Cl]_2$ (500 mg) in THF (50 mL) was added dropwise and the stirring was continued for another 2 h. The NaCl was removed by filtration through Celite and the THF was removed by distillation under reduced pressure at room temperature. The resulting yellow oil was chromatographed on silica gel using ether/pentane mixtures as eluent. Drying at 0.01 Torr for 24 h afforded the rhodium complex in 74% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.72 (t, J = 8 Hz, 4 H), 1.57–1.68 (m, 4 H), 1.95–2.07 (m, 8 H), 2.02 (t, J = 9 Hz, 4 H), 2.39–2.41 (m, 8 H), 3.53 (s, 18 H), 4.16 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.78, 25.53, 27.35, 31.37, 50.45, 78.92. $C_{28}H_{54}O_6Rh_2S_2Si_2$ (812.849): calcd. C 41.37, H 6.70; found C 41.17, H 6.74. The rhodium complex was redissolved in THF (20 mL) and kept under Ar in the refrigerator as a stock solution.

Preparation of {Rh(cod)[S(CH$_2$)$_3$Si(O)$_3$≡]}$_2$/5PPh$_3$@Hydrophobicized Sol-Gel: To the stock solution (2 mL) of $\{Rh(cod)[S(CH_2)_3Si(OMe)_3]\}_2$ in THF was added triphenylphosphane (133 mg), under exclusion of air. The resulting red solution was stirred for 2 h and then treated with tetramethoxysilane (TMOS) (5 mL), prehydrolyzed triethoxy(octyl)silane (2.1 mL) and triply distilled water (4 mL). After agitation for 3 h, a 0.1 M solution (0.2 mL) of tetrabutylammonium fluoride (TBAF) in THF was added. Gelation started immediately and was completed within 30 min. The gel was dried at 98 °C and 0.5 Torr for 24 h. The dry material was refluxed with dichloromethane (20 mL) for 1 h and then redried to give 3.5–3.6 g of $\{Rh(cod)[S(CH_2)_3Si(O)_3\equiv]\}_2/5PPh_3$@hydrophobicized sol-gel. Upon replacement of the triethoxy(octyl)silane by trimethoxy(phenyl)silane (1.5 g), 3.4–3.5 g of $\{Rh(cod)[S(CH_2)_3Si(O)_3\equiv]\}_2/5PPh_3$@phenylated silica was obtained.

Preparation of the Microemulsions: Typically, to a solution of *N*-dodecyl-*N*-(2-hydroxyethyl)-*N*,*N*-dimethylammonium bromide[7] (1.2 g) in water (10 mL) the substrate (13.1 mmol) was added dropwise under vigorous stirring. The emulsion so formed was titrated with *n*-butanol until a clear transparent mixture was obtained (1–3 mL). The w/w composition of the various microemulsions studied here are summarized in Table 1.

Catalytic Hydroformylations: A Teflon-lined microautoclave, equipped with a mechanical stirrer and a sampling device, was charged with the sol-gel entrapped catalyst and the substrate-containing microemulsion (typically 15–20 mL). The autoclave was sealed and purged three times with hydrogen and then pressurized with H_2 (6.9–13.8 bar) and with the same pressure of CO. The reaction mixture was then heated with stirring at the desired temperature for the required time. After cooling to room temperature, the gases were released and the remaining mixture was filtered. Upon addition of sodium chloride (200 mg) to the filtrate, the reaction mixture separated into two phases. The organic layer was diluted with dichloromethane (20 mL), dried with $MgSO_4$, concentrated and analyzed by GC, MS and NMR and compared with authentic samples. The filtered ceramic catalyst was suspended in refluxing methanol (20 mL) for 30 min, dried at room temperature and 0.5 Torr for 3 h, sonicated with dichloromethane (20 mL) for 30 min and dried again at room temperature and 0.5 Torr for 2 h before reapplication in a second catalytic run.

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