

Rhodium-catalyzed hydroformylation of 1-octene in micro-emulsions and micellar media

Christian C. Miyagawa, Jörg Kupka, Adrian Schumpe*

Institut für Technische Chemie, Technische Universität Braunschweig, Hans-Sommer Str. 10, D-38106 Braunschweig, Germany

Received 25 January 2005; received in revised form 14 February 2005; accepted 14 February 2005

Available online 19 March 2005

Abstract

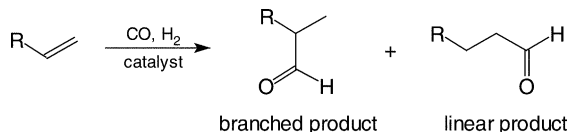
The rhodium-catalyzed hydroformylation of 1-octene and other higher olefins in an aqueous biphasic system was studied at pressures from 40 to 90 bar and temperatures of up to 393 K. The rhodium-TPPTS [tris (*m*-sulfonatophenyl) phosphine] catalytic system was used. Non-ionic amphiphiles of the alkyloxyethylene type were applied to promote the contact between the reacting species by enlargement of the interfacial area. The highest reaction rates were obtained at a surfactant concentration of only about 1 wt.%.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Hydroformylation; Biphasic catalysis; Micro-emulsion; Higher olefins; Rhodium catalyst

1. Introduction

1.1. Hydroformylation

The reaction of olefins with synthesis gas to aldehydes or alcohols is commonly known as hydroformylation or oxo synthesis. The reaction was discovered in 1938 by Otto Roelen at Ruhrchemie [1,2] and has become the most important industrial application of homogeneous catalysis. The present worldwide production capacities for oxo-products are close to 8 million tonnes per year [3].



While the bulk production of *n*-butyraldehyde via hydroformylation of propene is dominant, the conversion of olefins with five or more carbon atoms accounts for about 25% of the worldwide capacities of oxo-products [4]. The most important applications for higher oxo-products are plasticizers and detergent alcohols.

Since the introduction of the Ruhrchemie–Rhône-Poulenc (RCH–RP) process in 1984, the initially used cobalt-based catalyst for propene hydroformylation has now been replaced in nearly all major production plants by the more active rhodium-based catalyst [5]. The RCH–RP process is a liquid–liquid process, where the modified rhodium catalyst is dissolved in the aqueous phase, thus the catalyst can be considered to be heterogeneous with respect to the olefin [6,7]. This technique, which combines the advantages of homogeneous and heterogeneous catalysis, enables the product to be separated by simple phase separation. Thus, the catalyst can be recycled practically without any loss, due to its immiscibility with the organic products.

The solubilities of olefins in water as well as their reactivity, even in monophasic hydroformylation, decrease with increasing number of carbon atoms [8]. Higher olefins, with a chain length greater than six, are not suited for hydroformylation analogous to the RCH–RP process [9]. About 90% of high molar mass oxo-products are still being manufactured in homogeneous media using cobalt catalysts. Thus, a rhodium-based aqueous-organic process for conversion of long alkenes, which combines sufficiently high reaction rates with facile catalyst recycling by decantation, is highly desirable.

* Corresponding author. Tel.: +49 531 391 5365; fax: +49 531 391 5357.
E-mail address: a.schumpe@tu-bs.de (A. Schumpe).

Several approaches have been postulated in the literature to overcome the problem of mutual insolubility of the two phases and low space–time yields of biphasic hydroformylation. The use of phosphine ligands with amphiphilic properties [10–14] is reported to significantly enhance the reaction rate as compared to the Rh–TPPTS system. It was shown that the improved reaction rates were due to the surface activity of these new phosphines and that catalytic activity increased with the aggregation of the ligands becoming more likely [11]. Aqueous solutions of TPPTS show no aggregation at all concentrations of TPPTS [10].

Another type of amphiphilic ligands are the so-called “smart ligands” with an inverse temperature-dependency of their solubility in water [15]. Most of these ligands are tertiary phosphines containing polyethylene oxide (PEO) or block copolymers of ethylene oxide and propylene oxide (PPO) [16–20]. By increasing the temperature, the catalyst is transferred to the organic phase where it catalyzes the reaction and it is moved back to the aqueous phase to be separated from the products at lower temperatures. Amphiphilic properties can also be introduced into a sulfonated ligand by modifying its counter ion. The surface-inactive TPPTS ligand is reported to be converted into an amphiphile by replacing one Na^+ ion by a quaternary phosphonium ion [21]. While hydroformylation of 1-tetradecene with Rh–TPPTS showed no activity, the reaction using the modified ligand was performed successfully with a turnover frequency (TOF) of 186 h^{-1} .

Kanagasabapathy et al. [22] describe the use of methanol- and water-soluble phosphine-ligands. Hydroformylation is carried out homogeneously in methanol and the system is hydrogenised after the reaction by addition of water. This causes the organic product to separate from the aqueous phase and the catalyst can be recovered easily.

A different approach to hydroformylation of higher olefins is to deposit a thin film of water containing the catalyst on the hydrophilic surface of an inorganic support. This is known as supported aqueous phase catalysis (SAPC) [4].

Recently, the use of “modern” solvents as alternative reaction media for hydroformylation of higher olefins has gained much attention. Ionic liquids, for instance, have been found to be excellent solvents for catalysts, due to their polarity [23]. The use of ionic liquids in hydroformylation of higher olefins is reported by Waffenschmidt [24] and Karadia et al. [25]. Another approach is the use of highly fluorinated solvents in biphasic catalysis. Due to their immiscibility with many organic solvents, the fluorinated phase containing the catalyst can be separated easily from the products. The hydroformylation of 1-decene in such reaction systems was described by Horvath [26]. Leitner and co-workers [27,28] describe the application of supercritical CO_2 (scCO_2) as a solvent in hydroformylation. The advantages of this method are high miscibility of scCO_2 with the gaseous reactants and ease of separation of the solvent [29]. However, the catalyst must first be made soluble in scCO_2 , e.g., through co-ordination of fluorinated ligands.

Other efforts to overcome the mutual insolubility of catalyst and organic phase are the use of additives like cyclodextrins [30,31], co-solvents [32,33] or surfactants [34–37]. While the cyclodextrins are considered to enhance the mass transfer by acting as inverse phase transfer catalysts, the addition of co-solvents like ethanol increases the solubility of higher olefins in the aqueous phase, whereas the solubility of water in, e.g., 1-octene is not changed significantly [38]. Surfactants are known to decrease the interfacial tension and to form small aggregates above the critical micellar concentration (CMC). Thus, the reaction rate can be increased by enlargement of the interfacial area. The use of different alkyl polyethylene oxides (C_{10}E_j) as surface-active agents in 1-octene hydroformylation is considered in this paper.

1.2. Micro-emulsions

Micro-emulsions can be formed spontaneously from water (or an aqueous solution), a non-polar organic “oil” and a suitable surfactant in a determined composition [39]. Macroscopically, the mixtures are homogeneous. However, on a microscopic level, the ternary mixtures are structured as water-rich and oil-rich domains, which are separated by an amphiphilic film. Due to the very large interfacial area, micro-emulsions can be used as media for chemical reactions between two reactants with a mutual solubility gap. But also the reversibility of the solubilization of compounds with opposite polarity and the fact that the liquids are compartmentized in drops with given properties (e.g., shape and drop size) is counted as an advantage for the use of micro-emulsions as reaction media [40]. The composition of a micro-emulsion can be characterized through its content of organic liquid in the binary oil–water mixture, α , and the mass fraction of surfactant γ in the ternary mixture [41].

$$\alpha = \frac{m_{\text{oil}}}{m_{\text{oil}} + m_{\text{water}}} \quad (1)$$

$$\gamma = \frac{m_{\text{surfactant}}}{m_{\text{surfactant}} + m_{\text{oil}} + m_{\text{water}}} \quad (2)$$

The size and shape of the oil- and water-rich domains are a function of α and γ . Usually, the behavior of a micro-emulsion is studied in pseudo-binary phase-diagrams, where one variable is kept constant. For a given surfactant concentration, the microstructure of a micro-emulsion can vary from oil droplets dispersed in water (o/w) over a bi-continuous structure to a water in oil system (w/o) depending on the oil content α . The stability of micro-emulsions containing polyoxyethylenes as surfactants is strongly influenced by the temperature [42]. For a given oil mass fraction α , the temperature-dependent phase behavior is usually depicted as a function of the concentration of the amphiphile γ . At low temperatures, the surfactant solubility is higher in the aqueous phase. Therefore, an oil in water (o/w) micro-emulsion in equilibrium with an oil excess phase (2) is formed. With increasing temperature, the solubility of the hydrophilic head of the amphiphile in water decreases, whereas the

overall solubility of the molecule in the oil phase increases. At low surfactant concentrations, a new micro-emulsion phase (3) is formed between the oil- and the water-rich phase. At high concentrations of the amphiphile, both water and oil are completely solubilized in the micro-emulsion and the system consists of a single phase (1). A further increase of the temperature leads to a w/o micro-emulsion in equilibrium with an aqueous excess phase (2).

The observation that micro-emulsions show a temperature dependent and reversible phase behavior, gave rise to the idea of using them as reaction media for hydroformylation with water-soluble rhodium catalysts [34]. However, Tinucci and Platone [34] initially preferred monophasic micro-emulsions, and so high contents of surfactant and/or co-surfactant were needed to generate such pseudo-homogeneous systems. The use of smaller amounts of surfactant to form (2), (2̄) or (3) micro-emulsions would also produce some interesting reaction media. For instance, the reaction could be performed in a system containing a water-soluble surfactant, which generates a (2̄) w/o micro-emulsion at higher temperatures. After reaction, the catalyst droplets would be transferred back to the aqueous phase by cooling down the mixture, and the organic product could be separated by decantation. Haumann et al. [43,44] have applied this approach to the hydroformylation of 1-dodecene and 7-tetradecene, respectively. This study is concentrated on hydroformylation of 1-octene; 1-dodecene is used for comparison.

2. Experimental

2.1. Reagents

1-Octene (>99%, Acros Organics), 1-dodecene (95%, Fluka Chemie AG) and TPPTS tri-sodium salt (97%, Aldrich) were used without purification. Rhodium(III) acetate was purchased from Heraeus AG. Synthesis gas (51.5 vol.% CO, rest H₂) and the fatty alcohol polyoxyethylenes (Table 1), CH₃(CH₂)₉O(CH₂CH₂O)_{*n*}H, were kindly provided by BASF AG and used as received. Water was deionized, distilled and stripped with nitrogen gas prior to use.

2.2. Apparatus

All hydroformylation reactions were carried out in a 0.31 stainless steel autoclave (Parr Instrument) fitted with

a magnetic stirrer and an automatic temperature control unit. The reactor was connected to a thermostated reservoir containing the synthesis gas. From this reservoir, the reactor was fed with gas via a constant-pressure regulator. The reservoir was equipped with a pressure transducer, which was connected to a personal computer with an A/D converter card for data logging. The consumption of gas was recorded as a function of time throughout all experiments. The initial reaction rates R_0 (h⁻¹) were calculated from the syngas absorption up to 10% conversion of 1-octene. The turnover frequencies TOF (h⁻¹) were calculated from the moles of aldehydes at a reaction time of 2 h. Liquid samples were analyzed with a Shimadzu 14 B gas chromatograph, equipped with a FID. Rhodium concentrations were measured with a Perkin-Elmer 3110 atomic absorption spectrometer.

2.3. Procedure

The catalyst solution containing the active species HRh(CO)(TPPTS)₃ was prepared from the catalyst precursors rhodium(III) acetate, TPPTS and water, by contacting the mixture with synthesis gas at 30 bar and 353 K for a time of 3 h. This treatment is known as preforming and was carried out with amounts sufficient for 4–5 hydroformylation runs. The catalyst concentration is always referred to the aqueous phase. Usually, it was 100 ppm at a Rh–P ratio of 1:10.

The reactor was charged with the weighed amounts of 1-octene ($\alpha = 60$ wt.%), catalyst solution and surfactant. To remove oxygen, the gas phase in the reactor was first flushed with nitrogen, then with synthesis gas. After reaching the desired temperature, the reactor was pressurized with synthesis gas and the stirrer was started. Reproducibility was checked by carrying out some of the experiments twice or more. For determining the loss of rhodium, the reaction was stopped and the mixture was cooled down after a reaction time of 2 h. A sample of the organic phase was withdrawn and analyzed through atomic absorption spectrometry.

The phase behavior of micro-emulsions was studied in test tubes as described by Kahlweit et al. [45] and in an autoclave at high syngas pressures. The results agreed well, i.e., the effect of the dissolved gases is negligible. More experimental details are reported by Miyagawa [46].

3. Results and discussion

3.1. Micro-emulsions

Industrial fatty alcohol ethoxylates consist of a mixture of surface-active agents, rather than of one pure compound. However, an approximate degree of ethoxylation can be specified and the average alkyl chain length can be estimated. When added to water–oil mixture, the different surfactant molecules show a different distribution between the phases. This leads to the well-known effect [47], that the “fish” is not horizontal but inclined (Fig. 1).

Table 1
Specifications of the used surfactants

Surfactant	Formula ^a	Alcohol content ^b (wt.%)	HLB ^c value
Lutensol® ON 30	C ₁₀ E ₃	10	9
Lutensol® ON 50	C ₁₀ E ₅	6	11.5
Lutensol® ON 70	C ₁₀ E ₇	4	13
Lutensol® ON 80	C ₁₀ E ₈	2	14
Lutensol® ON 110	C ₁₀ E ₁₁	1	15

^a Alkyl-group carbon number and number of ethoxyl groups (mean).

^b Manufacturer's specification.

^c Hydrophilic–lipophilic balance.

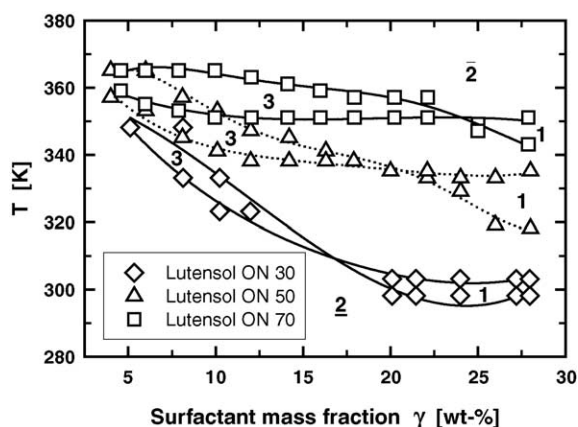


Fig. 1. Influence of the surfactant type on the phase behavior of water–1-octene micro-emulsions ($\alpha = 60$ wt.%).

The hydrophilicity of the surfactant increases with the degree of ethoxylation. The more water-soluble a surfactant, the higher will be the temperature required for the system to form a third or one single phase (phase inversion temperature). The oil-solubilizing power of the surfactant thus decreases with increasing hydrophilicity [48]. When using highly water-soluble surfactants, the systems remain biphasic at all investigated temperatures even at high values of γ . The investigation of the temperature dependent phase behavior of micro-emulsions as shown in Fig. 1 can be essential for choosing the appropriate amphiphile for biphasic hydroformylation. For several biphasic reactions in micro-emulsions, it has been reported that the reaction rate is strongly influenced by the phase condition. In the case of a bimolecular substitution reaction, Tjandra et al. [60] observed that the conversion rates were highest in a three-phase micro-emulsion, indicating that reaction took place in the middle phase.

The phase behavior of micro-emulsions is also affected by the properties of the oil. Fig. 2 shows the phase-diagram of the system water–oil–Lutensol[®] ON 30 with 1-octene and 1-dodecene. Due to the higher solubility of the less hydrophobic

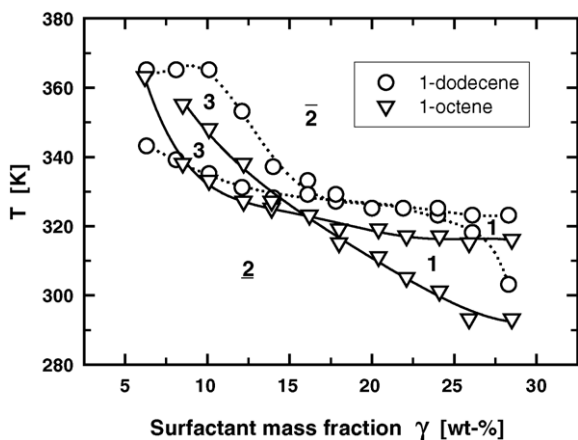


Fig. 2. Influence of the olefin chain length on the micro-emulsion phase behavior (Lutensol[®] ON 30, $\alpha = 80$ wt.%).

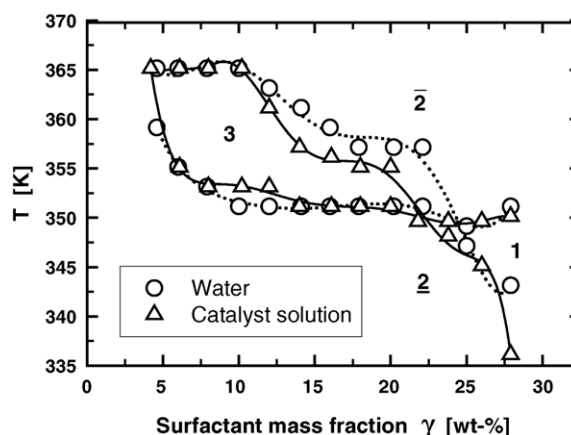


Fig. 3. Influence of the catalyst solution on the phase behavior (500 ppm Rh, P:Rh = 5:1, $\alpha = 60$ wt.% and Lutensol[®] ON 70).

1-octene in water, less surfactant is needed for the formation of a single-phase micro-emulsion. Also the temperature required to form a single-phase micro-emulsion is lower for 1-octene than for 1-dodecene. These results agree with the general trends reported in the literature [39].

The use of inorganic salt solutions, instead of pure water, can drastically change the phase behavior of a micro-emulsion [49]. Therefore, the influence of the electrolytes in the catalyst solution on the phase behavior was studied. As shown in Fig. 3, the phase behavior of the two systems is similar. The temperature for the (2) \rightarrow (3) phase transition remains constant, while the transition (3) \rightarrow 2-bar occurs at lower temperatures in the presence of the catalyst. The effect is more distinct at high surfactant mass fractions, where the (2) \rightarrow (1) transition temperature is lowered significantly compared to the system with water. Overall, the influence of the inorganic salts is relatively weak, as expected in systems with non-ionic surfactants [39].

3.2. Hydroformylation

3.2.1. Influence of the type of surfactant and its concentration

A variety of non-ionic surfactants with different degrees of ethoxylation were tested. Table 2 shows the results for the hydroformylation of 1-octene in micro-emulsions with

Table 2
Hydroformylation of 1-octene in micro-emulsions with various surfactants (70 bar, 373 K, $\alpha_0 = 60\%$, 100 ppm Rh, P:Rh = 10:1, $\gamma = 15\%$ and $t = 2$ h)

Run	Amphiphile	R_0^a (h ⁻¹)	TOF ^b (h ⁻¹)	Yield _{aldehydes} (%)	n^c (%)
1	Lutensol [®] ON 50	14161	4314	61	59
2	Lutensol [®] ON 70	6360	3437	49	59
3	Lutensol [®] ON 80	6485	3058	44	67
4	Lutensol [®] ON 110	6454	2746	40	68

^a Initial reaction rate calculated from the syngas absorption up to 10% conversion of 1-octene.

^b Calculated from the moles of aldehydes at a reaction time of 2 h.

^c Molar fraction of *n*-nonanal.

various Lutensol® ON amphiphiles after a reaction time of 2 h.

The highest initial reaction rates R_0 (aldehyde formation rate r_0 referred to moles of rhodium) were obtained with the hydrophobic surfactant Lutensol® ON 50, followed by the other three surfactants in the order of their degree of ethoxylation. However, with Lutensol ON 50 as well as with Lutensol ON 110, the reaction systems tend to foam. This hinders the separation of the catalyst solution from the organic products. Lutensol® ON 70 combines high hydroformylation rate with easy phase separation.

From a comparison of the initial reaction rates (Table 2) with the phase behavior (Fig. 4), it can be concluded that the latter has no intrinsic influence on the reaction kinetics. While the reaction mixture with Lutensol® ON 70 forms a biphasic micro-emulsion, the corresponding solution of Lutensol® ON 110 gives a system with an extended middle phase. The initial hydroformylation rates, however, are the same in both systems. On the other hand, both Lutensol® ON 70 and Lutensol® ON 50 form biphasic micro-emulsions with similar volumes but the initial hydroformylation rates differ.

The results of hydroformylation at various surfactant concentrations are depicted in Fig. 5. The strong increase of the rate at low surfactant concentrations is due to enlargement of the interfacial area, i.e., lower mass transfer resistance. This differs from the results of Chen et al. [50] who observed no enhancement of the hydroformylation rate of higher olefins when adding non-ionic surfactants. The reaction rate shows a maximum at about a surfactant mass fraction γ of only 1 wt.% and decreases rapidly at higher surfactant contents. Very similar observations were reported previously by Haumann et al. [44] for 1-dodecene hydroformylation in micro-emulsions. This trend is different from a monotonous increase encountered with bimolecular nucleophilic substitution [51]. To understand the trend in Fig. 5, it must be taken into account that the monomolecular surfactant film between the phases can act as a barrier limiting the contact between the reactants.

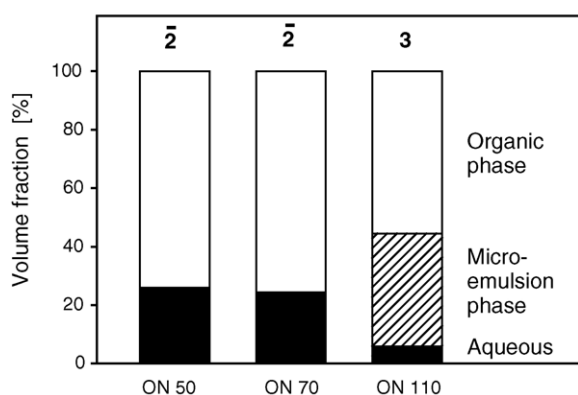


Fig. 4. Influence of the Lutensol® type on the phase behavior at reaction conditions (cf. Table 2) (373 K, $\alpha_0 = 60\%$, 100 ppm Rh, P:Rh = 10:1 and $\gamma = 15$ wt.%).

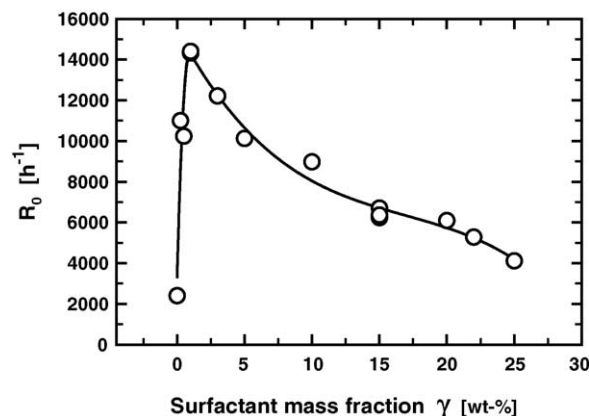


Fig. 5. Influence of the Lutensol® ON 70 concentration on the initial rate of nonanal formation (70 bar, 373 K, $\alpha_0 = 60\%$, 100 ppm Rh and P:Rh = 10:1).

According to Bauer et al. [52], the mass transfer rate in the presence of surfactants is highest at the critical micellar concentration. For the optimum surfactant concentration of 1%, a space-time yields of $200 \text{ kg m}^{-3} \text{ h}^{-1}$ is calculated from the TOF (Run 8 in Table 3). A further increase in surfactant concentration seems to hinder mass transfer although the interface may still be enlarged. Also the possibility that an increasing amount of amphiphile may interact with the rhodium catalyst should be taken into account as a possible explanation. According to Leckel [56] ethoxylated amphiphiles are able to coordinate to rhodium through their ether groups. The formation of a new rhodium–amphiphile complex could also explain the change of hydroformylation activity.

Noteworthy is the relation between the reaction rate and the selectivity (molar fraction of n -aldehyde): The higher the reaction rate, the lower the selectivity for the (usually desired) n -product (Table 3). The non-ionic surfactant could coordinate to rhodium, extract TPPTS-poor catalyst species into the alkene phase and solubilize water and TPPTS in the

Table 3
Hydroformylation of 1-octene at different surfactant concentrations (70 bar, 373 K, $\alpha_0 = 60\%$, 100 ppm Rh, P:Rh = 10:1, Lutensol® ON 70 and $t = 2$ h)

Run	γ (%)	R_0^a (h^{-1})	TOF ^b (h^{-1})	Yield _{aldehydes} (%)	n^c (%)
5	0	2404	–	16	73
6	0.25	10995	4515	40	n.o.
7	0.5	10231	4561	79 ^d	48
8	1	14320	5046	73	51
9	3	12206	4914	71	50
10	5	10125	4767	69	49
11	10	8974	4049	60	53
2	15	6360	3437	49	59
12	20	6093	3069	45	64
13	22	5276	2764	41	66
14	25	4110	3236	23	72

^a Initial reaction rate calculated from the syngas absorption up to 10% conversion of 1-octene.

^b Calculated from the moles of aldehydes at a reaction time of 2 h.

^c molar fraction of n -nonanal.

^d $t = 143$ min.

alkene phase. Thus, catalyst species of different activity and selectivity may prevail at different surfactant loadings.

The loss of rhodium through “leaching” into the organic phase is dependent on the type of surfactant. Table 4 shows the rhodium content in the organic phase after a reaction time of 2 h for systems with different Lutensol® surfactants. Best results were obtained with Lutensol® ON 70, with a rhodium loss ranging from 0.0 to 1.5 ppm for experiments under identical conditions.

Since the maximum tolerable loss of rhodium in biphasic hydroformylation is given as 0.3 ppm [2], further investigations have to be undertaken to optimize the micellar reaction system with regard to noble metal leaching.

3.2.2. Influence of the stirring speed

The influence of the agitation speed on the reaction rate was investigated at the surfactant contents of 15–20 wt.%. As expected for a reaction in the kinetic regime, the rate of hydroformylation shows a constant value at higher stirring speeds. Below 600 rpm, there may be gas–liquid mass transfer limitation. Liquid–liquid mass transfer is not expected to be limiting at any agitation speed. The large interface in the micro-emulsion is formed spontaneously and cannot be increased by mechanical agitation. All the other experiments were carried out at an agitation speed of 1000 min⁻¹.

3.2.3. Influence of pressure and syngas composition

The influence of the total pressure on the rate of the hydroformylation of 1-octene depends on the composition of the synthesis gas (Fig. 6). The reaction is accelerated with increasing pressure, when a CO:H₂-ratio of 1:1 is used. This is expected, as the concentrations of the gases in the liquid increase. If the composition of the gas is changed towards a higher proportion of one of the components, the acceleration of the reaction rate is less pronounced and, in the case of excess hydrogen, it reaches a maximum. Hydrogenation products were not observed, even at high partial pressures of hydrogen. No significant influence of the CO:H₂-ratio on the *n*:*iso*-selectivity and the amount of isomerization products could be determined.

The influence of the partial pressure of H₂ was studied at a constant CO partial pressure of 20 bar (and vice versa). The

Table 4

Rhodium loss by leaching ($\alpha = 60\%$, $\gamma = 15\%$, 100 ppm Rh, P:Rh = 10:1, 70 bar, 373 K and $t = 2$ h)

Surfactant	Rh-loss (ppm)
Lutensol® ON 50	3.4
Lutensol® ON 70 ^a	1.5
Lutensol® ON 70 ^a	1.0
Lutensol® ON 70 ^a	0.0
Lutensol® ON 70 ^b	0.2
Lutensol® ON 80	2.5
Lutensol® ON 110	n.o. ^c

^a At the same reaction conditions.

^b Agitation speed 1200 min⁻¹.

^c No phase separation.

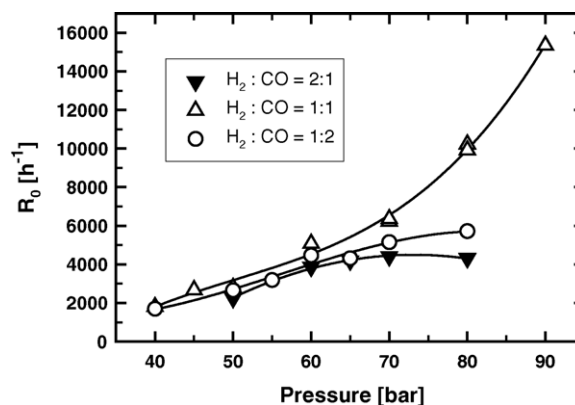


Fig. 6. Influence of the pressure at various compositions of the synthesis gas (1-octene, 373 K, $\alpha_0 = 60\%$, 100 ppm Rh, P:Rh = 10:1 and Lutensol® ON 70).

results are depicted in Fig. 7. The hydroformylation is accelerated with increasing partial pressures of both CO and H₂. The first order dependence on the hydrogen partial pressure observed in homogenous media [53] is not necessarily transferable to aqueous biphasic catalysis. Solvent interactions, as mentioned by Deshpande et al. [32], may be responsible for the observed partial order dependence on hydrogen.

The effect of the CO partial pressure on the rate of hydroformylation was studied up to 60 bar, i.e., a CO:H₂ ratio of 3:1. At this ratio, the reaction is still accelerated as compared to the rate at $p_{\text{CO}} = 40$ bar. This is different from the observed CO-inhibition for aqueous biphasic hydroformylation of 1-octene in the presence of ethanol as a co-solvent [32], which already occurs at a CO:H₂ ratio of 1:1 and a total syngas pressure of 20 bar. The absence of catalyst inhibition by CO is due to the lower solubility of carbon monoxide in aqueous solutions as compared to ethanol–water mixtures or organic solvents.

3.2.4. Influence of the temperature

The temperature has a very strong influence on both the reaction rate and the selectivity. The dependence of the initial

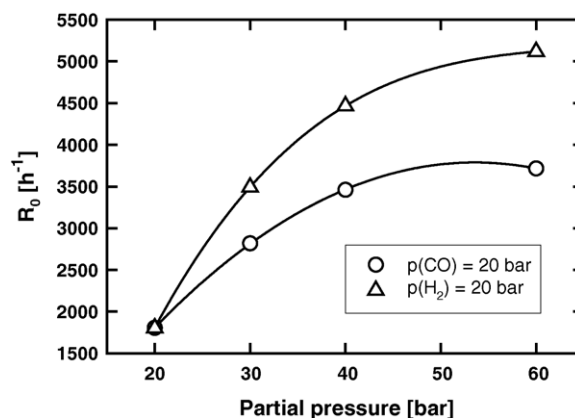


Fig. 7. Effect of the (○) H₂ or (△) CO partial pressure, respectively, on the reaction rate (1-octene, 373 K, $\alpha_0 = 60\%$, 100 ppm Rh, P:Rh = 10:1 and Lutensol® ON 70).

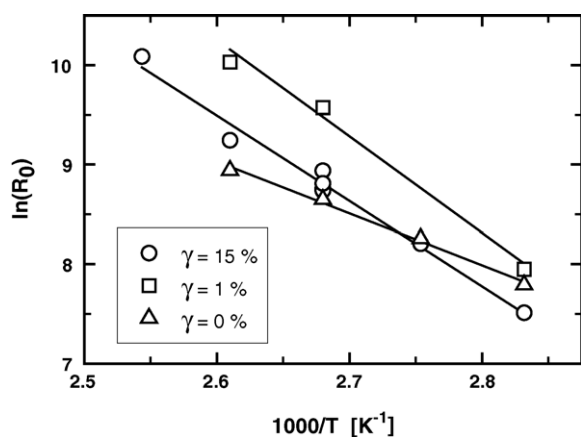


Fig. 8. Arrhenius plots for the hydroformylation of 1-octene (70 bar, 373 K, $\alpha_0 = 60\%$, 100 ppm Rh, P:Rh = 10:1 and Lutensol[®] ON 70).

reaction rates on the temperature is shown as an Arrhenius plot in Fig. 8 for three surfactant concentrations. The selectivities are listed in Table 5.

The apparent activation energies were 71 and 80 kJ/mol at surfactant contents of 15 and 1 wt.%, respectively. The activation energy of hydroformylation in the absence of surfactant is significantly lower (43 kJ/mol), indicating that mass transfer is the limiting step.

Although the hydroformylation rate of 1-octene is strongly accelerated with increasing temperature, the yield of aldehydes after a reaction time of 2 h is not affected significantly when changing the temperature from 383 to 393 K. This is due to the enhancement of the rate of the parallel isomerization of 1-octene to internal olefins, which are much less reactive. Significant amounts of 3-octene are observed at temperatures above 373 K. A catalyst system, which is able to suppress the formation of the thermodynamically more stable internal olefins, would be highly desirable. On the other hand, the synthesis of terminal aldehydes from internal olefins is of great industrial interest and is receiving more attention [57,58].

3.2.5. Influence of the catalyst concentration

The influence of the rhodium concentration was studied at a constant P:Rh ratio for different micro-emulsion systems. The initial reaction rate increases with increasing catalyst

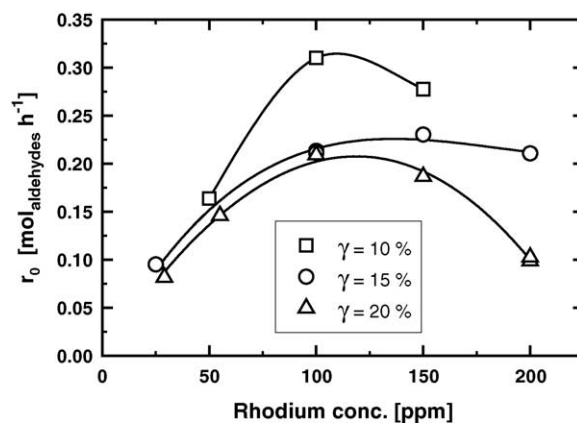


Fig. 9. Influence of the rhodium concentration at a constant P:Rh ratio of 10:1 on the aldehyde formation rate r_0 ($R_0 = r_0/n_{Rh}$) up to 10% conversion of 1-octene (373 K, 70 bar).

concentration but it reaches a maximum at about 100 ppm (Fig. 9) for all surfactant contents. Usually, in the kinetic regime a first order dependence is expected. The drop of the reaction rate at higher rhodium concentrations is probably due to aggregation of rhodium to inactive dimers as described by Borrmann [54] and Wilkinson and co-workers [59] for different rhodium species. At a catalyst concentration of 500 ppm, no hydroformylation was observed, at all.

3.2.6. Influence of the P:Rh ratio

The stability of the rhodium complex catalyst depends on the ligand-to-metal ratio and has an influence on the activity and selectivity of the reaction. But also the concentration of the ligand in solution plays an important role in homogeneous catalysis [55]. A catalyst solution containing 25 ppm rhodium with a P:Rh ratio of 10:1 is unstable under hydroformylation conditions and precipitated rhodium metal can be observed after the reaction. On the contrary, a 200 ppm solution is stable at the same P:Rh ratio, indicating that not only the ligand–metal ratio, but also the absolute concentrations have to be considered. Only the influence of the P:Rh ratio on the rate of hydroformylation and selectivity was investigated (Fig. 10). At the rhodium concentration of 100 ppm, neither the reaction rate nor the *n-iso* selectivity was affected

Table 5

Reaction rates and selectivities for various temperatures ($\alpha = 60\%$, $\gamma = 15\%$, 100 ppm Rh, P:Rh = 10:1, 70 bar, Lutensol[®] ON 70 and $t = 2$ h)

Run	γ (%)	T (K)	R_0^a (h^{-1})	TOF ^b (h^{-1})	Yield _{aldehydes} (%)	3-Octene (%)	2-Octene (%)	n^c (%)
41	15	353	1828	1568	22.4	0.9	16.4	69
42	15	363	3661	2439	35.9	2.4	31.5	71
2	15	373	6360	3437	49.0	20.2	27.2	59
43	15	383	10334	3533	55.4	24.7	15.1	47
44	15	393	24031	3811	50.6	27.5	16.6	43
45	1	353	2831	3446	51.4	2.4	28.9	68
46	1	373	14320	5046	73.5	15.7	9.3	51
47	1	383	22721	4958	74.6	19.2	12.2	45

^a Initial reaction rate calculated from the syngas absorption up to 10% conversion of 1-octene.

^b Calculated from the moles of aldehydes at a reaction time of 2 h.

^c Molar fraction of *n*-nonanal.

Table 6

Hydroformylation of various higher olefins ($\alpha = 60\%$, 100 ppm Rh, P:Rh = 10:1, 70 bar, 373 K, Lutensol[®] ON 70 and $t = 2$ h)

Run	Olefin	γ (%)	Olefin/Rh (mol/mol)	TOF (h^{-1})	Yield (aldehydes) (%)	Branched aldehydes ^b (%)	3-Olefin (%)	2-Olefin (%)
2	1-Octene	15	14451	3437	49	6.5	27.2	20.2
62	2-Octene	15	13036	881	13.5	1.6	23.1	61.2
63	Cyclooctene	15	14194	597	5.0	–	–	–
61	1-Octene	1	13752	5046	71.6	9.6	15.8	9.3
64	Di-isobutylene ^a	1	13803	–	1.5	–	–	–
65	1-Dodecene	1	8856	2356	55.1	2.5	–	22.9
66	1-Tetradecene	1	7536	2434	64.4	4.8	–	14.3

^a 393 K, 80 bar.^b Products of 2-octene and 3-octene.

significantly when doubling the P:Rh ratio from 5:1 to 10:1. A further increase of the ratio to 20:1 resulted in a dramatic drop of the reaction rate.

There are two possible explanations. At high concentrations of the ligand, the active center of the catalyst may be blocked, making the rhodium complex inactive for hydroformylation. On the other hand, the high concentration of salt at a P:Rh ratio of 20:1 may interact with the surfactant and change the hydrodynamic properties of the micro-emulsion (e.g., by diminishing the size of the interface, “salt effect”). To investigate which effect is responsible for the observed decrease of the reaction rate, a catalyst solution with a P:Rh ratio of 20:1, containing 50% of TPPOTS (oxidized TPPTS), was prepared and used for hydroformylation. As a phosphorous(V) species, triphenyl phosphine oxide trisulfonate (TPPOTS) is expected to be a much weaker ligand than TPPTS but represents the same salt content in solution. Any salt effect would therefore also be visible with this catalyst. As can be noted in Fig. 10, the hydroformylation rate with the mixture containing 50% TPPOTS is even higher than with P:Rh ratios of 10:1 or 5:1. A “salt effect” can therefore be excluded and the observed deactivation is ascribed to steric effects in the co-ordination sphere of the catalyst.

3.2.7. Hydroformylation of other higher olefins

Several higher molecular olefins were employed as starting materials for hydroformylation in micellar media with

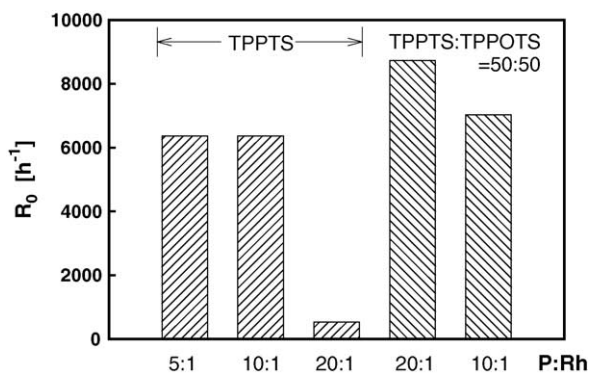


Fig. 10. Effect of the P:Rh ratio (1-octene, 70 bar, 373 K, $\alpha_0 = 60\%$, 100 ppm Rh, Lutensol[®] ON 70 and TPPOTS = triphenyl phosphine oxide trisulfonate).

Lutensol[®] ON 70. Among the alkenes used were several isomeric C₈-olefins. Reactions were performed at 70 bar and at a temperature of 373 K, using surfactant concentrations of $\gamma = 15$ wt.% and $\gamma = 1$ wt.%. As can be noted from Table 6, both 1-dodecene and 1-tetradecene are converted to the corresponding aldehydes at similar reaction rates at $\gamma = 1\%$. Since the solubility of olefins in water decreases with increasing number of carbon atoms, the aqueous phase can be excluded as the site where the reaction takes place. A comparison of experiments no. 61–64 leads to the conclusion that among isomeric C₈-olefins the reactivity drops in the order:

terminal olefin \gg internal olefin > cyclic olefin
 \gg branched olefin.

A significant conversion of di-*iso*-butylene was not observed, even at more severe reaction conditions.

4. Conclusions

The use of surfactants in biphasic hydroformylation of higher olefins like 1-octene can lead to highly efficient reaction systems. The choice of an appropriate surfactant is the key to a successful employment of micellar reaction media. The surfactant should be able to produce a sufficiently large interfacial area to promote mass transfer. On the other hand, the emulsification must be reversible so that the products can be separated by phase separation. Both requirements are fulfilled by using Lutensol[®] ON 70 or Lutensol[®] ON 80 as emulsifying agents. However, the temperature-mediated phase separation is not as neat as in the case of the Ruhrchemie–Rhône-Poulenc process. The presence of surfactants complicates the phase separation and in some cases a kinetically stable emulsion was obtained instead of a biphasic system, after cooling down the reaction mixture. It is not necessary to perform the reaction in a single-phase micro-emulsion, as high reaction rates can also be achieved in biphasic systems. Moreover, the hydroformylation rates are higher in systems with surfactant concentrations as low as 1 wt.%. The formation of foams, which hinder the separation of the organic phase, can be avoided by choosing a more hydrophobic amphiphile. Hydrophobically end-capped alkyl polyglycols would be interesting in this context.

Acknowledgement

The authors thank the BASF AG for providing the synthesis gas and the Lutensol[®] ON surfactants.

References

- [1] B. Cornils, W.A. Herrmann, M. Rasch, *Angew. Chem.* 106 (1994) 2219.
- [2] P.W.N.M. van Leeuwen, C. Claver (Eds.), *Rhodium Catalyzed Hydroformylation*, Kluwer Academic Publishers, 2000.
- [3] G. Protzmann, K.-W. Wiese, *Erdöl Erdgas Kohle* 117 (5) (2001) 235.
- [4] B. Cornils, W. Herrmann, *Aqueous-Phase Organometallic Chemistry, Concepts and Applications*, Wiley-VCH, 1998.
- [5] Ullmann's Encyclopedia of Industrial Chemistry, sixth ed., Electronic Release, Wiley-VCH, Weinheim, 1999.
- [6] E. Wiebus, B. Cornils, *Chem. Ing. Technol.* 66 (7) (1994) 916.
- [7] B. Cornils, W.A. Herrmann, R.W. Eckl, *J. Mol. Catal. A: Chem.* 116 (1997) 27.
- [8] O. Wachsen, K. Himmler, B. Cornils, *Catal. Today* 42 (1998) 373.
- [9] S. Bogdanovic, C.-D. Frohning, H. Bahrmann, DE 19700804 (1998).
- [10] H. Ding, B.E. Hanson, T. Bartik, B. Bartik, *Organometallics* 13 (1994) 3761.
- [11] B.E. Hanson, H. Ding, C.W. Kohlpaintner, *Catal. Today* 41 (1998) 421.
- [12] B. Fell, G. Papadogianakis, *J. Mol. Catal.* 66 (1991) 143.
- [13] M.S. Goedheijt, B.E. Hanson, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, *J. Am. Chem. Soc.* 122 (2000) 1650.
- [14] A. Solsona, J. Suandes, R. Mathieu, *J. Organomet. Chem.* 669 (2003) 172.
- [15] D.E. Bergbreiter, L. Zhang, V.M. Mariagnanam, *J. Am. Chem. Soc.* 115 (1993) 9295.
- [16] Z. Jin, Y. Yan, H. Zuo, B. Fell, *J. Prakt. Chem.* 338 (1996) 124.
- [17] S. Bogdanovic, C.-D. Frohning, H. Bahrmann, M. Beller, S. Haber, H.-J. Kleiner, DE 19630536 (1998).
- [18] X. Zheng, J. Jiang, X. Liu, Z. Jin, *Catal. Today* 44 (1998) 175.
- [19] E.A. Karakhanov, Yu S. Kardasheva, E.A. Runova, V.A. Semernina, *J. Mol. Catal. A: Chem.* 142 (1999) 339.
- [20] Y. Wang, J. Jiang, R. Zhang, X. Liu, Z. Jin, *J. Mol. Catal. A: Chem.* 157 (2000) 111.
- [21] H. Bahrmann, P. Lappe, EP 0602463 B1 (1994).
- [22] S. Kanagasabapathy, Z. Xia, G. Papadogianakis, B. Fell, *J. Prakt. Chem.* 337 (1995) 446.
- [23] P. Wasserscheid, W. Keim, *Angew. Chem.* 112 (2000) 3926.
- [24] H. Waffenschmidt, Thesis, Technical University Aachen, Germany, 2000.
- [25] N. Karadia, S. Guise, C. Newlands, J.A. Andersen, *Chem. Commun.* (1998) 2341.
- [26] I. Horvath, *Acc. Chem. Res.* 31 (1998) 641.
- [27] D. Koch, W. Leitner, *J. Am. Soc.* 120 (1998) 13398.
- [28] S. Kainz, D. Koch, W. Baumann, W. Leitner, *Angew. Chem.* 109 (1997) 1699.
- [29] P.G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* 99 (1999) 475.
- [30] E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2269.
- [31] E. Monflier, S. Tilloy, G. Fremy, Y. Castanet, A. Mortreux, *Tetrahedron Lett.* 36 (1995) 9481.
- [32] R.M. Deshpande, H. Purwanto, H. Delmas, *Ind. Eng. Chem. Res.* 35 (1996) 3927.
- [33] R.M. Deshpande, H. Purwanto, R.V. Delmas, Chaudhari, *J. Mol. Catal. A: Chem.* 126 (1997) 133.
- [34] L. Tinucci, E. Platone, US Patent 4,996,366 (1991).
- [35] T. Bartik, B. Bartik, B.E. Hanson, *J. Mol. Catal. A: Chem.* 88 (1994) 43–56.
- [36] F. Van Vyve, A. Renken, *Catal. Today* 48 (1999) 237.
- [37] M. Gimenez-Pedros, A. Aghmiz, C. Claver, A.M. Masdeu-Bulto, D. Sinou, *J. Mol. Catal. A: Chem.* 200 (2003) 157.
- [38] H. Purwanto, R.M. Deshpande, R.V. Chaudhari, H. Delmas, *J. Chem. Eng. Data* 41 (1996) 1414.
- [39] R. Schomäcker, *Nachr. Chem. Tech. Lab.* 40 (1992) 1344.
- [40] J.-H. Spilgies, Thesis, University of Cologne, Germany, 1966.
- [41] M. Kahlweit, R. Strey, G. Busse, *J. Phys. Chem.* 94 (1990) 3881.
- [42] D.F. Evans, H. Wennerström, *The Colloidal Domain*, VCH Publishers Inc., 1994.
- [43] M. Haumann, H. Yildiz, H. Koch, R. Schomäcker, *Appl. Catal. A Gen.* 236 (2002) 173.
- [44] M. Haumann, H. Koch, P. Hugo, R. Schomäcker, *Appl. Catal. A Gen.* 225 (2002) 239.
- [45] M. Kahlweit, R. Strey, D. Haase, H. Kunieda, T. Schmelting, B. Faulhaber, M. Borkovec, H.-F. Eicke, G. Busse, F. Eggers, Th. Funck, H. Richmann, L. Magid, O. Söderman, P. Stilbs, J. Winkler, A. Dittrich, W. Jahn, *J. Colloid Interface Sci.* 118 (1987) 436.
- [46] C. Miyagawa, Thesis, TU Braunschweig, 2002.
- [47] M. Kahlweit, *Tenside Surf. Det.* 30 (1993) 2.
- [48] B. Jakobs, T. Sottmann, R. Strey, J. Allgaier, L. Willner, D. Richter, *Langmuir* 15 (1999) 6707.
- [49] M. Brandt, A. Wehling, A. Schumpe, *Chem. Ing. Technol.* 69 (1997) 500.
- [50] H. Chen, Y. Li, J. Chen, P. Cheng, Y. He, X. Li, *J. Mol. Catal. A: Chem.* 149 (1999) 1.
- [51] M. Brandt, Thesis, TU Braunschweig, Germany, 1998.
- [52] F. Bauer, K.J. Hüttinger, *Chem. Ing. Technol.* 50 (1978) 477.
- [53] R.M. Deshpande, R.V. Chaudhari, *Ind. Eng. Chem. Res.* 27 (1988) 1996.
- [54] T. Borrmann, Thesis, University of Göttingen, Germany, 1998.
- [55] M. Beller, Dechema Study Course "Applied Homogeneous Catalysis", University of Dortmund, Germany, 2000.
- [56] D.O. Leckel, Thesis, Technical University of Aachen, Germany, 1993.
- [57] D. Selent, D. Hess, K.-D. Wiese, D. Rättger, C. Kunze, A. Börner, *Angew. Chem.* 113 (9) (2001) 1739.
- [58] H. Klein, R. Jackstell, K.-D. Wiese, C. Borgmann, M. Beller, *Angew. Chem.* 113 (18) (2001) 3505.
- [59] D. Evans, G. Yagupsky, G. Wilkinson, *J. Chem. Soc. A* (1968) 2660.
- [60] D. Tjandra, M. Lade, O. Wagner, R. Schomäcker, *Chem. Eng. Technol.* 21 (1998) 666.