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The effects of process variables in the hydroformylation of methyl methacrylate with the in situ formed (*o*-thiomethylphenyl) diphenylphosphine rhodium complex

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Abstract

The hydroformylation of methyl methacrylate (MMA) was studied with the in situ formed (*o*-thiomethylphenyl)diphenylphosphine (SP) rhodium catalyst to establish the effect of the rhodium precursor, temperature, ligand-to-rhodium ratio, and hydrogen and carbon monoxide partial pressures on the activity and selectivity of the reaction. The performance of the SP modified reaction was compared to the performance of unmodified and triphenyl phosphine (PPh_3) modified reactions.

In the case of the SP modified reaction, the rhodium precursor had a significant effect on the conversion, but only a minor effect on the selectivity. In contrast to the PPh_3 ligand, the regioselectivity of reaction did not change as the temperature and the total pressure were varied with a fixed $[H_2]/[CO]$ ratio. Unfortunately, the deactivation of the catalyst was strong at elevated temperatures. The increase in hydrogen partial pressure increased the conversion of MMA but had no effect on the selectivity. A minimum carbon monoxide pressure was needed to achieve good chemo- and regioselectivities. The increase in catalyst concentration accelerated the rate of parallel hydrogenation.

Keywords: Hydroformylation; Methyl methacrylate; (*o*-Thiomethylphenyl)diphenylphosphine; Temperature; Partial pressure

1. Introduction

Hydroformylation is one of the most important homogeneously catalysed reactions for functionalising olefins and thus offering powerful routes for preparing a wide variety of significant intermediates, most notably for pharmaceutical, cosmetics, adhesives and coating industries [1–5]. The most active research area in hydroformylation is ligand synthesis and their coordination chemistry [1].

Many alkenic compounds containing various functional groups, e.g. esters and alcohols, have been successfully hydroformylated. The hydroformylation of esters of unsaturated acids, particularly the industrially available acrylic and methacrylic acids, is an attractive synthetic route for the preparation of bifunctional compounds. The aldehydes derived from α-formylation can be easily converted into substituted malonic esters, and β-formylation products into 1,4-dicarboxylic acids and esters, which are useful

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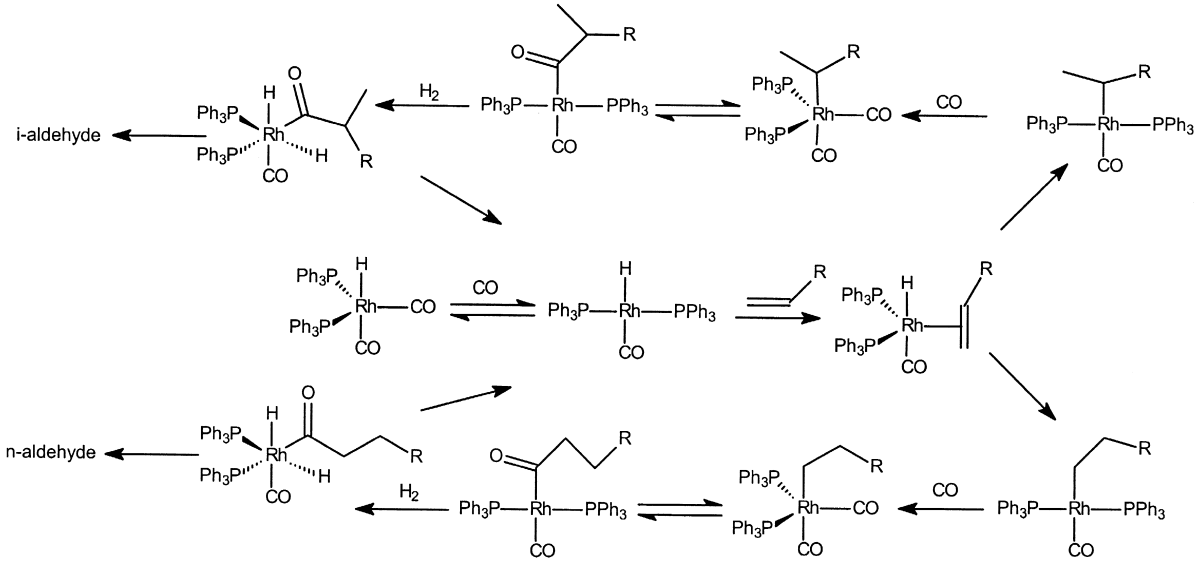
components for polyester manufacture [6]. Under hydroformylation conditions, methyl methacrylate (MMA) is mainly converted into branched methyl-α-formylisobutyrate (α-MFIB) or the linear isomer, methyl-β-formylisobutyrate (β-MFIB). Hydrogenation also occurs to some extent yielding methyl isobutyrate (MIB).

Hydroformylation of MMA with bidentate phosphine ligands was studied already in late 1970s by Tanaka et al. [7]. Later, triphenyl phosphine (PPh_3), the most used ligand in industrial hydroformylation processes, and its various derivatives were studied as possible ligand alternatives [8,9]. Recently, Alper and Zhou [10] introduced a zwitterionic rhodium 1,4-bis(diphenylphosphino)butane complex with high α-selectivity.

In the hydroformylation of MMA, branched-to-normal selectivity is highly dependent on reaction parameters [7,8]. In case of α,β-unsaturated esters, elevated pressure and low temperature favour the formation of the α-isomer, whereas the opposite is observed for the β-isomer. With PPh_3, the increase in ligand-to-rhodium ratio favours the formation of β-MFIB, whereas at low-ligand-to-rhodium ratios, the formation of α-MFIB is favoured [7–9]. In industrial use, the excess of a ligand is needed to preserve the stability of rhodium in the long run. However, the excess of a ligand also generally decreases the activity because of stabilisation of the species, which must dissociate the ligands during the catalytic cycle [2]. The effect of the excess depends strongly on the phosphorous ligand, e.g. Bergounhou et al. [11] reported that both activity and selectivity were independent of ligand-to-rhodium ratio with 1,2,5-triphenylphosphole ligand, whereas in the case of PPh_3 [2,8,9], selectivity is strongly dependent on the ligand-to-rhodium ratio.

It is generally accepted that when using the Wilkinson's catalysts, the active species are the same regardless the nature of the rhodium source (Scheme 1). On the other hand, the initial rhodium source modifies the nature of the in situ formed active complex and with some rhodium precursor–ligand combinations, the influence on activity and selectivity can be significant [12].

In our previous work [13], it was shown that in MMA hydroformylation, the potentially bidentate (*o*-thiomethylphenyl)diphenylphosphine (SP) ligand exhibited considerably higher



Scheme 1. Wilkinson's dissociative mechanism for rhodium catalysed hydroformylation.

selectivity to α-MFIB ($i/n \sim 27$) than did 1,2-bis(diphenylphosphino)ethane and 1,4-bis(diphenylphosphino)butane, which are known to be very effective in selective α-formylation of α,β-unsaturated esters. We also showed that even though regioselectivity of the reaction is known to be highly dependent on process variables [8], the pressure increase had no effect on the selectivity of the SP ligand. However, in order to become an industrially interesting option, the effect of various process parameters on the stability of the catalyst needs to be known. Therefore, the aim of this work was to establish the effect of the rhodium precursor, temperature, ligand-to-rhodium ratio, and hydrogen and carbon monoxide partial pressures on the activity and selectivity of the in situ formed SP-rhodium catalyst.

2. Experimental

All the hydroformylation experiments were carried out in a 250-ml autoclave (Berghof) equipped with a sampling system. The experiments were carried out in a semi-batch mode. A disposable inner Teflon reactor was used to avoid the accumulation of rhodium on the reactor walls. Furthermore, the purity of the system was checked with blank runs before each experiment. The rhodium precursors used in the experiments were $Rh(NO_3)_3$ (Fluka), $Rh_2(CO)_4Cl_2$ (Johnson Matthey), $[Rh(C_5H_7O_2)(CO)(PPh_3)]$ (Johnson Matthey), $Rh_4(CO)_{12}$ (Johnson Matthey), and $[Rh(norbornadiene)_2]BF_4$ (Johnson Matthey). The ligands used in the experiments were commercial PPh_3 (Fluka, ~99%) and SP (>95%) [13].

In a typical experiment, the autoclave was charged with the respective rhodium precursor (0.02 mmol calculated as rhodium), MMA (50 mmol, Merck, >99%), toluene (200 mmol, Fisher Scientific International, >99%), internal standards decane (7 mmol, Fluka, >98%), and cyclohexane (12 mmol, Riedel de Häen, >99%), and the respective phosphine. If not otherwise stated, the ligand-to-rhodium ratio was 4:1. The system was first flushed with nitrogen and heated to the reaction temperature (50–150°C) with continuous stirring, and then pressurised to the reaction pressure (20–80 bar) with a desired molar ratio of H_2 and CO (1:1, if not otherwise stated). Four samples were taken for analysis in each experiment; one immediately after pressurising with H_2 and CO, which was considered as the starting point of the reaction, and one after every first, third and fifth hour.

The products were analysed with a Hewlett Packard 5890 GC equipped with a capillary column (HP-1, 1.0 μm × 0.32 mm × 60 m) and a flame-ionisation detector. Products were quantified by the internal standard method. In addition, the aldehydes that formed were identified by GC-MS analysis, and after fractional distillation, by ^1H NMR spectroscopy.

Thermogravimetric analysis of the SP ligand was performed under air at a rate of 5°C/min up to 900°C.

Calculations of conversion, selectivity, yield, and i/n ratio were done on molar basis. Conversion was calculated with respect to MMA. The i/n ratio of the products was defined as the amount of branched product divided by the amount of linear product.

In order to estimate hydrogen and carbon monoxide concentrations in the liquid phase during reaction, phase equilibrium of the reaction was calculated with Soave's modification of the Redich Kwong equation of state [14]. The properties of the reaction mixture were simulated with the properties of toluene.

3. Results

The effect of the rhodium precursor on conversions and selectivities with the in situ formed SP rhodium catalyst is shown in Table 1. At 20 bar, $Rh(NO_3)_3$ and $[Rh(C_5H_7O_2)(CO)(PPh_3)]$ gave quite low conversions, 9% and 14%, respectively, whereas $Rh_2(CO)_4Cl_2$ gave virtually

Table 1
Effect of rhodium precursor on conversions and selectivities with the SP ligand in the hydroformylation of MMA[a]
n.a. = not applicable; n.r. = no detectable reaction; t.a. = trace amount.

Precursor	Pressure, bar	Conversion, %	Selectivity, %		
			MIB	α-MFIB	β-MFIB
$Rh(NO_3)_3$	20	9	9	86	5
$Rh_2(CO)_4Cl_2$	20	n.a.	–	t.a.	–
$[Rh(C_5H_7O_2)(CO)(PPh_3)]$	20	14	4	83	14
$Rh(NO_3)_3$	60	43	4	87	4
$Rh_4(CO)_{12}$[b]	60	24[c]	0[c]	95[c]	3[c]
$[Rh(norboynadiene)_2BF_4$	60	n.r.	–	–	–
$[Rh(norboynadiene)_2BF_4$[d]	60	n.a.	–	t.a.	–

[a] 100°C, $H_2/CO = 1:1$, MMA/Rh = 2500, L/Rh = 4, reaction time = 5 h.
[b] Due to experimental procedure, the reaction mixture was in contact with air for a short period.
[c] Reaction time = 3 h.
[d] L/Rh = 2.

no detectable reaction in 5 h. At 60 bar, $Rh(NO_3)_3$ and $Rh_4(CO)_{12}$ gave moderate conversions, 43% and 24%, respectively. Due to the experimental setup and the fact that MMA is easily polymerised under inert atmosphere (stabiliser hydroquinone deactivates under inert atmosphere), $Rh_4(CO)_{12}$ was in contact with air for a short time and thus carbonyl species started to decompose, explaining the low activity of the catalyst when compared to $Rh(NO_3)_3$. When $[Rh(norbornadiene)_2]BF_4$ was used as the rhodium source, there was no detectable reaction during 5 h, even though with plain $[Rh(norbornadiene)_2]BF_4$ the conversion was 87% after 5 h (β-form favoured).

The selectivity to α-MFIB was high regardless of rhodium precursor. Even in the case of $Rh_2(CO)_4Cl_2$ and $[Rh(norbornadiene)_2]BF_4$, trace amounts of α-MFIB were detected. However, with $[Rh(C_5H_7O_2)(CO)(PPh_3)]$, the β-MFIB selectivity was significantly higher (14%) than with other precursors.

The dependence of conversion and selectivity on L/Rh ratio is shown in Fig. 1 for both SP and PPh_3 ligands at 20 bar and 100°C. The addition of PPh_3 into the reaction mixture enhances conversion up to L/Rh ratio of 10, whereas the addition of SP immediately decreases conversion and at L/Rh ratio of 10, the conversion was almost negligible. With the PPh_3 ligand at L/Rh ratio of 10, β-MFIB was still the main product ($i/n < 1$) and the formation of α-MFIB became favoured only at L/Rh ratio of 100 ($i/n = 2$), whereas with SP, the α-MFIB

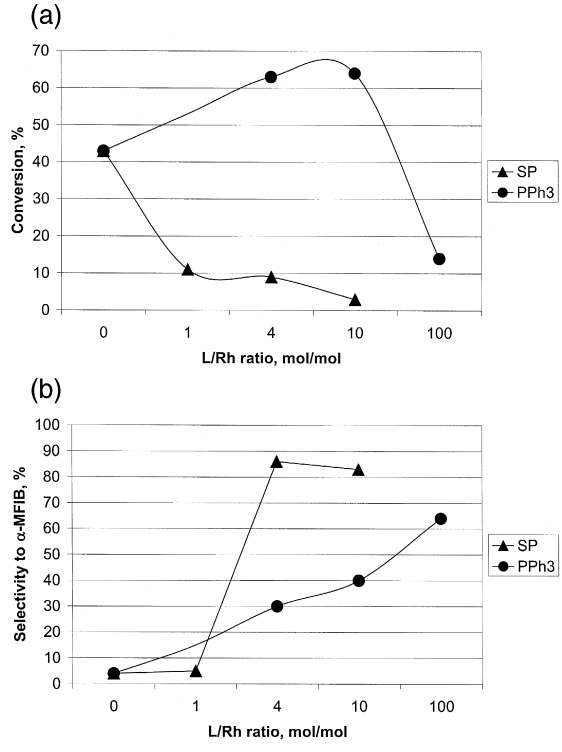


Fig. 1. (a) MMA conversion and (b) selectivity to α-MFIB as a function of L/Rh ratio with PPh_3 and SP ligands (100°C, 20 bar, MMA/Rh = 2500, reaction time = 5 h).

was practically the only hydroformylation product already at L/Rh ratio of 4 ($i/n = 19$).

Table 2 shows the influence of temperature on conversions and selectivities with unmodified rhodium ($Rh(NO_3)_3$), PPh_3, and the SP ligand modified reaction at 20 bar. In every case, the effect was different. With unmodified rhodium, the increase in temperature increased hydrogenation (S_{MIB}: from 6% to 52%) at the expense of β-MFIB formation, which was still the main hydroformylation product at 150°C. With PPh_3, conversion had a maximum at 100°C and selectivity changed from favouring α-MFIB at low temperatures to favouring β-MFIB at higher temperatures. Hydrogenation also increased with the temperature. In case of the SP ligand, the reaction occurred only at 100°C, where α-form was the favoured hydroformylation product.

Because conversion was low with the SP ligand at 20 bar and clearly improved at 60 bar [13], we decided to test the temperature behaviour of the SP ligand also at higher pressure. Fig. 2 shows the conversion and selectivity obtained as a function of temperature at 60 bar. The high selectivity to α-MFIB prevailed regardless of the temperature. However, as the temperature increased, the formation of β-MFIB was enhanced, but mainly at the expense of hydrogenation (i/n ratio = 13 at 120°C). As Fig. 2 shows, the conversion increased with temperature up to 100°C. Below 80°C, the reaction was slow, again at 50°C there was no detectable reaction probably due to the poor solubility of the ligand at low temperatures. Above 100°C, the catalyst showed activity loss so that conversion at 150°C was less than 1%.

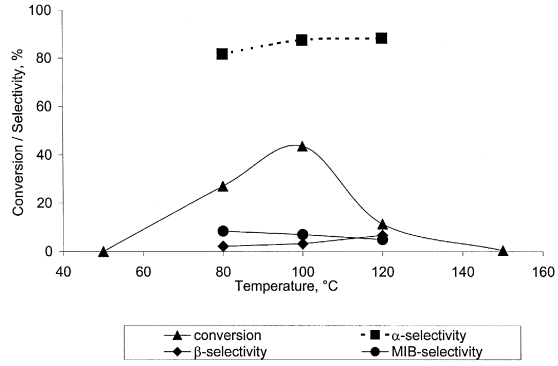


Fig. 2. Effect of temperature on conversion and selectivity with the SP ligand (60 bar, MMA/Rh = 2500, L/Rh = 4, reaction time = 5 h).

The rapid loss of activity raised the question of the SP ligands thermal stability and therefore the issue was studied further. Thermogravimetric analysis under air showed that the ligand did not decompose until 250°C. In addition, the SP ligand was refluxed in toluene for several days, and based on ^{31}P NMR measurements, no alterations had occurred. Nevertheless, when we did an experiment in which the reaction mixture was first heated to 120°C for 15 min (under nitrogen atmosphere) and then cooled back to reaction temperature of 100°C, the activity of the catalyst was about half of the activity of a standard experiment at 100°C and about twice as much as in a standard experiment at 120°C (Fig. 3). The selectivity to α-MFIB remained unchanged, but a slight increase in β-MFIB formation was observed again mainly at the expense of hydrogenation.

The obtainable conversion with the SP ligand modified reaction at 20 bar and 100°C was quite low (~9% after 5 h) and as an attempt to

Table 2
Effect of temperature on conversions and selectivities[a]
n.a. = not applicable; n.r. = no detectable reaction.

Ligand	Temperature, °C	Conversion, %	Selectivity, %		
			MIB	α-MFIB	β-MFIB
No ligand	100	43	6	4	91
No ligand	150	45[b]	52[b]	2[b]	45[b]
PPh_3	50	4	0	9	46
PPh_3	100	63	3	30	67
PPh_3	150	48	16	3	81
SP	50	n.r.	n.a.	n.a.	n.a.
SP	100	9	9	86	5
SP	150	n.r.	n.a.	n.a.	n.a.

[a] 20 bar, H_2/CO = 1:1, MMA/Rh = 2500, L/Rh = 4, reaction time = 5 h.
[b] MMA/Rh = 6000.

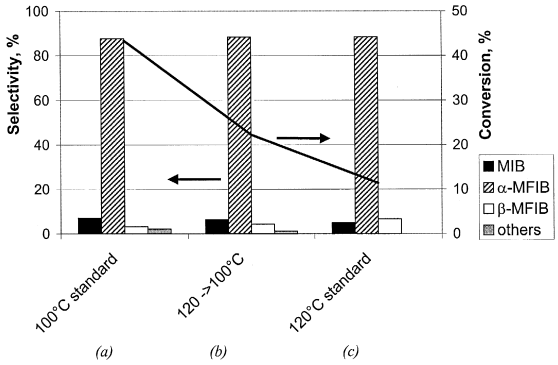


Fig. 3. Thermal stability of the in situ formed SP-rhodium catalyst (a) standard experiment at 100°C; (b) before the experiment, the reaction mixture was heated to 120°C for 15 min (under nitrogen atmosphere) after which it was cooled back to reaction temperature 100°C; (c) standard reaction at 120°C (60 bar, MMA/Rh = 2500, L/Rh = 4, reaction time = 5 h).

increase the conversion, the amount of the catalyst was tripled (L/Rh ratio was kept constant), whereas other reaction parameters were kept constant. However, as Fig. 4 shows, the increase in conversion was only 5 percentage points. Furthermore, selectivity of the catalyst changed significantly, α-selectivity decreased,

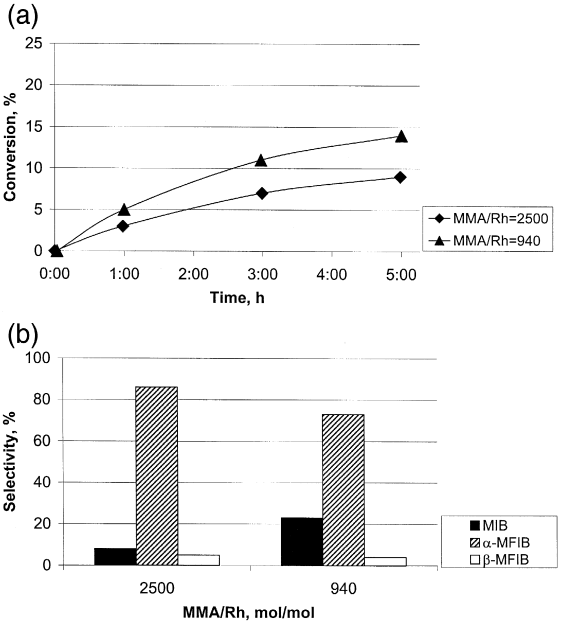


Fig. 4. Effect of catalyst concentration on (a) conversion and (b) selectivity with the SP modified hydroformylation (20 bar, 100°C, L/Rh = 4)

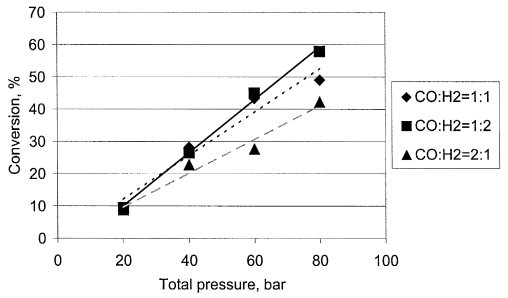


Fig. 5. Effect of total and partial pressures on MMA conversion with the SP modified hydroformylation (100°C, MMA/Rh = 2500, L/Rh = 4, reaction time = 5 h).

and selectivity to MIB increased 13 percentage points, whereas selectivity to β-MFIB remained rather constant.

In our previous work [13], we showed that, unlike with other ligands while the conversion increased with total pressure, chemo- and regioselectivities of the catalyst stayed constant with the SP ligand. Fig. 5 shows how the variation of carbon monoxide and hydrogen partial pressure influenced the conversion when total pressure was kept constant. At moderate pressures (20–40 bar), there was no difference between the conversion obtained with the syn gas mixtures in which there were either equal amounts of carbon monoxide and hydrogen or in which hydrogen was in excess (H_2/CO = 2:1). At higher pressures, the highest conversion was achieved with the syn gas mixture where hydrogen was in excess and the conversion was

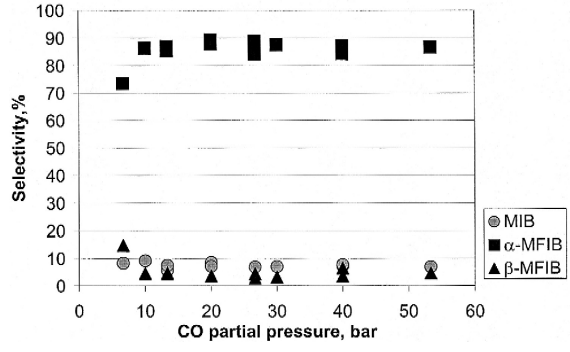


Fig. 6. Effect of CO partial pressure on selectivity (100°C, MMA/Rh = 2500, L/Rh = 4, L = SP, reaction time = 5 h).

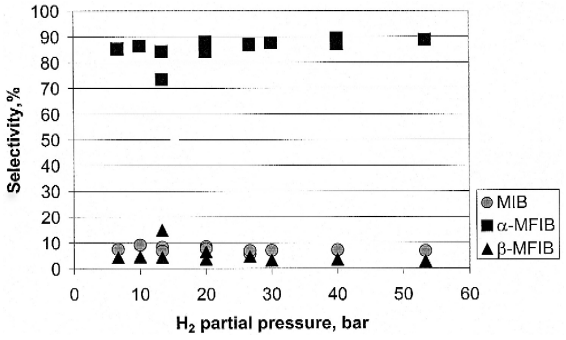


Fig. 7. Effect of H_2 partial pressure on selectivity (100°C, MMA/Rh = 2500, L/Rh = 4, L = SP, reaction time = 5 h).

substantially lower when carbon monoxide was in excess ($H_2/CO = 1:2$). Fig. 6 and Fig. 7 show the selectivity as a function of respective partial pressure. The chemo- and regioselectivities of the reaction were independent of the hydrogen partial pressure and after the minimum carbon monoxide partial pressure (10 bar in the feed), regioselectivity became independent of the carbon monoxide partial pressures as well.

4. Discussion

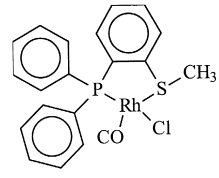
4.1. Precursor

It is commonly accepted that when using Wilkinson's catalyst, the active species in the hydroformylation of α-alkenes are the same regardless of the initial rhodium source (Scheme 1) [12]. However, in the case of the SP ligand, the rhodium source had a significant effect on the obtainable conversion and minor effects on the selectivity in MMA hydroformylation. As Table 1 shows, the best conversions and α-selectivities were obtained with the smallest rhodium precursors, $Rh(NO_3)_3$ and $Rh_4(CO)_{12}$, where there are no additional ligands hindering the formation of the catalytically active α-selective complex and the reaction thereafter. $[Rh(C_5H_7O_2)(CO)(PPh_3)]$ precursor contains 1 PPh_3 unit, thus, the reaction was actually modified with a mixture of phosphine ligands instead of just one ligand ($PPh_3/SP = 1:4$ on molar basis). This could lead to a mixture of two catalytically active species: one of the Wilkinson type and the other of the chelating SP type. The presence of Wilkinson type species enhanced the activity, and thus led to increased β-MFIB formation compared to the standard reaction. However, the formation of a complex containing both PPh_3 and SP ligands cannot at this stage be excluded.

Neither $Rh_2(CO)_4Cl_2$ nor $[Rh(norbornadiene)_2]BF_4$ gave any reaction with the SP ligand. According to Prókai-Tátrai et al. [9] in the hydroformylation of MMA, the chlororhodium species are active at low P/Rh ratios yielding β-MFIB, whereas at higher P/Rh ratios, or in the presence of NEt_3, α-MFIB is formed. Therefore, we tested a complex formed in the reaction between $Rh_2(CO)_4Cl_2$ and SP (Scheme 2) [15] without the excess of the SP ligand under the same conditions as the in situ formed complex, but the result was the same: no reaction. Apparently, even at low L/Rh ratios, the rhodium in the chlororhodium species was stabilised to the extent that it was not at all active in MMA hydroformylation. In the case of $[Rh(norbornadiene)_2]BF_4$, it seems that SP was unable to displace norbornadiene ligands and thus the complex became sterically too hindered for the catalytic cycle to take place.

4.2. Process variables

As the L/Rh ratio grows, the α-formation becomes favoured in the PPh_3 and SP modified



Scheme 2. RhSPCOCl complex formed in the reaction between $Rh_2(CO)_4Cl_2$ and SP.

reactions. As the α-formation becomes the main reaction, the conversion decreases. The change in regioselectivity cannot, however, be explained by the extent of the reaction so that α-MFIB would be favoured at lower conversion levels. The regioselectivity in both PPh_3 and SP modified reactions stayed constant regardless of the conversion level during one experiment [13], as well as in experiments (at 100°C and 60 bar) where the extent of the reaction varied (Fig. 8). Rather, the different stereoelectronic aspects of the ligands determined the regioselectivity.

The variation of hydrogen and carbon monoxide partial pressures clearly indicates that the conversion level is — particularly at higher pressures — dependent on the hydrogen partial pressure (Fig. 5). It has been suggested that the dependence of hydrogen partial pressure is a result of mass transfer limitations [2], e.g. hydrogen's poor solubility in the reaction mixture. Indeed, the estimation of H_2 and CO concentrations in the liquid phase revealed that when the H_2/CO molar ratio in the gas feed was 1:1, it was approximately 0.5:1 in the liquid phase. Since hydroformylation consumes equimolar amounts of both H_2 and CO, the solubility differences caused CO to be in excess in the liquid phase. The high CO concentration in turn may enhance the formation of a catalytically inactive rhodium species containing two CO ligands instead of one H and one CO ligand [16], thus deactivating the catalyst.

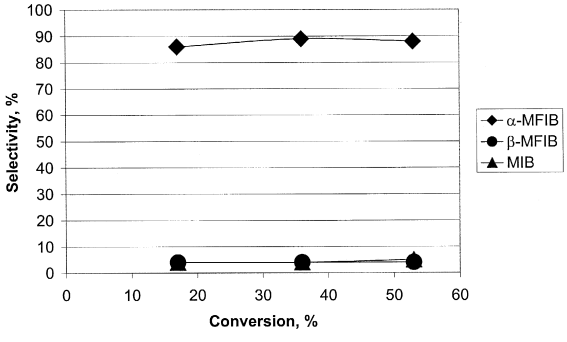


Fig. 8. Regioselectivity as a function of conversion with the SP modified reaction (100°C, 60 bar, MMA/Rh = 2500, L/Rh = 4, reaction time: 1, 3 and 11 h, 3 experiments).

Generally in the case of α,β-unsaturated esters, increasing temperature increases conversion, but changes the regioselectivity of the reaction so that the linear form becomes the main product [2,8] because the formation of the linear isomer is thermodynamically more favoured at higher temperatures [13]. Our results with PPh_3 obeyed this phenomenon, whereas with the SP ligand, even though the conversion increased with increasing temperature up to 100°C, regioselectivity remained approximately the same, favouring the α-isomer formation regardless of the temperature. In the cases of unmodified and PPh_3 modified reactions, the extent of hydrogenation increases steadily with temperature and selectivity to MIB, particularly with plain $Rh(NO_3)_3$, was quite high at 150°C. With the SP ligand, regioselectivity did not change and chemoselectivity even improved during deactivation (Fig. 3), thus the loss of catalytic activity observed at higher temperatures was due to the deactivation of α-selective complex rather than plain ligand degradation. Neither ligand nor rhodium precursor alone are decomposed at 150°C. However, deactivation affects the reaction in the same way as if the amount of catalyst was smaller — conversion is lower but regioselectivity is the same. Apparently, part of the rhodium activity was permanently suppressed without decomposition of all α-selective species. Indeed, it has been postulated [1,17] that the main reason for the deactivation of PPh_3 modified hydroformylation is the formation of complex phosphido bridged rhodium carbonyl clusters which are inactive for hydroformylation. According to Moser et al. [18], the deactivation starts as the most catalytically active intermediate, $RhH(CO)_2(PR_3)_2$, converts to a less active orange dimer, $[Rh(CO)(PR_3)_2]_2$, which eventually forms a totally inactive binuclear complex containing a bridged phosphido ligand. This deactivation process is irreversible and accelerated by high temperatures. Moreover, the deactivation was quite rapid in the case of PPh_3 ligands containing strongly electron donating sub-

stituents in the *para* position. Similarly, in the case of the SP ligand where the electron donating substituent is in *ortho* position, the slight increase in temperature accelerated the irreversible deactivation process even though the chelation control could have prevented deactivation by increasing the degree of coordinative saturation in the complex [17] as is the case with chelating diphosphines.

4.3. Selectivities

The hydrogenation tendency of the SP ligand deserves some discussion. According to Falbe [2], the increase of the $[H_2]/[CO]$ ratio at constant total pressure raises the hydrogenation tendency. However, with the SP ligand, the variation of $[H_2]/[CO]$ ratio from 0.5 to 2 had no effect on the yield of MIB (Table 3). Moreover, unlike the unmodified and the PPh_3 modified reactions, hydrogenation did not increase with increasing temperature. It seems that the SP modified reaction is more chemoselective to hydroformylation than the PPh_3 modified reaction. But, when the amount of catalyst — both ligand and rhodium — was tripled, chemoselectivity of the catalyst changed significantly.

There are contradictory reports [2,19] on the effect of catalyst concentration on regioselectivity in the ligand modified hydroformylation. Tucci [20] found no influence on the i/n ratio in the hydroformylation of 1-alkenes with the $HCo(CO)_3(PBu_3)$ whereas Rupilius et al. [21] noted, especially at low ligand to metal ratios, an increase in the formation of the linear product in the hydroformylation of 1-alkenes with the in situ from PPh_3 and $Co_2(CO)_8$ formed catalyst. Our results support the findings of Tucci [20]: only the chemoselectivity of the reaction is affected by the increase in catalyst concentration.

The increase in total pressure from 20 to 80 bar at 100°C with the SP ligand showed no such change in the regioselectivity, as observed in the case of the other ligands [8,13]. Moreover, unlike the PPh_3 modified MMA hydroformylation in which the selectivity to the normal product increases as the $[H_2]/[CO]$ increases [8], the regioselectivity of the SP modified reaction was fairly independent of the $[H_2]/[CO]$ ratio (Table 3). However, as Fig. 6 and Fig. 7 show, at low syn gas pressures, a critical initial CO pressure is needed in order to form an α-selective carbonyl complex from rhodium nitrate and SP ligand. Thus, the dependence of the α-MFIB selectivity on CO concentration is of positive order at low concentrations (up to 10 bar in the gas feed) and zero order at higher concentrations, whereas it is independent of the H_2 concentration within the tested pressure range.

Table 3
Effect of H_2/CO ratio on selectivities[a]

Total pressure, bar	$[H_2]/[CO]$	Selectivity, %		
		MIB	α-MFIB	β-MFIB
20	0.5	7	85	4
20	1	8	86	5
20	2	8	73	15
40	0.5	7	84	4
40	1	8	88	4
40	2	6	87	5
60	0.5	8	84	6
60	1	7	88	3
60	2	7	89	3
80	0.5	7	87	5
80	1	7	87	4
80	2	7	89	3

[a] 100°C, MMA/Rh = 2500, L/Rh = 4, reaction time = 5 h.

5. Conclusions

We have shown that in the in situ formed SP rhodium complex, the rhodium precursor has a significant effect on the conversion. In contrast to PPh_3 ligand, the regioselectivity of the reaction does not change as temperature and total pressure change with a fixed $[H_2]/[CO]$ ratio. However, operable temperature window is unfortunately narrow (90–110°C), at low temperatures the reaction is slow due to poor solubility of ligand and at higher temperatures the catalyst starts to deactivate strongly. The deactivation is likely caused by the formation of complex

rhodium clusters. The increase in hydrogen partial pressure increases conversion of MMA but has no effect on the selectivity, whereas a minimum carbon monoxide pressure is needed to achieve good chemo- and regioselectivities. The catalyst concentration is the best way to control the amount of hydrogenation in the SP modified hydroformylation. To summarise, in the SP modified hydroformylation of MMA, the activity of the reaction is most sensitive to the increase in the total pressure, temperature, and ligand-to-rhodium ratio, whereas — with the exception of ligand-to-rhodium ratio — the process variables do not alter regioselectivity. In addition, deactivation is strong at elevated temperatures ($> 120°C$), but otherwise no deactivation or shifts in selectivity were observed.

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References

[1] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Catal. A 104 (1995) 17.
[2] J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, 1980.
[3] G. Consiglio, L. Kollár, R. Kölliker, J. Organomet. Chem. 396 (1990) 375.
[4] A.M. Trzeciak, J.J. Ziólkowski, J. Organomet. Chem. 479 (1994) 213.
[5] T. Horiuchi, E. Shirakawa, K. Nozaki, H. Takaya, Organometallics 16 (1997) 2981.
[6] C. Botteghi, R. Ganzerla, M. Lenarda, G. Moretti, J. Mol. Catal. 40 (1987) 129.
[7] M. Tanaka, T. Hayashi, I. Ogata, Bull. Chem. Soc. Jpn. 50 (1977) 92351.
[8] C.U. Pittmann, W.D. Honnick, J.J. Yang, J. Org. Chem. 45 (1980) 684.
[9] K. Prókai-Tátrai, S. Tórrös, B. Heil, J. Organomet. Chem. 332 (1987) 331.
[10] H. Alper, J.-Q. Zhou, J. Org. Chem. 57 (1992) 3729.
[11] G. Bergounhou, D. Neibecker, R. Réau, J. Chem. Soc., Chem. Commun. (1988) 1370.
[12] C. Claver, A. Ruiz, A.M. Masdeu, N. Ruiz, Inorg. Chim. Acta 175 (1990) 77.
[13] H.K. Reinius, R.H. Laitinen, A.O.I. Krause, J.T. Pursiainen, Catal. Lett. 60 (1999) 65.
[14] R.C Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, McGraw-Hill, New York, 1988.
[15] J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, J.G. Sunley, J. Chem. Soc., Chem. Commun. (1995) 1579.
[16] T. Horiuchi, E. Shirakawa, K. Nozaki, H. Takaya, Organometallics 16 (1997) 2981.
[17] A.G. Abatjoglou, E. Billig, D.R. Bryant, Organometallics 3 (1984) 923.
[18] W.R. Moser, C.J. Papile, S.J. Weininger, J. Mol. Catal. 41 (1987) 293.
[19] C.D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds 1 VCH, Weinheim, 1996, p. 29.
[20] E.R. Tucci, Ind. Eng. Chem. Prod. Res. Dev. 7 (1968) 32.
[21] W. Rupilius, J.J. McCoy, M. Orchin, Ind. Eng. Chem. Prod. Res. Dev. 10 (1971) 142.