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Rhodium catalyzed hydroformylation of 1-octene in microemulsion: comparison with various catalytic systems

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In this work, we describe how addition of alkylpolyglycol ether type nonionic surfactant affects the hydroformylation of 1-octene in the presence of phosphine modified rhodium catalyst. Influence of different process parameters such as ligand excess and amount of surfactant on the reaction rate and selectivity were discussed. Direct comparison of microemulsion systems with classic processes was achieved by performing the reactions under comparable homogeneous and biphasic conditions. Thus, the experiments were carried out using catalysts such as unmodified rhodium carbonyl $HRh(CO)_4$ and $HRh(CO)(PPh_3)_3$ in homogeneous system, Rh–TPPTS complex in two-phase system and in association with co-solvent.

KEY WORDS: hydroformylation; microemulsion; 1-octene; nonionic surfactant; rhodium complex; water-soluble catalyst.

1. Introduction

Hydroformylation of olefins is an important, well-known commercial process for the production of aldehydes and alcohols, moreover it is one of the most important applications of homogeneous catalysis in industry as well [1].

The history of aqueous, biphasic homogeneous catalysis starts with the initial observation by Manassen [2]. Since the first industrial use of this system in 1984 by the hydroformylation of propylene in the plants of Ruhrchemie A.G., research into aqueous, two phase, homogeneous catalysis has become very active [3,4]. Two basic problems in classical homogeneous catalysis, namely the separation and subsequent recycling of the catalyst can be elegantly solved by using two-phase catalysis, in which the catalyst and the product enables to be separated by simple phase separation [5]. However, if we compare biphasic reactions with their monophasic equivalents, it is found that the rates are lower in the two-phase systems [6]. Although the use of water as a second phase has many advantageous [4], it has also its limitations, especially when the water solubility of starting materials is too low, preventing adequate transfer of the organic substrate into aqueous phase or at the phase boundary and consequently reducing the reaction rates [7]. Therefore, this process is not economically viable for long chain alkenes, which are not very soluble in water.

One useful way to overcome this solubility problem that is frequently encountered in organic reactions is performing the reaction in a microemulsion [8,9]. A microemulsion is formed by adding a suitable surfactant to biphasic system. The amphiphilic nature of this substance lowers the interfacial tension of water and oil and accelerates the rate of the reaction because aggregates such as micelles or microemulsion droplets form [10,11].

This strategy has been used in the hydroformylation of long chain alkenes [12,13]. The cationic surfactants such as cetyltrimethylammoniumbromide (CTAB) were used in the hydroformylation of various alkenes with Rh–TPPTS system [14]. High activity and selectivity was observed in the hydroformylation of 1-octene and 1-decene using rhodium complex associated with sulfonated diphosphines in the presence of ionic surfactants or methanol [15].

Understanding of the reaction mechanism and the characterization of the intermediates present during the reaction are important aspects of studies of the rhodium catalyzed hydroformylation [16,17]. High pressure (HP) spectroscopic techniques are regularly applied to identify organometallic compounds present under pressure [18,19].

The reaction kinetics and the resting state of unmodified rhodium carbonyl catalyst have been extensively studied [20,21]. The active species is generally assumed to be $HRh(CO)_3$, which is formed by dissociation of a CO ligand from the $HRh(CO)_4$ complex. Garland and co-workers [22] identified a rhodium acyl intermediate as the resting state of the catalyst using *in situ* IR spectroscopy.

The hydroformylation mechanism for phosphine modified rhodium catalysts and the coordination chemistry of several rhodium phosphine complexes that are

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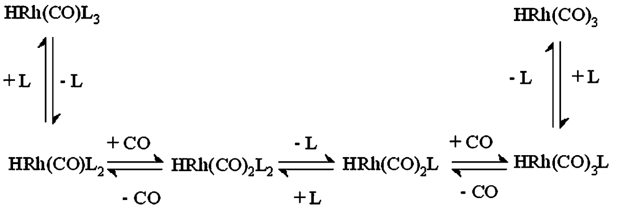

Figure 1. Equilibria between the active species. L = TPP, TPPTS.

potential intermediates in the reaction were studied by Wilkinson and co-workers [23,24]. It appeared that the principal active catalytic species was $HRh(CO)_2(PPh_3)_2$ under the conditions studied [25]. The active species are generated by preliminary equilibrium (figure 1). Depending on the reaction conditions, the predominant catalyst species are coordinated by one or more phosphine ligands.

Previously, we reported that the use of nonionic surfactants of alkylpolyglycolether results in high reaction rates in the hydroformylation of 7-tetradecene in a microemulsion [26]. At temperatures around 120 °C and under pressure of 100 bar 7-tetradecene is hydroformylated with high regioselectivity. More recently, hydroformylation of styrene, cyclohexene and 1,2-diacetoxy-2-butene have been studied using microemulsion stabilized by nonionic surfactant [27].

As a continuation of our investigation on microemulsion systems in hydroformylation reaction, we here described how addition of nonionic surfactant affects the hydroformylation of 1-octene by rhodium complex with triphenylphosphine sulfonate (TPPTS). The combination of the experiments under comparable homogeneous and biphasic conditions were performed in order to make direct comparison of microemulsion with classical systems. In addition, the influence of the ligand excess and the amount of the surfactant on the reaction rate and selectivity were discussed.

2. Experimental

2.1. General methods

All chemicals were purchased from Fluka or Sigma-Aldrich and used as received unless otherwise indicated. The technical grade surfactant Marlipal $O13/E_i$ (alkylpolyglycolether derived *via* ethoxylation of isodecanol), syngas (CO/H_2 1:1) were purchased from Condea Chemicals and Messer Griesheim, respectively. The ligand used was 30.7 wt% aqueous solution of TPPTS from Celanese.

The hydroformylation reactions were performed in 100 mL stainless steel autoclave (Premex) equipped with temperature controller (Huber CC3) and mechanical stirrer. The pressure inside the reactor was kept constant throughout the whole reaction time by using a gas reservoir along with a pressure regulator. Progress of the reaction was monitored by the pressure drop in the syngas reservoir. The reaction products were analyzed by gas chromatography (Sichromat 3) using Rtx-5MS capillary column and FID. The experiments were reproduced in order to gain confidence.

2.2. Standard hydroformylation reaction

Standard experiments were carried out at temperature 85 °C and syngas pressure of 60 bar (CO/H_2 1:1). The rhodium concentration of the reaction mixtures was 200 ppm with respect to substrate in all experiments. Preparation of the reaction mixtures was carried out as follows:

2.2.1. Microemulsion

The catalyst precursor rhodium dicarbonyl acetylacetonate $Rh(acac)(CO)_2$ (0.05 mmol) and a proper amount of water soluble ligand tris-(3-sulfophenyl)-phosphine trisodium salt (TPPTS) in 2.5 mL degassed water were stirred under nitrogen atmosphere for 24 h. The resulting catalyst solution was added to 24.7 g olefin and 3.9 g nonionic surfactant to give the microemulsion. Composition of the microemulsions was 79 wt% of alkene, 13 wt% of surfactant and 8wt% of aqueous catalyst solution.

2.2.2. Biphasic

Composition and preparation procedure of the catalyst solution was the same with the solution that was prepared for the microemulsion. This solution was added to the olefin phase.

2.2.3. Biphasic associated with co-solvent

The catalyst solution was prepared as in microemulsion and the resulting solution was added to a proper amount of olefin in 30 mL toluene.

2.2.4. Homogeneous

The rhodium precursor $Rh(acac)(CO)_2$ (0.05 mmol) and proper amount of triphenylphospine (TPP) were dissolved in 2.5 mL toluene and added to the olefin.

2.2.5. Unmodified

The rhodium precursor $Rh(acac)(CO)_2$ (0.05 mmol)-was dissolved in 2.5 mL toluene and added to the olefin.

3. Results and discussions

One of the purposes for developing microemulsions was to generate a catalysis system capable of transforming long chain alkenes. For this purpose, 1-octene was chosen to test the concept of microemulsion catalysis.

The product identification and the material balance were examined under microemulsion condition with ligand/metal (L/M) ratio 10. Major byproducts formed were internal alkenes 2-octene and 3-octene due to isomerization of the substrate.

The typical course of the reaction at standard conditions is shown in figure 2. As can be easily seen from the figure, the octene conversion increases linearly with the reaction time up to 80% of the total conversion. The linear aldehyde selectivity (n/b) is constant during that time and the amount of the isomerization products reach a maximum value of 37%. The internal octenes formed *via* isomerization are hydroformylated when the reaction of 1-octene begins to slow down. The internal double bond is converted into the branched aldehydes. Therefore, hydroformylation of the isomerization products causes a decrease of the initial linear to branched aldehyde ratio. Because of this concentration–time profile of the reaction, linear aldehyde selectivities of a catalyst should be observed before the disturbance by isomerization products in order to make consistent discussion. This is probably the reason why some authors observed low linear aldehyde selectivities with high reaction rates and *vice versa* [28].

The possible sources of the branched aldehyde formation include alkene isomerization, regioselectivity of the addition of the metal carbonyl to the alkene and isomerization of the alkyl and acyl species. Lazzaroni [29,30] studied the relation between the observed isomerization and the linear to branched ratio and showed that isomerization is a result of β-hydride elimination of the isoalkyl bonded to the rhodium. The amount of the isomerization is expected to increase with higher temperatures and lower pressures because this reaction has higher free energy of activation than hydroformylation and requires vacant site. For hydroformylation of hex-1-ene, at a reaction temperature of 100 °C, for linear alkyl, the hydroformylation predominates β-hydride elimination, for branched alkyl, elimination predominates hydroformylation.

Because only the isoalkyl rhodium forms internal alkenes, the amount of the branched aldehyde diminishes during the isomerization in the present system. Since the internal alkenes are less reactive than the terminal alkenes, hydroformylation of isomerization products take place at high conversions and the regioselectivity depends on the conversion.

3.1. *Variation of the catalytic system*

In order to make a comparison of our microemulsions with the other systems, experiments were also carried out using catalysts such as, unmodified rhodium $HRh(CO)_4$ and $HRh(CO)(PPh_3)_3$ in homogeneous system, water-soluble Rh–TPPTS complex in two-phase system and in association with co-solvent. A comparison of the performance of these catalysts is shown in figure 3.

First, all the reactions were performed with L/M ratio of 4. Conversion to aldehyde, i.e. mol of aldehyde per mole of substrate transformed, is plotted against reaction time for each catalytic system. It indicates considerable high reaction rates in homogeneous systems (in both unmodified rhodium $HRh(CO)_4$ and $HRh(CO)(PPh_3)_3$), as expected.

The result of Rh–TPPTS catalyst in water/toluene showed high activity with respect to biphasic equivalent. This is probably due to the increase in the solubility of catalyst in the organic layer.

The catalytic activity that is observed in the biphasic system is higher than expected for this kind of poorly water-soluble organic reagent. This surprising result raised the question whether the active species is still the water-soluble Rh–TPPTS complex or unmodified rhodium carbonyl complex ($HRh(CO)_3$) which is formed by loosing of the TPPTS ligand as indicated in figure 1. To answer this question, the experiments under microemulsion and biphasic conditions were repeated with higher ligand/metal ratio (L/M = 10). Conversion to

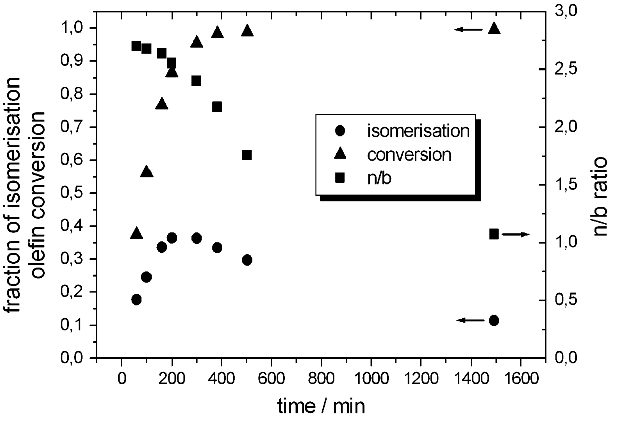

Figure 2. Typical course of the hydroformylation reaction of 1-octene. 85 °C, 60 bar, 200 ppm Rh, L/M = 10.

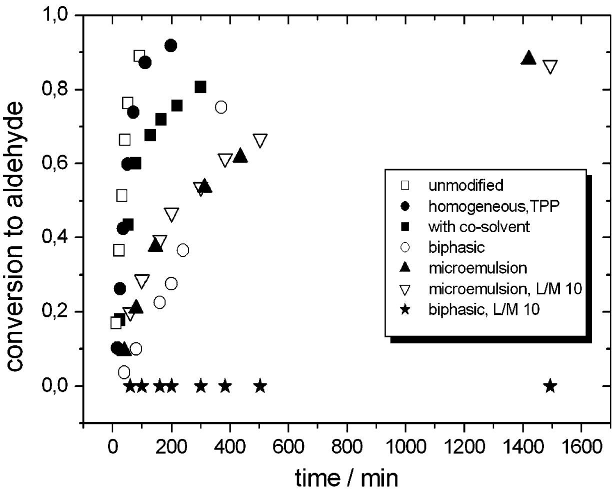

Figure 3. Hydroformylation of 1-octene with various catalytic system. 85 °C, 60 bar, 200 ppm Rh, L/M = 4.

the aldehydes was only 0.3% after 24 h under biphasic condition. This observation indicates that the L/M ratio of 4 is not sufficient to convert all the rhodium into the water-soluble complex. The organic-soluble rhodium carbonyl is dominantly present in two-phase system with this low ligand excess.

It seems that the water-soluble rhodium complex is the active species with both L/M ratios under microemulsion condition, hence the concentration time profile remained identical as the L/M ratio was increased. Furthermore, the active species during the hydroformylation of 1-octene in microemulsion medium has been investigated using HP infrared spectroscopy(HP-IR) (Yildiz-Ünveren *et al.* submitted). The results reveal that $HRh(CO)_2(L)_2$ is the resting state of the catalyst at the L/M ratios greater than 2 under the microemulsion conditions studied.

The influence of the catalytic system on linear aldehyde selectivity and the amount of isomerization product are presented in figures 4 and 5, respectively. The change in the initial selectivity is observable with all catalyst systems and the results correspond well with the typical reaction pattern under microemulsion conditions shown in the previous section. Surprisingly, no significant change in the initial linear aldehyde selectivity is observed as the catalytic systems have changed. Neither addition of the surfactant or the co-solvent to the two-phase system nor change of the catalyst from unmodified rhodium carbonyl to Rh–TPP or Rh–TPPTS complexes has any considerable influence on the selectivity.

The isomerization products increase with reaction time up to total olefin conversion of 80% (50% conversion to the aldehydes) and reach a maximum value. A change of the catalytic system has also no remarkable effect on the ratio of rate hydroformylation to rate of isomerization.

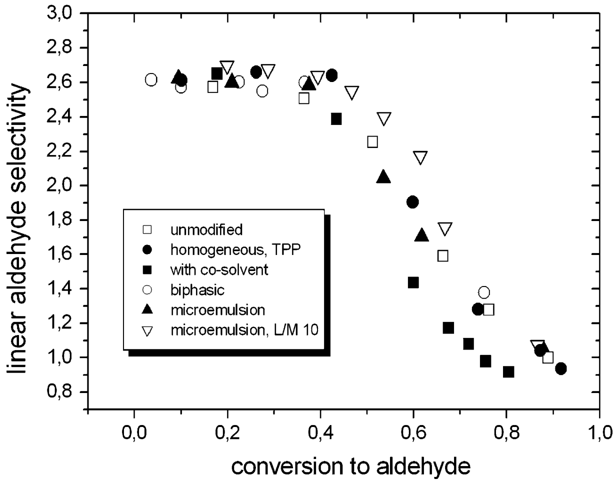

Figure 4. Effect of variation of the catalytic system on linear aldehyde selectivity. 85 °C, 60 bar, 200 ppm Rh, L/M = 4.

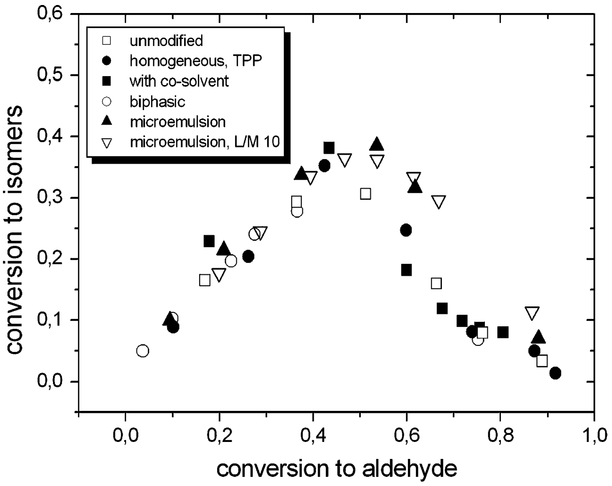

Figure 5. Effect of variation of the catalytic system on amount of isomerization product. 85 °C, 60 bar, 200 ppm Rh, L/M = 4.

3.2. *Influence of the ligand excess*

In order to gain better understanding of the behavior of the microemulsions, further investigations were carried out on the ligand excess. Thus, the L/M ratio was varied between 4 and 40. The effect of the ligand excess on the initial reaction rate is illustrated in figure 6.

Under biphasic conditions, the initial reaction rate at L/M ratio of 4 is higher than expected for the poor water-soluble substrate. As previously indicated, high initial reaction rate reveals that the equilibrium between various active species shifts towards unmodified rhodium carbonyl complex under biphasic condition at low ligand concentrations. At higher ligand concentration the rhodium species are modified by the ligand and no hydroformylation of the water-insoluble substrate is obtained.

The initial reaction rates are increased towards higher ligand excess under homogeneous ($HRh(CO)(PPh_3)_3$) condition. This effect was already described by Olivier

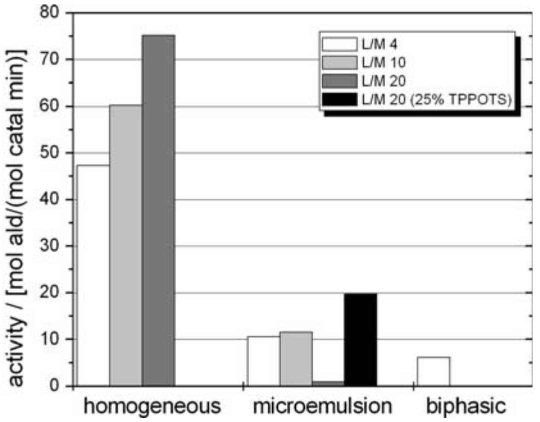

Figure 6. Influence of ligand excess on initial reaction rate. 85 °C, 60 bar, 200 ppm Rh.

et al. [31]. The catalytic activity varies in nonlinear fashion as a function of phosphine concentration. The activity increases as the phosphine concentration increases and reaches a maximum, further increase in ligand concentration leads to lower rates. This is due to hindrance of the formation of the active species $HRh(CO)_2(L)_2$ at high ligand concentration.

Under microemulsion condition, the initial reaction rates remain constant as the ligand concentration increases from 4 to 10 and decreases with further ligand excesses. It is reasonable to state that even with low ligand concentrations, the active species are modified and the decreasing trend in the catalytic activity begins at lower ligand excess in comparison homogeneous equivalent. These effects are due to the high local ligand concentration inside the small reverse micelle.

In order to avoid any question on oxidized TPPTS under our reaction conditions, we tested indirectly for the presence of oxidized TPPTS. Thus, the reaction was performed at the L/M ratio of 20 with 25 mol% oxidized TPPTS under microemulsion conditions. The catalytic activity is even higher than the activity observed at lower ligand concentrations. The result suggests that oxidation of the ligand is not pronounced under the conditions studied.

Table 1 shows the influence of the ligand excess on linear aldehyde selectivity. The selectivities were recorded at low conversions (< 30%) before the disturbance by isomerization products. In general the linear products show a gradual increase with increasing L/M ratio. Coordination of the ligands to the metal center enhances the steric bulkiness and linear products are favored. However, this effect is very weakly pronounced, thus the n/b ratio varies between 2.6 and 2.9 as the L/M ratio increases from 4 to 20. Moreover, as mentioned previously, change of the reaction medium or the ligand has no influence on the selectivity. It can be concluded that the selectivity is mainly affected by the structure of the 1-octene.

Another remarkable result is that the amount of the isomerization is slightly suppressed towards high L/M ratios in homogeneous and microemulsion systems. Under such conditions the metal center presents a more sterically hindered environment to the alkene and the formation of linear alkyl and acyl species are favored.

With the L/M ratio of 20 (cf. figure 7), the internal octenes that are formed *via* isomerization are not hydroformylated as the 1-octene conversion begins to slow down, therefore no change of the initial linear aldehyde selectivities is observable. Because the formation of the active species $HRh(CO)_2(L)_2$ is hindered by high ligand excesses, hydroformylation of the internal alkenes that is much more difficult than 1-alkenes is not possible under these conditions. Decrease in the amount of internal alkenes may due to backward isomerization to 1-octene.

3.3. Variation of the surfactant concentration

The influence of the surfactant concentration within the microemulsion system on the hydroformylation reaction was studied by varying the amount of the surfactant between 0 and 3%. Figure 8a shows the effect of surfactant on conversion. For more convenient discussion figure 8b is plotted in following way: the linear aldehyde selectivities were recorded after 60 min reaction time (before the disturbance) in order to be sure about the consistency of the data and the conversions were recorded after 400 min in order to obtain a clear picture about the differences in rates (cf. figure 8b).

In the limit of no surfactant, no hydroformylation of 1-octene is observed. Addition of small amount of the surfactant (0.5 wt%) causes a considerable increase in the conversion. Further increase in the surfactant concentration leads to lower conversions again. This increase in the reaction rate can be explained by an increase in the interfacial area between organic and water phases when the surfactant is added to the system.

Table 1
Variation of the ligand excess with various catalytic systems

Catalytic system	Ligand	L/M[a]	n/b[b]
Homogeneous	TPP	4	2.66
		10	2.71
		20	2.93
Microemulsion	TPPTS	4	2.62
		10	2.70
		20	2.91
		40	*
	TPPTS + TPPOTS[c] (25 %)	20	2.61
Biphasic	TPPTS	4	2.61
		10	*

* No reaction.

[a] Ligand per metal ratio.

[b] Ratio of linear to branched aldehyde.

[c] Oxidized TPPTS.

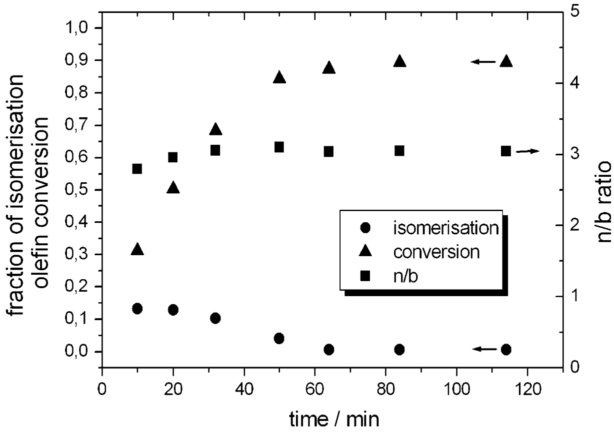

Figure 7. Course of the hydroformylation of 1-octene at high ligand concentration. 85 °C, 60 bar, 200 ppm Rh, L/M = 20, under homogeneous conditions.

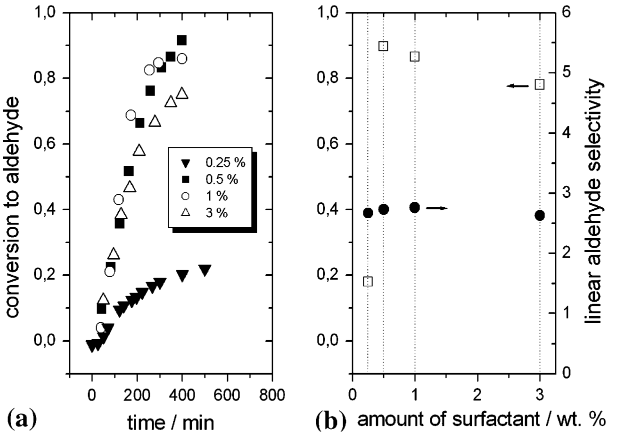

Figure 8. Effect of the surfactant concentration on conversion and linear aldehyde selectivity. 85 °C, 60 bar, 200 ppm Rh, L/M = 10.

The maximum of the reaction rate correlates with the critical microemulsion concentration (cμc) at which the reverse micelles are formed that act as host for the catalyst in the organic phase.

All the selectivities remain constant as the amount of the surfactant increases. We were not able to take any information from the selectivity values on any possible change in the active species by the addition of the surfactant, because even the change of the catalyst does not show any influence on the selectivity of 1-octene hydroformylation.

Figure 9 represents the effect of the surfactant concentration on the amount of the isomerization products and clearly indicates that there is no influence of the amount of surfactant.

4. Conclusion

Isomerization and hydroformylation of the 1-alkene are in competition during the reaction. When the hydroformylation of 1-alkene begins to slow down, hydroformylation of the isomerization products causes a disturbance in the initial linear aldehyde selectivity. This disturbance should be taken in consideration in order to ascribe all the observed effects to the varied conditions.

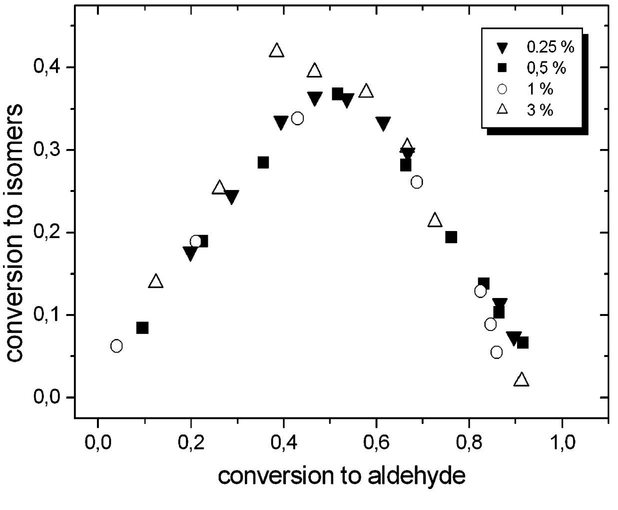

Figure 9. Effect of the surfactant concentration on amount of isomerization product. 85 °C, 60 bar, 200 ppm Rh, L/M = 10.

Following criteria show no considerable influence on the initial linear aldehyde selectivity for the hydroformylation of 1-octene;

- change of the reaction medium from homogeneous to two-phase system, addition of the co-solvent or surfactant to two-phase system.
- change of the catalyst from unmodified rhodium carbonyl to Rh–TPP or Rh–TPPTS complexes.
- amount of the surfactant in microemulsion.

As 1-octene was hydroformylated at all reaction condition with a moderate selectivity of about 2.65, the selectivities appeared to be more affected by the nature of the substrate.

Under biphasic conditions the equilibrium between various active species is shifted towards the unmodified rhodium carbonyl with low ligand excess. Formation of the unmodified complex is suppressed when the L/M ratio increases to 10. Because of the high local ligand concentration inside a small reverse micelle, the hydroformylation reaction is mainly catalyzed by water-soluble Rh–TPPTS complex even with low ligand excess under microemulsion conditions. Therefore, microemulsions allow working at lower L/M ratios with respect to biphasic equivalent. The catalytic activity varies in nonlinear form as a function of the surfactant concentration of the microemulsion. The concentration of the surfactant does not have any influence on the selectivity. Therefore, it would be beneficial to determine the effect of surfactant concentration by using other substrates that enable to obtain information from the selectivities on any possible change in the active species by the addition of the surfactant.

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