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Hydroformylation in microemulsions: conversion of an internal long chain alkene into a linear aldehyde using a water soluble cobalt catalyst

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Abstract

The hydroformylation of 7-tetradecene with Co-TPPTS was studied in microemulsions as reaction media at various temperatures, pressures and surfactant concentrations. The influence of metal concentration and ligand excess on activity and selectivity has been investigated. The use of cobalt based catalysts resulted in isomerization of the internal double bond of 7-tetradecene to yield more than 50% terminal aldehydes. A change in the selectivity for linear aldehydes at different temperatures and metal to ligand ratios indicates a shift in the equilibrium between modified and unmodified cobalt species.
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1. Introduction

The hydroformylation, discovered by Otto Roelen at Ruhrchemie in 1938 [1], is one of the most important reactions using homogeneous catalysis in industry with production capacities of more than 6 million tonnes per annum [2]. Alkenes react with carbon monoxide and hydrogen in the presence of a transition metal catalyst to a mixture of linear or branched aldehydes. Industrial important catalysts consist of rhodium and cobalt, exclusively [3]. For the hydroformylation of short chain alkenes like propene or butene, the use of ligand modified rhodium catalysts enabled mild reaction conditions and resulted in high yield of linear aldehydes. Due to the high price of rhodium, continuous improvements have been made to ensure complete catalyst recovery [4]. Application of the water soluble phosphine ligand TPPTS (*meta* triphenylphosphine trisodiumsulfonate) in the Ruhrchemie/Rhône-Poulenc process has made the catalyst recovery easy and complete with rhodium losses in the range of ppb [5]. However, this biphasic process is limited to short chain alkenes due to the required olefin solubility in water [6]. Alkenes with carbon numbers higher 8 are hydroformylated in the presence of cobalt based catalysts under more severe reaction conditions with temperatures between 150 and 200 °C and total syngas pressures between 200 and 300 bar. Cobalt recovery can be achieved either by oxidation (BASF) [7] or by chemical transition (Exxon) [8], each followed by catalyst recovery and regeneration. Ligand modified cobalt catalysis only gained importance in the Shell process [9], operating with triphenylphosphine (TPP) as ligand. Beller combined the concept of ligand modification with the technique of two phase catalysis by using water

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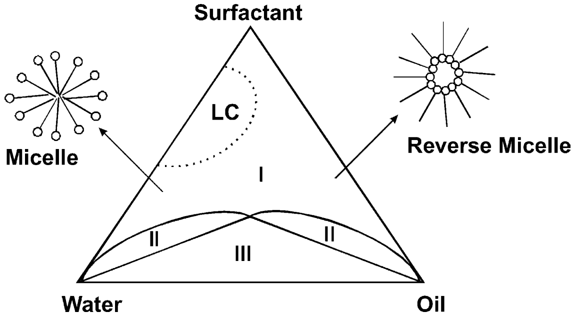

Fig. 1. Schematic phase triange with illustration of normal and reverse micelles.

soluble Co-TPPTS [10]. He reported high reaction rates and *n*/*iso* selectivities for the hydroformylation of 3-pentene. Temperatures were in the range of 100 to 190 °C with pressures between 80 and 100 bar. In order to ensure solubility between the aqueous and the organic phase, co-solvents (1-butanol) were added.

An alternative for solving the problem of miscibility between oil (higher alkene) and water (aqueous catalyst solution) is the addition of surfactants to form microemulsions [11]. They form spontaneously and are thermodynamically stable dispersions. The phase behaviour of these ternary mixtures can be described by using the Gibbs phase triangle depicted in Fig. 1. At low oil concentrations micelles are formed, small oil droplets surrounded by a surfactant layer in a continuous water phase. At high oil concentrations reverse micelles are formed, consisting of small water droplets in a continuous oil phase.

These reverse micelles, containing the water soluble rhodium catalyst complex, act as microreactors for the hydroformylation [12]. Alkenes, carbon monoxide and hydrogen approach from the oil phase to the interface of the micelle. After the reaction is completed, phase separation can be achieved by changing the temperature of the reaction mixture. When the mixture is cooled down an aqueous bottom phase, containing most of the surfactant separates from the organic upper phase, consisting of unreacted alkene, aldehydes and small amounts of surfactant.

A first attempt at hydroformylation in a micellar system using a water soluble rhodium catalyst (Rh-TPPTS) was made by Tinucci and Platone from Eniricherche in 1990 [13]. They converted 1-alkenes with carbon numbers up to 12 in a mixture of an anionic surfactant (SDS) and 1-butanol (as co-surfactant). It has been shown that ternary systems containing nonionic surfactants from the alkyl-polyglycolether type (Marlipal) form stable microemulsions without the need of co-surfactant [14]. 1-Dodecene was hydroformylated using Rh-TPPTS at moderate reaction conditions with temperatures around 80 °C and pressures between 60 and 80 bar [12]. Linear aldehydes could be obtained in 75% yield using low ligand excess (L/M = 4). Catalyst recycling is simplified by temperature induced phase separation, followed by an ultrafiltration step. The internal alkene 7-tetradecene could not be converted to terminal aldehydes due to the highly reactive rhodium catalyst [15]. Hydroformylation of the internal double bond occurred before isomerization towards terminal positions, thus resulting in a broad product distribution of branched aldehydes. In this work, we report on the application of water soluble catalysts based on cobalt for the combined isomerization and hydroformylation of 7-tetradecene. Water soluble cobalt catalysts are able to allow shifting of the internal double bond towards terminal positions before hydroformylation [10].

2. Experimental setup

All hydroformylation experiments were carried out in a 100 ml stainless steel autoclave equipped with a gas dispersion stirrer and flow spoiler. The reaction was performed in semi-batch mode by syngas being permanently made up to maintain a constant pressure inside the reactor. Samples were taken at intervals and analyzed by gas chromatography. All chemicals were purchased from Sigma–Aldrich or Fluka and used without further purification. The water soluble cobalt complex was synthesized and purified according to the literature. The technical grade surfactants were purchased from Sasol, Germany. A 1:1 mixture of carbon monoxide and hydrogen from Messer Griesheim was used.

All experiments were carried out using a microemulsion with 79 wt.% of 7-tetradecene, 13 wt.% of surfactant Marlipal O13/80 and 8 wt.% of aqueous catalyst solution. Standard reaction conditions: cobalt concentration 200 ppm with respect to the microemulsion, ligand to metal ratio 1:1, olefin to metal ratio 2500. The catalyst was prepared from $Co_2(CO)_8$

and TPPTS according to a procedure described in [18,19].

3. Results

3.1. Variation of temperature

As known from literature, cobalt is less reactive than rhodium and internal alkenes are less reactive than terminal alkenes in hydroformylation. Reaction temperatures have to be higher for cobalt catalysts in order to ensure acceptable reaction rates. The influence of temperature was studied between 120 and 160 °C. At temperatures around 140 °C, a single phase microemulsion could not be established by the use of the available Marlipal surfactants. Therefore, not all of the alkene was emulsified with the water, resulting in an upper organic phase which could act as a substrate reservoir. All experiments were carried out at 120 bar syngas pressure. For all experiments summarised in Table 1 the overall cobalt concentration was 200 ppm and the ligand/metal (L/M) ratio was 1:1. The products were analysed for their content of linear and branched aldehydes, expressed as l:b-ratio, and the conversion of 7-tetradecene, expressed as:

$$X = \frac{c_{\text{olefin},0} - c_{\text{olefin}}}{c_{\text{olefin},0}}$$

At temperatures below 160 °C the cobalt catalyst is almost inactive with only small conversion at 140 °C. At 160 °C the system becomes highly active with 86% alkene conversion after 10 h of reaction time. Two reasons may account for this effect: the low activity of the cobalt species at lower temperatures and the increased mobility of the internal double bond with higher temperatures. GC–MS experiments proved 45% yield of terminal aldehydes (l:b = 0.83), which are only accessible from 7-tetradecene after isomerization of the double bond. All further experiments were carried out at 160 °C due to the low activity of the cobalt complex at lower temperatures.

Table 1
Hydroformylation of 7-tetradecene as a function of temperature at 120 bar syngas pressure

Temperature (°C)	Conversion X (after 10 h)	l:b	Alcohols (%)
120	–	–	–
140	0.14	n.d.	n.d.
160	0.86	0.83	25

200 ppm cobalt, L/M = 1.

3.2. Influence of total syngas pressure

Using a 1:1 mixture of hydrogen and carbon monoxide, the conversion as a function of pressure was studied at 160 °C between 40 and 120 bar as shown in Fig. 2.

The conversion is strongly dependent on the pressure applied. At lower pressures the conversion is very low, probably due to poor solubility of the syngas in the organic phase, thus the reaction becomes transport limited. This limitation is overcome at pressures above 80 bar. In Table 2, the conversion and the selectivities are compiled.

With increasing pressure, the reaction is accelerated, resulting in higher conversion. The ratio between terminal and branched aldehydes is 1.06 both for 80 and 100 bar, thus indicating that 51% of the internal double bond were isomerized and converted into linear products. This value drops towards 45% isomerization (l:b = 0.83) when operating at 120 bar syngas pressure. In the Shell process using Co-TPP catalysts, the formed aldehydes are mainly (80%) converted into alcohols by consecutive hydrogenation. The amount of alcohols formed in the microemulsion experiments is significantly lower, increasing from 20% at 80 bar to 25% at 120 bar. However, the amount of alcohol formed is higher than comparable results by Beller, who reported only minor alcohol formation (∼1.5%) under similar conditions. These results are interesting because traces of water are known to enhance the formation of alcohols in the Shell process.

Table 2
Hydroformylation of 7-tetradecene as a function of total syngas pressure at 160 °C

Pressure (bar)	Conversion X (after 10 h)	l:b	Alcohols (%)	k_{obs} ($\times 10^{-3}$ min^{-1})
40	0.05	n.d.	n.d.	0.1
60	0.36	1.08	15	0.7
80	0.84	1.06	21	1.2
100	0.85	1.06	22	2.0
120	0.86	0.83	25	3.5

200 ppm cobalt, L/M = 1.

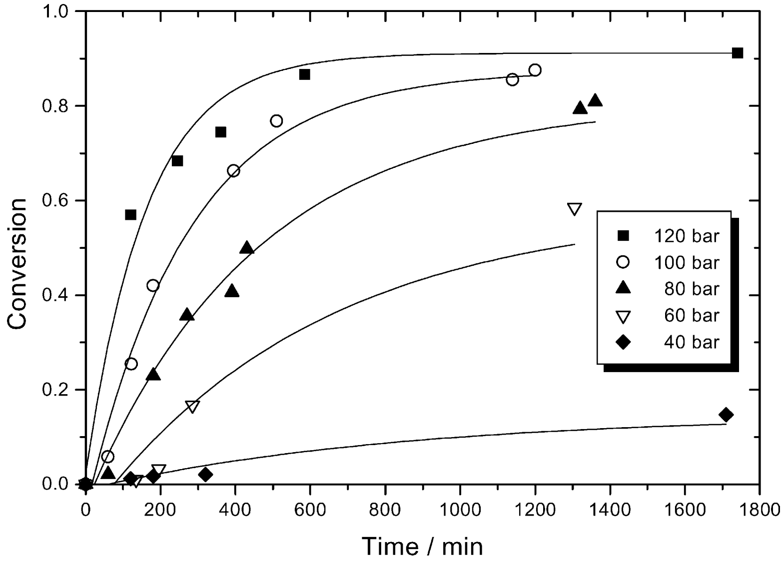

Fig. 2. Hydroformylation of 7-tetradecene at various pressures: 160 °C, 200 ppm cobalt, L/M = 1, Marlipal O13/80.

For the water soluble Rh-TPPTS catalysts the observed reaction rate is a function of olefin and catalyst concentration and partial pressure of both hydrogen and carbon monoxide [16]. The rate constant k_{obs} was determined using data fitting software tools derived by Hugo at TU Berlin from the rate equation developed by Desphande et al. [17].

$$
\begin{aligned}
-\frac{\mathrm{d}c_{\mathrm{Olefin}}}{\mathrm{d}t} &= k_{\mathrm{obs}} \times (c_{\mathrm{olefin}})^n \quad \text{with}\, k_{\mathrm{obs}} \\
&= k_{\mathrm{r}} \times c_{\mathrm{catalyst}} \times (p_{\mathrm{CO}})^x \times (p_{\mathrm{H_2}})^y \\
&\quad \text{with}\, x = 0.7,\ y = 1
\end{aligned}
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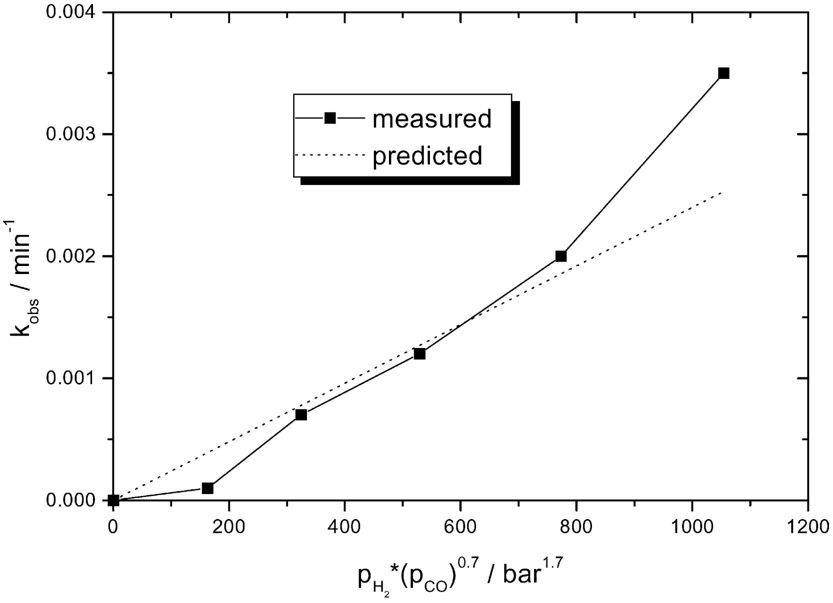

Fig. 3. Pressure dependence of the observed rate constants k_{obs} at 160 °C.

A first order dependence with regard to the olefin was observed in all experiments. Fig. 3 shows the determined k_{obs} as a function of the partial pressure product $p_{H_2} \times (p_{CO})^{0.7}$. A linear dependence should be expected between the rate constant k_{obs} and the product of the partial pressures, indicated by the dotted line. This was true for pressures between 40 and 100 bar. Above 100 bar, the observed value was significantly higher than the predicted one. One reason for this up curved shape could be the formation of an unmodified cobalt carbonyl species. Under the more severe conditions at 160 C and 120 bar the cobalt complex can loose the TPPTS ligand L according to the given equilibrium:

$$HCo(CO)_3L + CO \rightleftharpoons HCo(CO)_4 + L$$

The formation of unmodified cobalt at 120 bar syngas pressure would explain the drop in selectivity towards the linear aldehydes. $HCo(CO)_4$ is far more active than the modified species $HCo(CO)_3L$ and less selective. After the reaction mixture was cooled down and depressurized, the organic upper phase was analyzed by atomic absorption spectroscopy (AAS) for cobalt content. No significant amount of cobalt was detected. However, no in situ experiments were performed to detect the possible unmodified cobalt hydride species.

Table 3
Hydroformylation of 7-tetradecene with Co-TPPTS as a function of ligand to metal ratio at 160 °C

$c_{catalyst}$ (ppm)	L:M	Conversion (after 10 h)	l:b
200	1	0.86	0.83
200	5	0.85	1.40
200	9	0.53	3.30
100	1	0.05	n.d.
150	1	0.09	n.d.
400	1	0.95	0.92

3.3. Variation of the catalyst composition

In a recent publication we have shown that changing the excess of ligand and the concentration of catalyst in a microemulsion system does not have the same effects as in homogeneous or two phase media. Overloading the small micelles with catalyst can result in formation of inactive metal clusters, whereas at high ligand excess the formation of the active species is less favoured. For the cobalt catalyzed hydroformylation

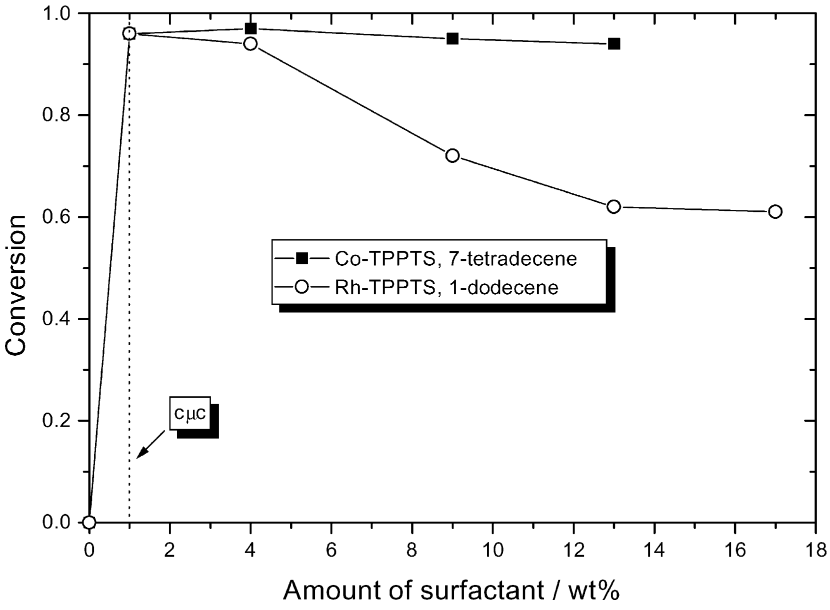

Fig. 4. Conversion of hydroformylation of 7-tetradecene/1-dodecene after 10 h with Co-TPPTS and Rh-TPPTS at different amounts of Marlipal O13/80 in the microemulsion.

of 7-tetradecene the catalyst concentration has been varied between 100 and 400 ppm and the ligand to metal ratio in the range of 1:1–9:1, respectively. The results are shown in Table 3.

The conversion after 10 h reaction time drops to 51% when operating with a ligand to metal ratio of 9. The selectivity towards the linear aldehyde increased under the same conditions to 77%. This behaviour is in good agreement with results for the rhodium 1-dodecene system [12]. However, increasing the overall catalyst concentration to 400 ppm has a positive effect on the conversion. Formation of $HCo(CO)_4$ might account for this result, however could not be verified because no cobalt was detected in the organic phase after the reaction.

3.4. *Variation of the surfactant concentration*

The amount of surfactant was varied between 0 and 13 wt.%. Without any surfactant the reaction rate was zero with no conversion after 10 h. Addition of small amounts of surfactant resulted in a dramatic increase of conversion as depicted in Fig. 4.

Below 1% no aggregation of surfactants to form micelles was observed. Micelles were formed spontaneously at values above 1%, the so called critical microemulsion concentration $c\mu c$. These micelles exhibit a large interfacial surface, resulting in high reaction rates. For rhodium catalyzed hydroformylation of 1-dodecene we noticed a decrease when adding more surfactant. The reason for this was reduced catalyst concentration within the interface layer on the one hand and an increased obstacle for the reactants to pass the surfactant monolayer. This decrease was not observed for cobalt complexes. This might be due to the fact that at 160 °C the reactants were able to pass the interface without any hindrance.

4. Conclusion and outlook

In a recent publication, we have outlined the application of microemulsions as useful reaction media for the hydroformylation of even less reactive higher alkenes using Rh-TPPTS [15]. The catalyst is highly active and converts the internal alkene into the corresponding branched aldehyde with high regioselectivity. In order to obtain linear aldehydes from an internal alkene feedstock, cobalt based catalysts can be used. The cobalt catalyst allows isomerization of the double bond first, followed by hydroformylation. More than 50% of the internal alkene are isomerized into a 1-alkene before hydroformylation although there is no detectable concentration of 1-alkene. In order to increase the linear to branched (l:b) ratio of the obtained aldehydes, either the reaction temperature had to be lowered or the excess of ligand had to be increased. Both ways resulted in decreased reaction rates.

An important aspect for an economical process is the recovery of both metal and ligand. Because surfactants are present in the reaction mixture, simple phase separation is not complete. Recovery of catalyst and ligand can be achieved by consecutive ultrafiltration of the reaction mixture. Only aldehydes, unreacted alkenes and small amounts of surfactant (according to the $c\mu c$ of the system) are able to pass the ultrafiltration membrane. Aggregated surfactants, containing the water soluble catalyst, are retarded, accumulated and reused. Phase separation of the microemulsion after the reaction is very much depending on the total conversion and composition. By different modes of phase separation and ultrafiltration the catalyst recovery can be further optimized. Current research results account for cobalt losses below 1 ppm.

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