Hydroformylation with Dendritic-Polymer-Stabilized Rhodium Colloids as Catalyst Precursors

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Hydroformylation of 1-hexene with rhodium colloids stabilized by poly(ethylene imine) amides with a hyperbranched polyamine core and a lipophilic periphery is reported. The catalyst selectivity for aldehydes increases with increasing temperature or pressure. The ratio of linear to branched aldehydes decreases with increasing temperature. At 80 °C and 90 atm, 1-hexene is converted completely with 96% selectivity for aldehydes, with a ratio of linear/branched aldehydes of 58:42. Turnover numbers up to 3×10^4 (calculated with respect to the entire amount of Rh present) were observed. The results indicate that the catalyst precursor colloids serve as a reservoir for the formation of soluble Rh(I) complexes as the active species.

Introduction

Catalysis by transition metal colloids has received increasing interest in recent years. Among the reactions studied, a large number of reports has dealt with hydrogenation.^[1] Hydrogenations are well known to occur on metal surfaces, thus they are catalyzed by a variety of colloidal dispersions based on different metals and stabilizing agents. In some cases, chemo- and enantio-selectivities have been achieved with colloids which differ from those achieved with classical heterogeneous catalysts based on highly disperse metals.^[2]

More recently, metal colloids have also been studied as catalysts for reactions, for which it is not obvious that they can occur on a metal surface. Most notably, Heck and Suzuki coupling by palladium colloids has been investigated intensely.^[3] In homogeneous catalysis with soluble

metal complexes, the mechanism of both reactions is known to involve changes in oxidation state between Pd(0) and Pd(II) by oxidative addition of substrate and reductive elimination of product, respectively. The question arises whether these reactions can occur on a metal surface, as present in a colloid, or whether the colloidal particles serve as a reservoir for soluble (mononuclear) complexes, i.e., classical homogeneous catalysts, which represent the actual active species.^[4] Detailed studies have been carried out which come to the conclusion that catalytic coupling occurs on the metal colloid surface.^[3d] Strict unambiguous proof remains challenging due to the complexity of the issue and the difficulty of absolutely excluding that catalysis occurs by a small portion of palladium complex in solution (it is known from studies of homogeneously soluble metal precursors that activities in the Heck reaction can be extremely high^[5]). On the other hand, it has been demonstrated that palladium colloids (and the metal nanoparticles of classical heterogeneous catalysts) can dissolve under the conditions of the coupling reaction by oxidative addition of aryl halide to afford solutions of palladium(II) complexes.^[3e,6]

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Scheme 1. Possible functions of rhodium colloids in hydroformylation. (a) mononuclear soluble complexes as active species, (b) catalysis on the surface of a colloidal nanoparticle (active species of the catalytic cycle exemplified by rhodium hydride only).

In contrast to the aforementioned reactions, hydroformylation by metal colloids has received little attention to date, despite the fact that hydroformylation is by far the largest homogeneously catalyzed reaction by volume. Most often, rhodium catalyzed hydroformylations are carried out with Rh^{I} phosphine complexes. “Ligand-free” catalysts, that is, catalysts not containing phosphines or similar strongly coordinating ligands, usually form substantial amounts of branched aldehydes also.

There are scattered brief reports that Rh^0 colloids can be active for hydroformylation.^a For example, hydroformylation of 1-hexene in the presence of a rhodium colloid stabilized with a styrene–butadiene polymer was claimed to result in 95% conversion to aldehydes with an *n*-selectivity of ca. 67% [reaction temperature 100 °C and 42 bar of H_2/CO (1:1)].^[7] Liu et al. reported hydroformylation of propylene in a biphasic aqueous system employing an aqueous rhodium colloid stabilized by PVP. From determination of rhodium particle sizes before and after the reaction and from XPS studies, the authors conclude that catalysis occurs in a heterogeneous fashion, however without further considerations on the underlying mechanism.^[8] Investigations by Bönemann et al. of 1-octene hydroformylation in an aqueous biphasic system with a rhodium colloid stabilized by oligo(ethylene glycol)-substituted phosphine show that the catalytic reaction is insensitive to the mercury test probing for heterogeneous catalysis, overall this study concludes that the nature of the active sites is unclear to date and does not further comment the mechanism of catalysis.^[9]

It is generally recognized that hydroformylation can occur by Rh^{I} species. Rh^0 compounds can be converted to Rh^{I} by oxidative addition of hydrogen. For example, the formation of the transient $[\text{HRh}(\text{CO})_4]$ – known to be active

for hydroformylation^[10] – by reaction of $[\text{Rh}_4(\text{CO})_{12}]$ with H_2/CO was observed recently.^[11]

Regarding the aforementioned hydroformylation reactions with metal colloids as catalyst precursors, the question arises whether colloidal particles themselves can be active at their surfaces, or whether the colloidal particles act as a reservoir for mononuclear species (Scheme 1).

Studies of hydroformylation of alkenes in a single phase homogeneous system require metal colloids stable in apolar organic solvents. Based on investigations of noble metal colloids stabilized by amphiphilically modified hyperbranched polyglycerols^[12] and their catalytic properties,^[13] we had turned to amidated poly(ethylene imine)s as models for the structure of metal colloids stabilized by amphiphilic polymers with a polar hyperbranched core.^[14] Amidated poly(ethylene imine)s were shown to form unimolecular inverted micelles in aromatic hydrocarbon solvents.^[14d] This structure is retained upon loading with silver ions and reduction to silver nanoparticles, when a polymer of appropriate core molecular weight is used.^[14c] These findings prompted us to utilize these polymers for the preparation of rhodium colloids.

It is worth noting that Geissler et al. have studied hydroformylation reactions employing Rh^{I} complexes in combination with alkoxyated or amidated poly(ethylene imine)s. The recovery of the catalyst from the high boiling residue obtained after distillation of the reaction mixture by membrane techniques was studied. As an example, hydroformylation of 1-octene at 280 bar H_2/CO (1:1) and 100 °C by a catalyst formed by mixing an amidated poly(ethylene imine) with $[\text{Rh}^{\text{I}}(\text{acac})(\text{CO})_2]$, (acac = acetylacetonate) resulted in 99.7% conversion of 1-hexene, yielding 99.3% nonanals with an *n*-selectivity of 54%.^[15]

Results and Discussion

The preparation of poly(ethylene imine)-amide stabilized rhodium colloids was studied for different reducing agents and metal precursors in toluene solution.^[16] For the studies reported here, colloids prepared by reduction of $[\text{Rh}^{\text{I}}(\text{acac})(\text{C}_2\text{H}_4)_2]$ with hydrogen were utilized, as these

^a The phenomenon of “activation” of pressure reactors used for hydroformylation, that is the observation that in a reactor previously used for studies of rhodium catalyzed hydroformylation conversion of substrates to hydroformylation products will also occur without added catalyst, is also well known. This is considered to be due to rhodium deposited on the reactor walls.

Figure 1. TEM micrograph and corresponding number weighted histogram of a rhodium colloid.

were found to have a high colloidal stability, being stable for weeks and longer. Under the concentration conditions and with the composition of polymer employed (cf. Experimental Part), particle sizes were typically 2 ± 0.5 nm (cf. Figure 1).

The hydroformylation of 1-hexene was studied with such colloids. For comparison, hydroformylation by polymer-coordinated non-reduced rhodium(I) precursor complexes and also by the Rh(0) carbonyl $[\text{Rh}_6(\text{CO})_{16}]$ in the presence of polymer was investigated (Table 1). Reactions were performed at 120°C under 50 bar H_2/CO (1:1). In all cases, virtually complete conversion is observed. Also with the colloids as catalyst precursors, hydroformylation prevails over hydrogenation and isomerization products (*n*-hexane and hexene isomers). The overall course of reaction was studied by following the gas uptake over time by means of mass-flow meters (supporting information). For a rhodium colloid, and for non-reduced $[\text{Rh}^{\text{I}}(\text{acac})(\text{C}_2\text{H}_4)_2]/\text{polymer}$, very similar profiles were observed. In

detail, a difference between rhodium colloids and rhodium complexes as catalyst precursors is observed. With the colloids as catalyst precursors, a higher portion of hydrogenation and isomerization side-products is found. This is particularly pronounced for a colloid prepared by reduction with $\text{Li}[\text{BHEt}_3]$ instead of the usually employed reducing agent hydrogen (entry 1-3), which was less colloidal stable and partially coagulated. It is well known that noble metal surfaces, as present in the rhodium nanoparticles, catalyze olefin hydrogenation. The observation that the formation of hexane and internal hexenes is most pronounced with the less colloidal stable and partially aggregated colloid as a precursor (entry 1-3) can be interpreted as formation of hydroformylation active species being less rapid in this case.

Reducing the amount of rhodium in the reaction mixture from $10\ \mu\text{mol}$ down to $2.5\ \mu\text{mol}$ under otherwise identical conditions as in entry 1-1, complete conversion was still achieved in 3 h reaction time. This corresponds

Table 1. Hydroformylation of 1 hexene with rhodium colloids and rhodium complexes as catalyst precursors. Reaction conditions: $T = 120^\circ\text{C}$, $p = 50$ bar (H_2/CO 1:1); $[\text{1 hexene}] = 0.8\ \text{mol L}^{-1}$ (10 mL in 90 mL toluene); $10^{-5}\ \text{mol Rh}$; metal to N atoms of polymer ratio 1:2; reaction time: 3 h.

Entry	Catalyst precursor	Conversion of 1-hexene	Selectivity for aldehydes
		%	%
1-1	colloid ^{a)} (prepared via H_2 reduction)	98	96
1-2	comparative: $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]/\text{PEI}$ amide	>99	99
1-3	colloid ^{a)b)} (prepared via $\text{Li}[\text{BHEt}_3]$ reduction)	>99	88
1-4	comparative: $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PEI}$ amide	>99	99
1-5	comparative: $\text{Rh}_6(\text{CO})_{16}/\text{PEI}$ amide	>99	99

^{a)}Prepared by reduction of $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]$ in the presence of PEI amide with the reducing agent given; ^{b)}Partially coagulated.

Table 2. Conversion and selectivity versus pressure. Reaction conditions: $T = 120^{\circ}\text{C}$, H_2/CO 1:1; [1 hexene] 0.8 mol L^{-1} (10 mL in 90 mL toluene); 10^{-5} mol Rh ; metal to N atoms of polymer ratio 1:2; reaction time: 3 h.

Entry	Pressure	Conversion of 1-hexene	Selectivity for aldehydes	Linear/branched aldehydes
	bar	%	%	
2-1	10	98	7	40:60
2-2	20	98	40	42:58
2-3	30	99	61	41:59
1-1	50	98	96	41:59

to a total of 3×10^4 TO (TO = turnover, mole 1-hexene converted per mole Rh), calculated with respect to all rhodium present in the reaction mixture.

The influence of the synthesis gas pressure on selectivity was studied in the range from 10 to 50 bar total pressure (Table 2).

Hydrogenation and isomerization products of 1-hexene are formed preferentially rather than hydroformylation products at lower pressures. The formation of hydroformylation products increases with increasing pressure, and hydroformylation is the major reaction at pressures above 30 bar. The prevalence of hydrogenation and isomerization at low pressures of H_2/CO can be interpreted as the formation of hydroformylation-active species being slow under these conditions such that hydrogenation on the colloid surface can compete with hydroformylation effectively.

The selectivity for the different aldehyde isomers does not vary much with pressure at the reaction temperature of 120°C studied (Table 2). Heptanal and 2-methylhexanal are formed in equal amounts, the amount of 2-ethylpentanal is ca. 40% of the linear aldehyde.

The influence of reaction temperature was studied in the range of 80 – 120°C , at a constant 50 bar total synthesis gas pressure (Table 3).

At 80°C , 95% conversion are observed after 3 h of reaction time, at temperatures of 90°C and higher, conversion is virtually complete. The selectivity for hydroformylation increases with temperature, at 80°C about one-third

of the substrate is converted to by-products from hydrogenation and isomerization, whereas at 120°C byproducts account for only 3%. The selectivity for *n*-aldehyde versus branched aldehydes is higher at lower temperature. At 80°C , 70% of the aldehydes formed are heptanal, and no 2-ethylpentanal is observed.

The aforementioned findings show that high selectivities for aldehydes, and a relatively high selectivity for *n*-aldehyde at the same time should be expected at high pressures and low reaction temperatures. At 80°C reaction temperature, pressures up to 90 bar were studied (Table 4). Within the aldehyde product fraction, selectivity for the *n*-aldehyde decreases slightly with pressure at this reaction temperature. At 90 bar, virtually complete conversion is observed in the reaction time of 3 h also at this relatively low temperature. Aldehyde selectivity is 96%, with about 60% of the aldehydes formed being *n*-aldehyde (entry 4-2).

Summary and Conclusion

In conclusion, rhodium nanoparticles (2–3 nm size) stabilized by poly(ethylene imine)-amide are active for the hydroformylation of 1-hexene. Selectivities are similar to comparative experiments with Rh(I) complexes or with $[\text{Rh}_6(\text{CO})_{16}]$ as a catalyst precursor in the presence of the polymer. In detail, selectivity for hydrogenation and isomerization of olefin as side reactions are significantly

Table 3. Conversion and selectivity versus reaction temperature. Reaction conditions: $p = 50 \text{ bar}$ (H_2/CO 1:1); [1 hexene] 0.8 mol L^{-1} (10 mL in 90 mL toluene); 10^{-5} mol Rh ; metal to N atoms ratio 1:2; reaction time: 3 h.

Entry	T	Conversion of 1-hexene	Selectivity for aldehydes	Linear/branched aldehydes
	$^{\circ}\text{C}$	%	%	
3-1	80	95	62	70:30
3-2	90	99	82	50:50
3-3	100	>99	88	45:55
1-1	120	98	96	41:59

Table 4. Conversion and selectivity versus pressure at 80 °C. Reaction conditions: T 80 °C, H_2/CO 1:1; [1 hexene] 0.8 mol L⁻¹ (10 mL in 90 mL toluene); 10^{-5} mol Rh; metal to N atoms of polymer ratio 1:2; reaction time: 3 h.

Entry	Pressure	Conversion of 1-hexene	Selectivity for aldehydes	Linear/branched aldehydes
	bar	%	%	
3-1	50	95	62	70:30
4-1	70	>99	75	66:34
4-2	90	>99	96	58:42

higher for the colloids. Both the latter reactions are well known to occur on metal surfaces. An activation of the colloids for hydroformylation occurs rapidly. From the similar course of the reaction observed with colloids and complexes as catalyst precursors, we speculate that colloidal rhodium is converted to catalytically active $[HRh(CO)_nL_m]$ complexes under reaction conditions. That is, in terms of Scheme 1 the colloidal rhodium metal particles serve as a reservoir from which soluble active species are formed (pathway a in Scheme 1). The somewhat higher selectivity for hydrogenation and isomerization with colloids as a catalyst precursor is considered to be due to these reactions occurring on the intact metal nanoparticles, present particularly in the early stages of the reaction. Selectivities for aldehydes increased with pressure in the range studied, and with temperature (80 to 120 °C, 50 bar). A productivity of up to 3×10^4 TO was observed (calculated with respect to all rhodium present). Concerning the selectivity of the reaction, at 80 °C and 90 bar 1-hexene is converted completely with 96% selectivity for aldehyde and about 60% selectivity for the linear aldehyde. Overall, the selectivities observed are in line with the extensive previous studies of hydroformylation of alkenes and the known necessity for phosphines or similar ligands if high n -selectivities are desired.

The foregoing considerations are of interest in the context of the development of more robust catalysts for hydroformylation and carbonylation reactions in general. Formation of elemental metal precipitates is a notorious deactivation mechanism in carbonylations with soluble noble metal catalysts. Colloidal stabilization at the stage of small nanoparticles, i.e., prevention of irreversible precipitation of bulk metal, in combination with oxidation reactions (e.g., oxidative addition of substrate) could increase catalyst lifetime and stability.

Experimental Part

TEM analyses were performed on a LEO 912 Omega microscope at an acceleration voltage of 120 kV. A copper grid, covered with a carbon film, was shortly immersed in the colloidal solution, and

the residual solvent was evaporated. Gas chromatographic analyses were performed on a Chrompack CP9003 instrument equipped with a 30 m CP-Sil-5-CB fused-silica column (diameter 0.25 mm) and an FID detector. After 10 min isothermal at 35 °C, the temperature was raised to 250 °C with a rate of 25 °C min⁻¹ (nitrogen as a carrier gas; injector temperature 270 °C; detector 290 °C). Aldehydes were determined versus methylhexanoate added as an internal standard.

Toluene was distilled from sodium under argon. 1-hexene (99%) supplied by Aldrich was degassed prior to use. A carbon monoxide/hydrogen 1:1 mixture of 99.999% purity was supplied by Messer Griesheim. $[Rh(acac)(C_2H_4)_2]$ ^[17] and $[Rh(acac)(CO)_2]$ ^[18] were prepared according to published procedures. Poly(ethylene imine)amide with a degree of amidation of 57% was prepared from poly(ethylene imine) with $\overline{M}_w$ 5 000 g mol⁻¹ (BASF Lupasol; $\overline{M}_w/\overline{M}_n$ 1.1)^[19] and palmitic acid as previously reported.^[14d]

Colloid Preparation

A solution of $[Rh(acac)(C_2H_4)_2]$ in dry toluene (1 Rh per 2 N atoms) was added to a solution of PEI/amide in toluene (10 g L⁻¹). The resulting clear yellow solution was stirred at room temperature for 2 h and transferred to a Kontes flask. The solution was degassed briefly by bubbling with H₂, and the flask was pressurized with a slight overpressure of hydrogen (1.5 bar). The flask was left lying for 3 d. The dark solution obtained was brought to a precise volume by dilution with toluene, and stored under argon.

Hydroformylation

A Büchi model Limbo 350 high-pressure autoclave consisting of a 285 mL stainless steel vessel equipped with a magnetically coupled mechanical stirrer (1000 rpm) and a heating/cooling jacket controlled by a thermocouple dipping into the reaction mixture was utilized. A toluene solution of the catalyst precursor (polymer-stabilized nanoparticles or polymer-bound metal complex) was added to a toluene solution containing 10 mL 1-hexene and ca. 1.5 mL methyl hexanoate (weighed precisely) as an internal standard. The solution was cannula-transferred under argon to the reactor, previously flushed with argon. The reactor was closed, flushed three times with argon and once with H₂/CO. The reactor was heated to the reaction temperature. The H₂/CO pressure was kept constant over the entire experiment by means of a pressure controller, also allowing for monitoring of

the gas flow by means of mass flow meters. After 3 h, the vessel was cooled and the pressure released, and the reaction medium was transferred to a flask under argon by means of a syringe.

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