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Hydroformylation with rhodium phosphine-modified catalyst in a microemulsion: comparison of organic and aqueous systems for styrene, cyclohexene and 1,4-diacetoxy-2-butene

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Use of microemulsion as a reaction media in the hydroformylation of different alkenes, namely styrene, cyclohexene and 1,2-diacetoxy-2-butene have been studied using alkylpolygylcol ether-type nonionic surfactant in the presence of phosphine-modified rhodium catalyst. The combination of the experiments under comparable homogeneous and biphasic conditions were performed in order to make direct comparison of microemulsion with classical systems. Thus, the experiments were also carried out using catalysts such as unmodified rhodium carbonyl H $Rh(CO)_4$ and H $Rh(CO)(PPh_3)_3$ in homogeneous system, Rh–TPPTS complex in two-phase system and in association with co-solvent.

KEY WORDS: hydroformylation; microemulsion; substituted alkene; nonionic surfactant; rhodium catalyst.

1. Introduction

Hydroformylation reaction represents the best technology for the synthesis of aldehydes from olefins [1]. The concept of biphasic catalysis was applied to the hydroformylation first in the Ruhrchemie/Rhône-Poulenc (RCH/RP) process. The simple aqueous/hydrocarbon system provides rapid product catalyst separation. However, the application of this system is limited to low molecular mass olefins which have adequate water solubility [2]. This solubility problem can be solved by adding a suitable surfactant to the biphasic system. Reverse micelles are formed by association of polar head groups of the surfactant with colloid drops of water in an organic medium [3]. Catalytically active groups are carried by the reverse micelles and these reverse micelles act as a catalyst.

Hydroformylation of alkenes with carbon number up to 12 in microemulsion using sodium dodecyl sulfonate (SDS) and butanol has been investigated by Tinucci and Platane [4]. The use of cationic surfactant such as cetyltrimethylammomiumbromide (CTAB) has been studied in the hydroformylation of unsaturated fatty acids [5] and 1-dodecene [6,7].

In recent years, the hydroformylation of substituted olefins is gaining importance and the applications for several valuable organic intermediates for pharmaceuticals and fine chemicals are emerging [8]. Styrene and 1,4-diacetoxy-2-butene (DAB) are important examples of these classes of substrates.

Several kinetic and mechanistic studies of the hydroformylation of styrene have been performed [9, 10]. Using unmodified rhodium, the detailed kinetic analysis reported that the hydrogen activation on the 4 coordinate species is the rate limiting step and product formation is accompanied by the formation of a transient species H $Rh(CO)_3$ [11].

The effect of the reaction conditions on the regioselectivity in the hydroformylation of styrene has been studied by Lazzaroni *et al.* [12]. Branched aldehyde is found as a major product and it decreases with decrease in CO or H_2 partial pressure. By means of deuterioformylation, it is showed that the regioselectivity depends on the reaction conditions. At high temperatures, β-hydride elimination of the branched alkyl intermediate forms back styrene, therefore the branched to linear ratio diminishes. However, the formation of branched and linear alkyl intermediates is irreversible at room temperature.

In another study, kinetics of hydroformylation of styrene, cyclohexene and octene using rhodium-[tris(2-*tert*-butyl-4-menthylphenyl)phosphite] catalyst has been reported [13].

Chaudhari and coworkers [14] have reported the kinetics of hydroformylation of styrene using H $Rh(CO)(PPh_3)_3$. The rate was found to be independent of styrene concentration and first order with respect to catalyst concentration and hydrogen partial pressure. The activation energy was found to be 68.80 kJ mol^{-1} in a temperature range of 333–353 K.

In the manufacturing of vitamin A, hydroformylation using rhodium catalyst is a key step (cf. figure 1). Major producers, BASF and Hoffmann–La Roche have

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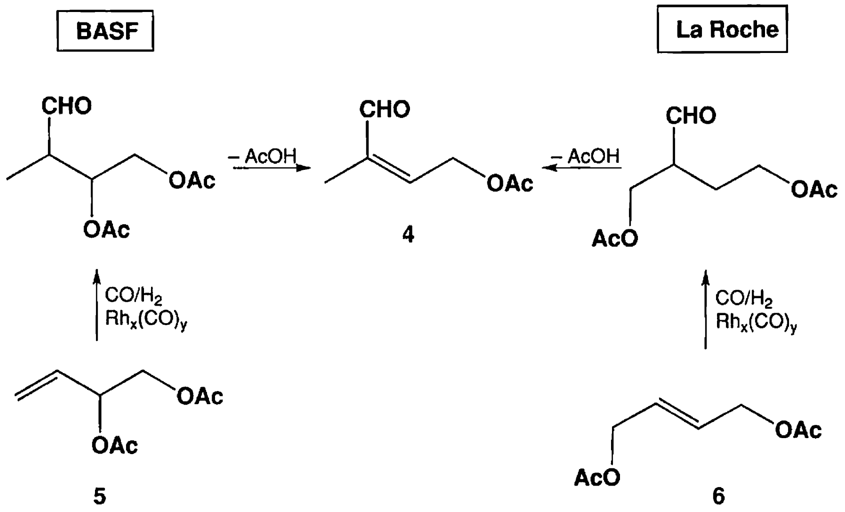

Figure 1. The hydroformylation step in the synthesis if vitamin A precursor 4.

developed processes starting from DAB. 1,4-Diacetoxy-2-butene is hydroformylated using phosphine-modified rhodium catalyst to yield 1,4-diacetoxy-2-formylbutane in the Hoffmann–La Roche process [15], whereas it isomerizes to 1,2-diacetoxy-3-butene at the first stage which is hydroformylated using unmodified rhodium carbonyl catalyst at a high reaction temperature in the BASF process [16]. In a recent paper, kinetics of hydroformylation of DAB using a homogeneous H $Rh(CO)(PPh_3)_3$ has been studied in a temperature range of 338–358 K [17]. The reaction was found to be zero order with substrate concentration and first order with respect to catalyst and H_2 partial pressure.

Several analysis has been reported on hydroformylation of cyclohexene [18, 19]. Kinetics of hydroformylation of cyclohexene has been studied by Marko [20] using $Rh_4(CO)_{12}$ as the catalyst precursor. Addition of the cyclohexene to the hydrido–rhodium carbonyl complex was the rate determining step under the conditions studied.

Marko *et al.* have also shown that reactivity of alkenes in hydroformylation followed systematic trend: Styrene > terminal alkenes > internal alkenes > cyclic alkenes. In our ongoing work on the rhodium-catalyzed hydroformylation in microemulsion medium [21, 22], we have recently described how adding nonionic surfactant effects the hydroformylation of 1-octene in the presence of rhodium complex associated with triphenylphosphine sulfonate [Yildz-Ünveren and Schomäcker, submitted]. The active species during the hydroformylation of 1-octene in microemulsion medium have been investigated using high-pressure infrared (HP-IR) spectroscopy [Yildz-Ünveren et al., in preparation].

Here, we report on the extension of the scope of microemulsion as a reaction media in the hydroformylation of long-chain olefins. Thus, hydroformylation of styrene, cyclohexene and 1,2-diacetoxy-2-butene have been studied using microemulsion stabilized by nonionic surfactant. In addition, all the organic reactants were also tested under homogeneous and biphasic conditions.

2. Experimental

2.1. Materials

Rhodium dicarbonyl acetylacetonate $Rh(acac)(CO)_2$ (Sigma-Aldrich), and 30.7 wt.% aqueous solution of tris-(3-sulfophenyl)-phosphine trisodium salt (TPPTS) were used as received without further purification. The substrates styrene and cyclohexene were purchased from Sigma-Aldrich and DAB was purchased from Narchem Cor. in its highest purity available. The technical grade surfactant Marlipal O13/70 (alkylpolyglycolether derived via ethoxylation of isodecanol), syngas (CO/H_2 1:1) were from Condea Chemicals and Messer Griesheim, respectively. Toluene was used as co-solvent and purchased from Sigma-Aldrich.

2.2. Experimental procedure

Hydroformylation experiments were carried out in a 100-mL autoclave supplied by Premex. Preparation of the reaction mixtures, details of the experimental set-up and procedure were identical as described earlier [21, Yildz-Ünveren and Schomäcker, submitted].

Standard experiments were carried out at syngas pressure of 60 bar and temperature of 85 °C. Composition of the microemulsion was 79 wt.% of alkene, 13 wt.% of surfactant and 8 wt.% of aqueous catalyst solution. The rhodium concentration of the reaction mixtures was 200 ppm with respect to the substrate. The analysis of the products and the reactants were carried out by gas chromatography (Sichromat 3 with Rtx-5MS capillary column). Reproducibility of all the experiments was checked by at least one duplicate experiment in order to gain confidence.

3. Results and discussions

3.1. Hydroformylation of styrene

In preliminary experiments, the material balance of styrene hydroformylation was examined using Rh–TPPTS complex in microemulsion medium at standard reaction conditions (ligand/metal (L/M) = 4). The products formed were 2-phenyl-propionaldehyde and 3-phenyl-propionaldehyde under the condition studied (see figure 2). No hydrogenation or isomerization products were observed.

For the comparison of the performance of the microemulsion, the reaction was also tested under homogeneous and biphasic conditions. Thus, styrene was hydroformylated using unmodified rhodium H $Rh(CO)_4$ and H $Rh(CO)(PPh_3)_3$ catalysts in homogeneous system and using Rh–TPPTS complex in two-phase system and in association with co-solvent. Aldehyde selectivities (b/n) and initial catalytic activities, i.e. mol of substrate transformed per mol of catalyst per minute at 10–20% conversion, are summarized in table 1.

First, the reactions were performed at ligand to metal ratio of 4. Regioselectivities are directed towards the formation of the branched aldehyde for the all catalytic systems. Preference of styrene to form branched aldehyde has been suggested by several authors [23,24].

Under homogeneous conditions (unmodified, TPP modified), catalytic activities appear to be very high, as expected. The initial catalytic activity and more noteworthy the selectivity of the system is improved as the catalyst is changed from unmodified rhodium carbonyl H $Rh(CO)_4$ to H $Rh(CO)(PPh_3)_3$. The catalytic activity of biphasic system is somewhat lower than the analogous reactions under homogenous conditions due to low solubility of styrene in water phase. However, the activity is still higher than expected for Rh–TPPTS complex in two-phase system. Moreover, the selectivity under biphasic condition is almost equal to that of unmodified rhodium. These results indicate that unmodified rhodium carbonyl complex H $Rh(CO)_3$ which is formed by loosing the ligand is the predominant species under biphasic condition with L/M ratio of 4.

Addition of the co-solvent to the biphasic system leads to an enhancement of the catalytic activity, but more note worthy, to a decrease in the selectivity toward the branched aldehyde. As known, the unmodified rhodium complex is soluble in nonpolar solvents and leads to high rates and low selectivities. Therefore, such an increase in activity and a decrease in selectivity can be attributed to an increase in the fraction of the unmodified rhodium carbonyl species in biphasic system by addition of the co-solvents.

Under microemulsion conditions, the selectivity towards the branched aldehyde and the total conversion after 24 h was 2.13 and 94.1%, respectively. From the selectivity point of view, the microemulsion system is slightly better than the biphasic and the unmodified systems at L/M ratio of 4.

As previously indicated, it seems that the L/M ratio of 4 is not sufficient to convert all the rhodium into the water-soluble complex under biphasic conditions. In order to examine this, the experiments under biphasic, microemulsion and homogeneous (Rh–TPP) conditions were repeated with higher L/M ratio (L/M = 10).

At high ligand concentration, all the rhodium species are modified by the ligand and converted into the water-soluble complex. Therefore, no hydroformylation of the water insoluble substrate is observed under biphasic conditions.

Under homogeneous H $Rh(CO)(PPh_3)_3$ conditions, a significant improvement is observed both in the catalytic activity and the aldehyde selectivity by increasing the L/M ratio from 4 to 10. Finally, under microemulsion conditions higher selectivity is observed along with poorer catalytic activity with higher ligand excess. All these observation can be attributed most probably to the shift of the equilibria between various active species by the addition of more ligand.

From the reaction rates point of view, it is known that the catalytic activity varies nonlinearly as a function of phosphine concentration [25]. The activity increases as the phosphine concentration increases, until it reaches to a maximum value. Further increase in the ligand concentration leads to lower rates due to the hindrance of the formation of the active species. The selectivity of the reaction is improved by increasing the phosphine

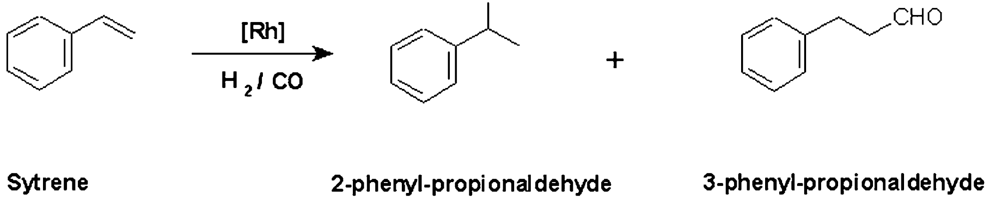

Figure 2. Reaction scheme for hydroformylation of styrene.

Table 1
Hydroformylation reaction of styrene

Catalytic system	Ligand	L/M[a]	Time (min)[b]	r_o[c]	b/n[d]
Unmodified	–	–	119	69.8	1.60
Homogeneous	TPP	4	67	82.7	3.20
Biphasic	TPPTS	4	450	34.0	1.74
With co-solvent	TPPTS	4	116	70.2	1.63
Microemulsion	TPPTS	4	1440	10.0	2.13
Microemulsion	TPPTS	10	1440	2.1	3.66
Homogeneous	TPP	10	45	124.9	8.54
Biphasic	TPPTS	10	*	*	*

*No reaction.
[a]Ligand per metal ratio.
[b]Optimized reaction time for total conversion except for microemulsion L/M 4: 94.1% con.; microemulsion L/M 10: 2.8% con.
[c]Initial activity; mol of substrate transformed per mol of catalyst per minute.
[d]Ratio of branched to linear aldehyde.

concentration and it remains constant at a point where the activity has reached a maximum.

In the present system, the increase in the catalytic activity and the selectivity can be clearly seen as the L/M ratio increases from 4 to 10 under homogeneous conditions (Rh–TPP). However, in the case of microemulsion, decrease in the catalytic activity is observed with the variation of the ligand excess from 4 to 10. Therefore, it is reasonably to state that under microemulsion conditions the decreasing trend of the catalytic activity begins at lower ligand excess with respect to homogeneous equivalent due to high local ligand concentration in the small reverse micelle. All the observations are in good agreement with the results obtained for 1-octene in our previous study [Yildz-Ünveren and Schomäcker, submitted].

3.2. Hydroformylation of cyclohexene

Cyclohexene was chosen as an example of cyclic olefins in order to test the application of microemulsion as a reaction medium in the hydroformylation reaction. As in the case of styrene, the performance of the microemulsion was compared with its monophasic and biphasic equivalents. The catalytic systems were tested with two different L/M ratios, 4 and 10, respectively. Cyclohexanecarboxaldehyde and cyclohexane carboxylicacid were the products formed under the reaction conditions studied (see figure 3).

Table 2 summarizes the results of the varying catalytic systems. As known, the hydroformylation of the cyclic alkenes is rather difficult due to their internal double bonds. Thus, for the all catalytic systems the observed catalytic activities are lower than the activities which were found for styrene or 1-octene. The aldehyde selectivities are greater than 99% in all cases.

As expected, the highest catalytic activity is observed with unmodified rhodium carbonyl catalyst. The change of the catalyst from unmodified rhodium carbonyl H $Rh(CO)_4$ to H $Rh(CO)(PPh_3)_3$ and the change of the reaction medium from homogeneous to biphasic and from biphasic to microemulsion result in a systematic decrease in the catalytic activity. Moreover, in all these cases increase in the L/M ratio leads to lower catalytic activities. Thus, no hydroformylation of cyclohexene is observed under biphasic and microemulsion conditions with L/M ratio of 10. Therefore, it is reasonable to conclude that the unmodified rhodium carbonyl is the only active species for the hydroformylation of cyclohexene. Since only the unmodified rhodium carbonyl is the active species, the increase in the catalytic activity under biphasic conditions by addition of the co-solvent is attributed to an increase in the proportion of the unmodified rhodium carbonyl complex. This effect was also observed for the hydroformylation of the styrene as mentioned before. In the table 3 the influence of the reaction pressure on the total conversion under biphasic conditions at the L/M ratio of 4 is presented. Increasing the reaction pressure causes an increase in the catalytic activity. At higher pressures the reaction seems to be further accelerated, thus, going from 60 to 100 bar the reaction proceeds faster by a factor of 132. This

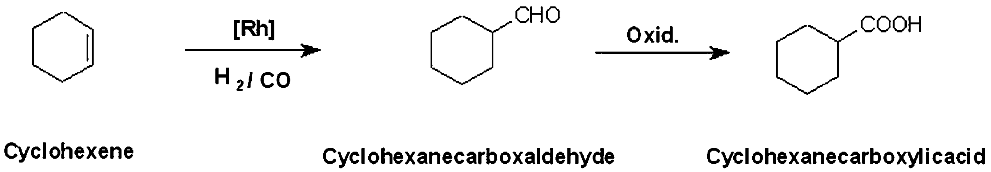

Figure 3. Reaction scheme for hydroformylation of cyclohexene.

Table 2
Hydroformylation reaction of cyclohexene

Catalytic system	Ligand	L/M[a]	X_T (%)[b]	r_o[c]	S[d]
Unmodified	–	–	100	31.1	99.8
Homogeneous	TPP	4	57.2	5.5	99.2
Biphasic	TPPTS	4	2.1	0.3	100
With co-solvent	TPPTS	4	100	8.6	100
Microemulsion	TPPTS	4	0.42	udl	100
Microemulsion	TPPTS	10	*	*	*
Homogeneous	TPP	10	33.2	3.21	99.1
Biphasic	TPPTS	10	*	*	*

*No reaction.
udl, under detection limit.
[a] Ligand per metal ratio.
[b] Total conversion after 1200 min, optimized reaction time for unmodified and associated with co-solvent system is 300 and 800 min.
[c] Initial activity; mol of substrate transformed per mol of catalyst per minute.
[d] Aldehyde selectivity, oxidation product accounts for the balance.

Table 3
Influence of syngas pressure on hydroformylation of cyclohexene[a]

Pressure (bar)	X_T (%)	r_o[b]	S[c]
60	0.7	0.3	100
80	86.5	16.7	99.7
100	100	39.6	99.8

[a] Biphasic system, L/M 4, $t = 200$ min.
[b] Initial activity; mol of substrate transformed per mol of catalyst per minute.
[c] Aldehyde selectivity, oxidation product accounts for the balance.

acceleration is probably because of the formation of unmodified rhodium carbonyl by higher syngas pressure.

3.3. *Hydroformylation of 1,4-diacetoxy-2-butene*

Investigation of the heterogenized catalysts can have many advantages in the hydroformylation of DAB, because of the high boiling points and thermal instability of the corresponding aldehydes. This is the reason why we chose the substrate to test the microemulsion.

For the product identification 1,4-diacetoxy-2-butene was hydroformylated by using H Rh(CO)$(PPh_3)_3$ catalyst with L/M ratio of 10 at the standard reaction conditions. The major product formed was 1,4-diacetoxy-2-formyl butane (DAFB). As indicated by Chansarkar *et al.* [17], the elimination of the acetic acid from DAFB appeared as a side step reaction. The involved reactions are presented in figure 4. The comparison of the performance of the catalytic systems is summarized in table 4. The use of unmodified rhodium catalyst results in isomerization of the substrate (6.2% after 24 h). However, the hydroformylation of this isomer is not observed during the reaction. Although high reaction rates can be obtained using unmodified rhodium and H Rh(CO)$(PPh_3)_3$ catalysts, the selectivities for FAB are in the range of 25–35%. The use of biphasic system results in higher selectivity along with a poor activity. Addition of the surfactant to the biphasic system causes enhancement in the catalytic activity. However, the activity is still lower than the one that was observed under homogeneous condition (both for unmodified and TPP modified rhodium). In spite of this relatively low activity, the use of microemulsion represents the best selectivity for FAB and it offers the possibility of simple catalyst recovery. Therefore, microemulsion might be an interesting approach for the hydroformylation of DAB.

The influence of the reaction temperature and pressure on selectivity and conversion under microemulsion conditions is shown in table 5. The effect of the temperature was investigated over a range

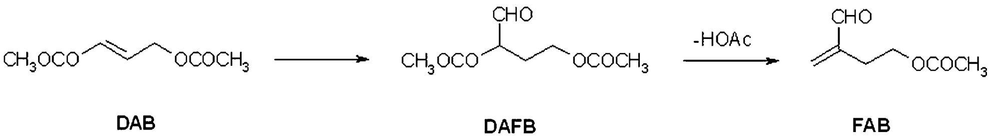

Figure 4. Involved reactions in hydroformylation of 1,4-diacetoxy-2-butene.

Table 4
Hydroformylation reaction of 1,4-diacetoxy-2-butene[a]

Catalytic system	Ligand	L/M[b]	X_T (%)[c]	S_{DAFB} (%)	S_{FAB} (%)
Unmodified	–	–	97.4	67.4	26.4
Homogeneous	TPP	10	95.8	66.0	33.9
Biphasic	TPPTS	10	21.4	43.1	56.9
Microemulsion	TPPTS	10	31.1	41.7	58.3

[a] At standard reaction conditions, $t = 1440$ min.
[b] Ligand per metal ratio.
[c] Total conversion of DAB.

Table 5
Effect of reaction temperature and pressure on hydroformylation reaction of DAB[a]

Pressure (bar)	Temperature (°C)	X_T (%)[b]	S_{DAFB} (%)	S_{FAB} (%)
60	60	8.9	53.6	46.4
60	85	31.1	41.7	58.3
60	100	22.1	27.3	72.7
80	85	39.2	45.1	54.9

[a] Microemulsion, L/M 4, $t = 1440$ min.
[b] Total conversion of DAB.

of 60–100 °C. The increase in the selectivity towards deacetoxylation product (FAB) is observed at high temperatures. Drop in the catalytic activity appears as the reaction temperature increase from 85 to 100 °C. This surprising result is due to the change of the phase behavior of the microemulsion. Formation of the two phases from the microemulsion at higher temperatures is the reason of such a decrease in the catalytic activity.

The effect of the reaction pressure is less pronounced on the FAB selectivity and the proportion of FAB decreases upon increasing syngas pressure.

Deacetoxylation of DAFB to produce FAB is only a function of temperature, whereas the hydroformylation of DAB is a function of both temperature and synthesis gas pressure. Therefore, at high temperatures FAB is favored but at high pressures DAFB.

4. Conclusion

In the all catalytic systems which were studied here the hydroformylation of styrene is somewhat faster than the hydroformylation of cyclohexene and DAB. With the exception of unmodified rhodium carbonyl catalyst reactivity of the olefins show the following order: styrene > DAB > cyclohexene

When unmodified rhodium carbonyl is used as a catalyst, cyclohexene is hydroformylated faster than DAB.

As also observed in our previous study, addition of the co-solvent to the biphasic system leads to an increase in the proportion of the unmodified rhodium species. Therefore, use of the co-solvent results in high catalytic activity along with poor regioselectivity.

The unmodified rhodium carbonyl is found to be the only active species in the hydroformylation of cyclohexene. At high syngas pressures the equilibrium between the active species shifts towards unmodified rhodium complex. Therefore, the catalytic activity is further accelerated.

The use of microemulsion in the hydroformylation of the DAB gives the best selectivity toward deacetoxylated product (FAB) among the catalytic systems. The selectivity for FAB increases upon increasing reaction temperature and decreasing syngas pressure.

The corresponding aldehydes of DAB are unstable and non-volatile. Therefore, the use of microemulsion as a reaction medium might be a good alternative to homogeneous processes, because the microemulsion offers simple catalyst recovery by temperature-induced phase separation.

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References

[1] B. Cornils and W. Herrmann, eds. *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 2 (VCH, 1996).
[2] B. Cornils and W.A. Herrmann, eds. *Aqueous Phase Organometallic Catalysis* (VCH, 1998).
[3] K.V. Schubert and E.W. Kaler, Ber. Bunsenges. Phys. Chem. 100 (1996) 190.
[4] L. Tinucci and F. Platone, Enichircherche SpA EP 0.380.154.
[5] B. Fell, C. Schobben and G. Papadogianakis, J. Mol. Catal. A: Chem. 111 (1995) 179.
[6] H. Chen, H. Liu, Y. Li, P. Cheng and X. Li, Chin. J. Mol. Catal. A: Chem. 9 (1995) 145.
[7] H. Chen, Y. Li, J. Chen, P. Cheng, Y. He and X. Li, J. Mol. Cat. A: Chem. 149 (1999) 1.
[8] K. Othmer, ed. *Encyclopedia of Chemical Technology*, 4th edn. Vol. 25 (Wiley/Interscience, 1998).
[9] I. Rio, O. Pamies, P.W.N.M. Leeuwen and C. Claver, J. Organomet. Chem. 608 (2000) 115.
[10] K. Nozaki, T. Matsuo, F. Shibahara and T. Hiyama, Organometallics 22 (2003) 594.
[11] J. Feng and M. Garland, Organometallics 18 (1999) 417.

[12] R. Lazzaroni, A. Rafaelli, R. Settambolo, S. Bertozzi and G. Vitulli, J. Mol. Catal. 50 (1989) 1.
[13] A. Rooy, E.N. Orij, P.C.J. Kamer and P.W.N.M. Leeuwen, Organometallics 14 (1995) 34.
[14] V.S. Nair, S.P. Mathew and R.V. Chaudhari, J. Mol. Catal. A: Chem. 143 (1999) 99.
[15] P. Fitton and H. Moffet, US Patent 4.124.619.
[16] W. Himmele, W. W. Aquila, US Patent 3.661.980.
[17] R. Chansarkar, K. Mukhopadhyay, A. Kelkar and R. Chaudhari, Catal. Today 79–80 (2003) 51.
[18] J. Feng and M. Garland, Organometallics 18 (1999) 1542.
[19] G. Liu, R. Volken and M. Garland, Organometallics 18 (1999) 3429.
[20] B. Heil, L. Marko and G. Bor, Chem. Ber. 104 (1971) 3418.
[21] M. Haumann, H. Yildiz, H. Koch and R. Schomäcker, Appl. Catal. A Gen. 236 (2002) 173.
[22] M. Haumann, H. Koch, P. Hugo and R. Schomäcker, Appl. Catal. A Gen. 225 (2002) 239.
[23] M. Tanaka, T. Hayashi and I. Ogata, Bull Chem Soc. Jpn. 50 (1997) 2351.
[24] I. Ojima, Chem. Rev. 88 (1988) 1011.
[25] K.L. Olivier and F.B. Booth, Hydrocarbon Process. 49 (1970) 112.