

Cobalt-catalyzed biphasic hydroformylation of internal short chain olefins

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Received 2 June 1998; accepted 31 July 1998

Abstract

Hydroformylation of short chain internal olefins to linear aldehydes is an interesting subject due to the enormous importance of the resulting oxo products. Here we report a systematic study of the hydroformylation of 2-pentenenes in an aqueous two-phase system with a Co/TPPTS catalyst. At elevated temperatures and pressures good yields of the desired aldehydes were obtained. Linear to branched ratios (*n/iso*) of up to 70:30 were observed. Recycling of the catalyst and reuse up to four times without loss of activity has been demonstrated. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Two-phase catalysis; Biphasic catalysis; Hydroformylation; Internal olefins; Cobalt; TPPTS

1. Introduction

The hydroformylation of olefins, especially propene, is the most important homogeneous transition metal catalyzed process in industry today.¹ In 1997, more than 6 million tons of oxo products were produced by this method and it is estimated that the volume of these products will increase each year by 3–5%. Commercial hydroformylation processes use exclusively rhodium or cobalt catalysts. Since the technical and economical success of the homogeneous Union Carbide process in 1976 [7], a substitution of cobalt complexes by rhodium complexes

has occurred. Therefore, most of the hydroformylation studies in the last decade focused on rhodium catalysts. Nevertheless, a significant amount of oxo products (ca. 2.5 million tons/a) is still produced using cobalt catalysts, especially $\text{HCo}(\text{CO})_4$ and $\text{HCo}(\text{CO})_3\text{PR}_3$. However, the technology of cobalt-based processes has remained unchanged over the years, whereas, new rhodium based hydroformylation processes have been introduced. The last important industrial development in this area is the so-called Ruhrchemie/Rhône-Poulenc process [8–12], whereby, a water-soluble rhodium catalyst is employed in a two-phase hydroformylation process. Based on the original idea of Kuntz [13,14], a Rh/TPPTS complex (TPPTS = tris sodium salt of *meta* trisulfonated triphenylphosphine) is used as catalyst for this process which reached a production level of almost 600,000 tons per year nowadays. The economical advantages of

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¹ For recent reviews on hydroformylation reactions see: Refs. [1–6]

the Ruhrchemie/Rhône-Poulenc process are based on the simple principle of catalyst recycling and the low-cost catalyst/product separation. Due to the advantages of the biphasic operation mode for the production of butyraldehyde (from propene), and valeraldehyde (from 1-butene) the use of water-soluble catalysts in a biphasic system has received much attention [15–27]. However, the Rh/TPPTS catalyst has limitations, e.g., the catalyst system is only applicable in water to the hydroformylation of terminal olefins. With branched or internal olefins as substrates only very low conversion rates are achieved [28]. In this respect, there is considerable industrial interest in the development of new catalysts which are able to hydroformylate internal olefins to *n*-aldehydes in a two phase solvent system. Of special importance is the conversion of *E*-2-butene and *Z*-2-butene to *n*-valeraldehyde due to the economical availability of raffinate II as feedstock. Currently raffinate II which is a mixture of isomeric butenes (1- and 2-butenes, and butane) is hydroformylated in a two step process to *n*-valeraldehyde and 2-methyl butyraldehyde [29]. There is increasing interest in *n*-valeraldehyde, a precursor to *n*-valeric acid, which is the basis of a new ester-type lubricant for CFC-substituents in refrigeration systems. Apart from this application, *n*-valeraldehyde may partly substitute *n*-butyraldehyde for the production of plasticizers.

Although there is a number of catalysts known that can hydroformylate internal olefins to linear aldehydes in a one phase reaction,² especially rhodium–phosphite complexes or unmodified cobalt carbonyl complexes, only one patent from 1979 exists to the best of our knowledge, that deals with the liquid/liquid biphasic hydroformylation of internal olefins [39]. This lack of knowledge is explained by the fact that rhodium–phosphine complexes are in generally not active for the hydroformylation of internal olefins. On the other hand up to now only little

attention has been put on two phase catalysis using cobalt catalysts [39–45]. Hence, it was our concept to combine the advantages of biphasic catalysis with the properties of cobalt catalysts which are able to hydroformylate internal olefins selectively to linear aldehydes [46, 47]. In this paper, we report the first study of a cobalt-catalyzed biphasic hydroformylation of an internal olefin.

2. Experimental

All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. All solvents, internal standard, and olefin were dried and deoxygenated by distillation under argon. Chemicals were purchased from Fluka or Aldrich and used without further purification. The syngas (CO/H₂ 50/50, purity 99.98) used in the hydroformylation experiments was purchased from Messer Griesheim.

The cobalt analyses were done by the Mikroanalytisches Labor der Technischen Universität München. The reaction product distribution in the hydroformylation reactions was analyzed by gas chromatography on a Hewlett Packard 6890 series GC system equipped with a Hewlett Packard HP 5 column (30 m × 0.32 mm × 0.25 μm) and FID detector.

Two-phase hydroformylation reactions of 2-pentene (60% *E*-2-pentene, 40% *Z*-2-pentene, > 98% purity) were carried out in a 300 ml stainless steel Parr autoclave with a glass inlet and stream breakers. The autoclave was charged under argon with 40 ml anisole and 40 ml water, catalyst, internal standard (5 ml isooctane) and 2-pentene (10 ml). After pressurizing the autoclave to the desired syngas pressure, the reaction mixture was constantly stirred at 1100 min⁻¹ until the end of the reaction. After cooling the vessel was depressurized and the organic phase was analyzed by gas chromatography (temperature program: 37°C (hold 8 min), 60°C (8°C/min), 60°C (hold 5 min), 310°C

² See for example, Refs. [30–38]

(35°C/min), 310°C (hold 1 min); carrier gas flow: 0.5 ml/min (hold 8 min), 1.5 ml (0.6 ml/min²), 1.5 ml (hold 23 min)).

3. Results

3.1. The test system

Although our main interest focuses on the reaction of raffinate II, a mixture of *Z*- and *E*-2-pentenes was chosen as test olefins due to the easier handling compared to 2-butenes. The well-known TPPTS complex of cobalt $\text{Co}_2(\text{CO})_6(\text{TPPTS})_2$ (**1**) in the presence of a 10-fold excess of TPPTS was used as catalyst in all reactions. Complex **1** was prepared according to the literature from $\text{Co}_2(\text{CO})_8$ and TPPTS in a reaction mixture of water and toluene [48]. The figure lists all possible reactions products (except condensation products and formates) which could be formed during the hydroformylation of 2-pentenes (Fig. 1).

Apart from the desired linear aldehyde or hydrogenated alcohol (*n*-products), two different branched products (*iso*-products) are possible. The quotient of the amount of linear products to *iso*-products will be referred to as the *n/iso* ratio or *n/iso* selectivity.

3.2. Hydroformylation results

3.2.1. Influence of temperature and pressure on aldehyde and alcohol yields

It was observed that in the range of conditions investigated here, the products formed were

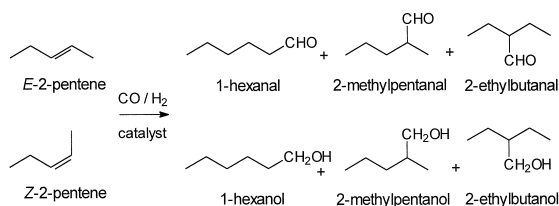


Fig. 1. Possible reaction products from the hydroformylation of the isomeric 2-pentenes.

the isomeric aldehydes, 1-hexanal, 2-methylpentanal, and small amounts of 2-ethylbutanal, which could not be separated from 2-methylpentanal by GC. In addition, the corresponding alcohols were obtained in up to 5% yield. Olefin isomerization and hydrogenation occurred only to a small extent (< 1%). In Fig. 2 the results of the hydroformylation of 2-pentenes concerning alcohol and aldehyde yields using 0.1 mol% **1**, a Co/P ratio of 1:10, and a CO/H₂ ratio of 1:1 are depicted.

Alcohol and aldehyde yields (each sum of *n*- and *iso*-products) were studied as a function of five different reaction pressures and four different temperatures. As shown in Fig. 2, aldehydes were formed almost exclusively between 130–170°C and 20–100 bar. Minor amounts of alcohols (< 5%) were formed when forcing conditions were employed, e.g., 190°C, 80–100 bar. In agreement with results in organic phase it is observed that the yield of aldehydes increases when the pressure for a given temperature was increased. This general trend was not seen while varying the temperature for a given pressure. In case of low CO/H₂ pressures (20–40 bar) an increase of the aldehyde yield was observed when the temperature was increased. However, increasing the temperature above 170°C resulted in a decrease in the yield. Above 60 bar, the aldehyde yield increases with increasing temperature. Apparently, at low CO pressures there is not enough carbon monoxide available to stabilize the catalyst, hence the yield of products decreased. This effect has also been described for unmodified cobalt catalysts [49].

3.2.2. Influence of temperature and pressure on aldehyde and alcohol *n/iso* selectivity

The regioselectivity (*n/iso* selectivity) was studied between 130–190°C and 20–100 bar. As shown in Fig. 3, the *n*-product was favored under all conditions studied (i.e., *n/iso* ratio > 50:50). This was true for both aldehydes and alcohols.

Hydroformylation at 130°C and 100 bar CO/H₂ yielded a linear to branched ratio of

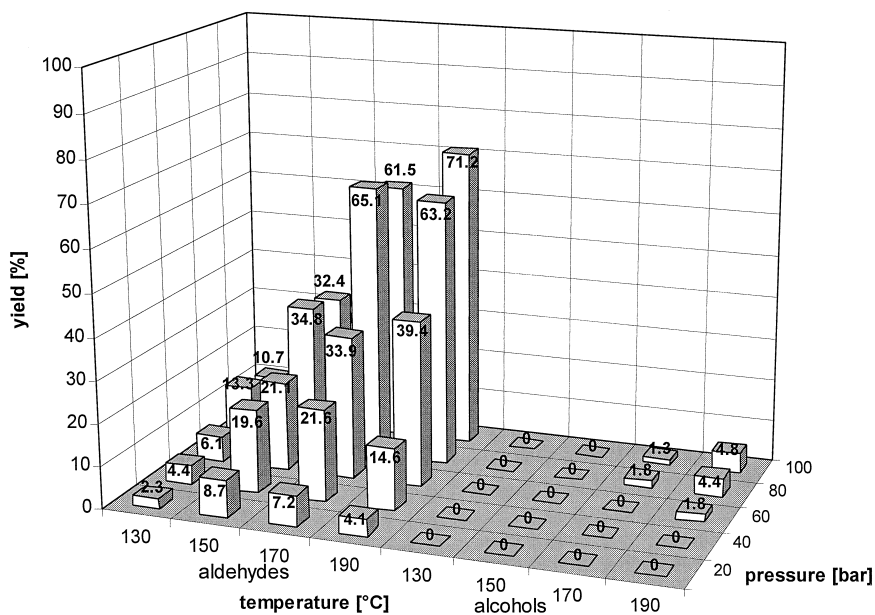


Fig. 2. Aldehyde and alcohol yields in dependence on temperature and pressure.

almost 75:25. Higher temperatures and lower pressures lead to significantly lower selectivity of the linear aldehyde, giving the lowest selec-

tivity (*n/iso* 50:50) at 190°C and 20 bar. In general, similar selectivities were observed for pentanols as products. However, due to the

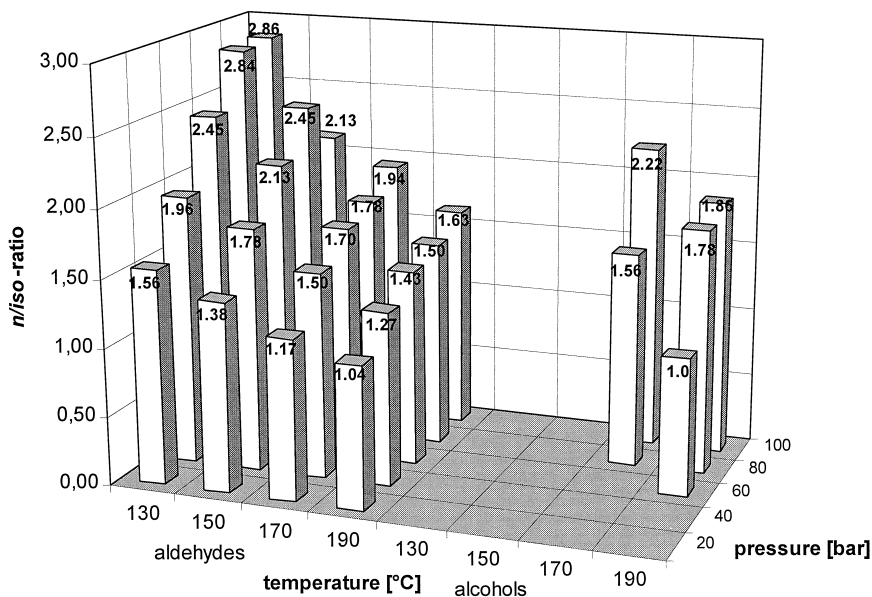


Fig. 3. Aldehyde and alcohol *n/iso* selectivity in dependence on temperature and pressure.

small amounts of alcohol formed there is certainly a larger error made when calculating the *n/iso* selectivity.

3.2.3. Variation of temperature and catalyst amount

Industrial hydroformylation processes which use cobalt as catalyst generally require high catalyst amounts, i.e., up to 0.5 mol% $\text{HCo}(\text{CO})_4$. In the aforementioned model system, we used significantly less catalyst (0.1 mol%). Thus, we were interested to study the effect of an increased amount of catalyst on product yields and selectivities. For this purpose, the reaction pressure was kept constant at 100 bar CO/H_2 (1:1). The results of the catalysis are shown in Fig. 4.

As far as the aldehyde yield is concerned the expected trend—an increase of aldehyde yield with an increase of catalyst amount—is observed at reaction temperatures between 130–170°C. The yield of hexanals also increased by a factor of 2.5 to 2.0 at 130 and 150°C, respectively. The aldehyde yield was only slightly better (factor of 1.1) at 170°C. Interestingly, at

190°C the aldehyde yield obtained with 0.1 mol% catalyst is even better by a factor of 1.2 compared to the reaction using 0.5 mol% cobalt catalyst. The effect of an increased amount of catalyst on the alcohol yield is even more pronounced. While at 130°C no alcohol formation is observed regardless of the amount of catalyst, a 5.6-fold increase of hexanols is obtained at 190°C in the presence 0.5 mol% **1** compared to 0.1 mol% **1**. As depicted in Fig. 5, the *n/iso* selectivity in both aldehydes and alcohols is independent of catalyst concentration.

3.2.4. Recycling of the catalyst

A prerequisite for the technical use of water-soluble cobalt catalysts are the efficient reuse of the aqueous catalyst phase and a small loss of cobalt in the reaction products. The efficiency of the cobalt recycling system was determined in two ways. The first method involves subsection of the recovered catalyst phase to additional hydroformylation runs. Second, determination of the amount of cobalt metal which went into the organic phase was investigated by AAS. Initially we studied retention of the catalyst

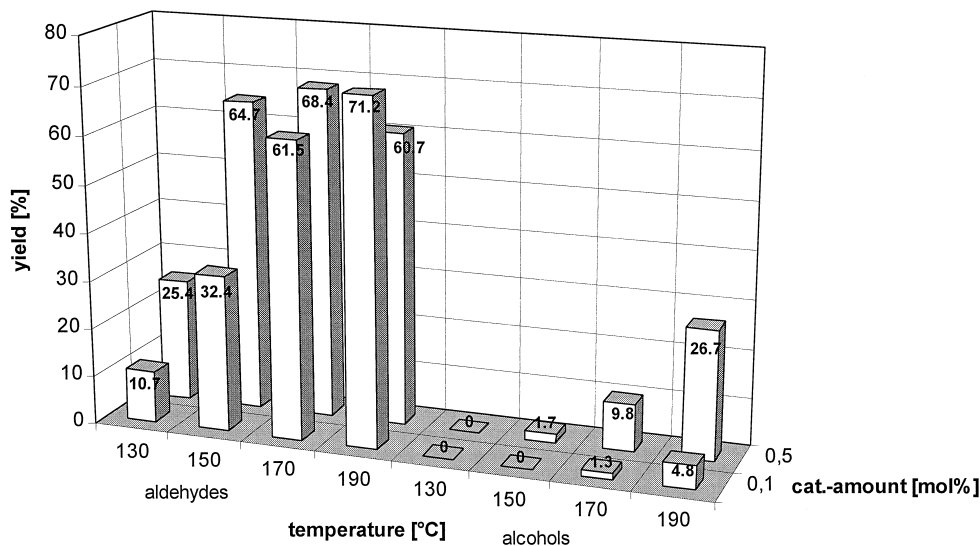


Fig. 4. Aldehyde and alcohol yields in dependence on temperature and catalyst amount.

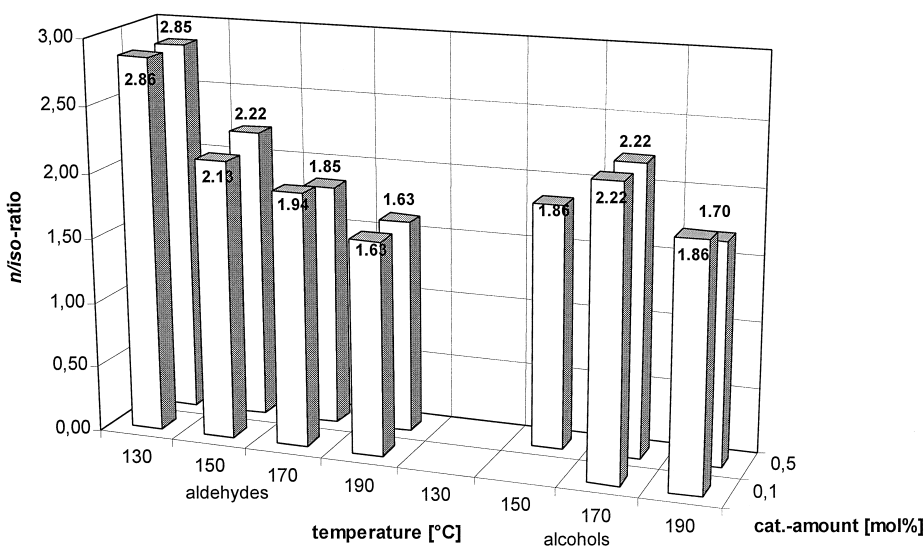


Fig. 5. Aldehyde and alcohol *n/iso* selectivity in dependence on temperature and catalyst amount.

activity by reusing the hydrophilic catalyst phase three times. Thus, the yellow colored aqueous phase was separated under argon from the organic phase after a standard hydroformylation reaction (150°C, 40 bar, 12 h, 0.1 mol% **1**, Co/P 1:10, CO/H₂ 1:1, 1100 min⁻¹) and treated with a fresh solution of 2-pentene in anisole. This procedure was repeated three times. In Fig. 6 the yield of hexanals and the *n/iso* ratio are depicted for the four runs.

Interestingly, the aldehyde yield significantly increases from 13% (1st run) to 19% (4th run). The *n/iso* selectivity remained constant at 64:36. As stated above, another important feature of the quality of a biphasic reaction is the

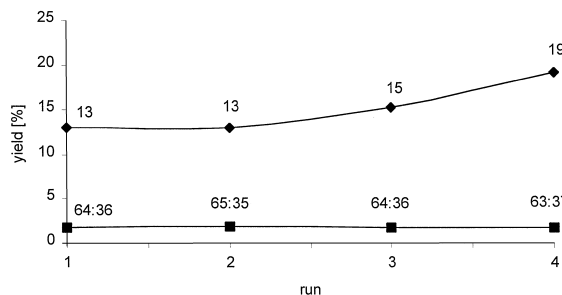


Fig. 6. Recycling of the catalyst phase.

determination of the metal amount that is extracted into the organic phase during the reaction. In Table 1, the amount of cobalt which was lost to the organic phase, as detected by AAS, is shown for various reaction temperatures and pressures.

Depending on the reaction conditions, between 0.9% (9 ppm) and 6% (60 ppm) of the total cobalt amount was found in the organic phase. The differences of catalyst leaching are not fully understood so far, however, they were independent of cobalt amount, reaction temperature, or applied pressure.

Table 1
Cobalt leaching into the organic phase

Temperature (°C)	Pressure (bar)	Co (%)	Co (ppm)
150	20	1.7	17
150	60	3.9	39
150	80	1.5	15
150	100	1.4	14
190	20	0.9	9
190	60	6.0	60
190	100	1.7	17

Reaction conditions: [Co] = 0.1 mol% = 1000 ppm; CoP = 1:10; reaction time = 12 h; stirring rate = 1100 min⁻¹; the [Co] is determined by atomic absorption spectroscopy (AAS).

4. Discussion

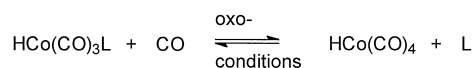
The aim of this work was to study the feasibility of a water-soluble Co/TPPTS catalyst for the biphasic hydroformylation of internal olefins. Indeed, as demonstrated by the experimental data the hydroformylation of 2-pentenes in an aqueous biphasic system with a Co/TPPTS complex is viable. Thus, we show for the first time that the superior performance of homogeneous cobalt catalysts compared to rhodium systems regarding the hydroformylation of internal olefins to *n*-aldehydes can be transferred to a biphasic reaction. Aldehyde yields up to 75% were realized at 190°C and 100 bar CO/H₂ = 1:1 using 0.1 mol% of cobalt. *n/iso* Selectivities from 50:50 to 75:25 are typical for triphenylphosphine modified cobalt catalysts and are of the same magnitude as for terminal olefins [50]. For comparison, 2-hexene is hydroformylated with HCo(CO)₃PBu₃ in benzene (170°C, 250 bar, 5 h, 20 mol%, P/Co 2:1) with an *n/iso* selectivity of 86:14 [51]. As expected, *n/iso* selectivity is independent of catalyst amount. The dramatic increase of alcohol formation with increasing catalyst amount (0.1 mol% to 0.5 mol%) at 190°C is rationalized by a consecutive reduction of the already produced aldehyde. Since the reaction time (12 h) was the same regardless of the catalyst amount, the formed aldehydes have more time to be reduced. In order to show that this reduction takes place, a 50:50 mixture of 1-hexanal and 2-methylpentanal was reduced with syngas in the presence of 0.5 mol% cobalt catalyst. After 12 h at 190°C and 100 bar, a 50:50 mixture of 1-hexanol and 2-methylpentanol was observed in 46% yield.

Recycling experiments (4 times) of the aqueous catalyst phase demonstrated that the concept of liquid/liquid biphasic catalysis works for this reaction. Remarkably, the aldehyde yield increases from 13% to 19% with reuse of the catalyst phase. We explain this behaviour by the fact that not all cobalt is transformed into the catalytically active species in one run even at

150°C and 40 bar syngas pressure, hence full catalyst activity is reached after several runs. For aqueous TPPTS modified rhodium catalysts, similar effects are known [52]. Obviously more runs have to be done in order to reach maximum catalyst activity. Nevertheless, our recycling experiments demonstrate that reuse of water-soluble catalysts is possible. So far, metal extraction from the aqueous into the organic phase is more problematic than with rhodium catalysts. This behaviour is determined by the coordination chemistry of cobalt as described below (see Scheme 1).

It is known that cobalt, in contrast to rhodium, carries only one phosphine ligand during catalysis (HCo(CO)₃L) [53]. Under oxo-conditions ligand dissociation takes place more easily compared to rhodium [54]. The resulting HCo(CO)₄ is 200-fold more active than HCo(CO)₃L [55], it is less selective and most importantly it is not water-soluble. In order to perform the oxo reaction in the water phase, and to recycle the catalyst efficiently it needs to be guaranteed that the equilibrium between HCo(CO)₃L and HCo(CO)₄ is on the left side. This can be achieved either by using an excess of a weak coordinating ligand such as TPPTS or a strong coordinating ligands (strong basic ligands). As can be seen from Table 1, only minor amounts of cobalt are leached into the organic phase if a surplus of ligand (TPPTS) is employed. However, the amount of HCo(CO)₄ in the organic phase during the reaction is not known because all cobalt measurements were done with the cooled reaction mixture.

Since the unmodified cobalt catalyst is capable of the hydroformylation of internal olefins with a 200-fold higher rate compared to a phosphine-modified catalyst, it is not clear where catalysis actually takes place. To answer this



Scheme 1. Equilibrium of phosphine modified cobalt catalysts under oxo-conditions.

question, we performed additional experiments in homogeneous medium. After a successful catalytic run (experiment: 150°C, 80 bar, 12 h, 0.1 mol% = 1000 ppm, Co/P 1:10, CO/H₂ 1:1, Co in organic phase 15 ppm; entry 3 in Table 1) the organic phase was separated from the aqueous phase, washed with water, and reused. While the initial two-phase reaction leads to 34% yield of aldehydes, the reaction performed in the reused organic phase leads only to an additional yield of 4%. Thus, the leached cobalt present at room temperature in the organic phase is only responsible for a negligible yield of aldehydes. In addition, we used Co₂(CO)₆(TPPTS)₂ (0.1 mol%) in the presence of 10 equivalents of dry TPPTS in anisole as solvent. Without any water present no aldehyde products were observed. This shows that no TPPTS modified cobalt catalyst is soluble in anisole and no conversion of **1** to HCo(CO)₄ takes place in the organic phase.

Clearly the catalyst activity of the present system is much lower than the Rh/TPPTS catalyst for the hydroformylation of propene. There are several reasons for this: (a) the solubility of 2-pentenes in water compared with propene is rather low; (b) catalysis with cobalt is, in general, slower than with rhodium; (c) hydroformylation of internal olefins is slower by a factor of about 3 [55] compared to terminal olefins. However, at present there exist no water-soluble rhodium catalyst that hydroformylates internal olefins predominately to *n*-aldehydes, and secondly cobalt is cheaper than rhodium by a factor of 4000 [1]. In this respect the Co/TPPTS catalyst is very promising for large scale applications. Our present efforts focus on minimizing the cobalt leaching into the organic phase and on the investigation of the catalyst system for the hydroformylation of other internal olefins.

Acknowledgements

We gratefully acknowledge support of this work from Bundesministerium für Bildung und

Forschung (bmb + f) and we thank Prof. Dr. B. Cornils for initiating this project, and Dr. S. Bogdanovic, Dr. R. Fischer, Dr. H. Geissler, and Prof. Dr. K. Kühlein (all CRT Hoechst) for stimulating discussions. We also thank Dr. G. Stark for valuable comments on this manuscript.

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