ELSEVIER

Journal of Molecular Catalysis A: Chemical 139 (1999) 139–147

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Biphasic and SAPC hydroformylation catalysed by rhodium phosphines bound to water-soluble polymers

Torsten Malmström [a], Carlaxel Andersson [a,*], Jes Hjortkjaer [b]

[a] *Department of Inorganic Chemistry 1, Chemical Center, Lund University, P.O. Box 124, S-22100 Lund, Sweden*
[b] *Department of Chemical Engineering, Technical University of Denmark, Building 229, DK 2800, Lyngby, Denmark*

Received 11 March 1998; accepted 18 May 1998

Abstract

Coupling of the triphenylphosphine moiety to poly-acrylic acid and poly-ethyleneimine, respectively, afford the macromolecular ligands PAA–PNH and PEI–PNH. Reaction of the ligands with $[Rh(CO)_2(acac)]$ give water-soluble complexes that are active as catalyst in the hydroformylation of different olefins. SAP-catalysts based on PAA–PNH are efficient in gas phase hydroformylation of propene and in liquid phase hydroformylation of 1-octene. Hydroformylations under biphasic conditions are very slow but addition of sodiumdodecyl sulphate (SDS) or methanol increases the rate significantly. Catalysts using PEI–PNH as ligands show lower stability and activity in both SAPC and biphasic applications.

Keywords: Water-soluble phosphines; Poly-acrylic acid; Rhodium; Biphasic; SAP; Hydroformylation

1. Introduction

The most severe drawback in homogeneous catalysis is the inherent difficulty to separate the catalyst from the reaction mixture. Different immobilisation methods using ligand functionalised solid supports, e.g., silica and crosslinked poly-styrene have been extensively studied over the years, but none of these attempts have been successful, mainly due to metal leakage or decomposition of the catalyst [1]. However, immobilisation of the catalyst in a water phase, i.e., using an aqueous phase containing the catalyst and an immiscible organic phase containing the substrate, and after the reaction the product [2–4] has been shown to be a feasible way to solve the separation problem. This concept has been developed to an industrial process for rhodium catalysed hydroformylation of propene by Ruhrchemie/Rhone-Poulenc [5,6].

The introduction of charged or polar groups as substituents on a parent phosphine renders catalyst based on such ligands water-soluble. Tri- and mono-sulfonated triphenylphosphine (TPPTS [7,8] and TPPMS [9,10], respectively) are probably the most well-known water-soluble phosphines and TPPTS is the ligand used in the Ruhrchemie/Rhone-Poulenc process.

Ligand synthesis is of great importance in the development of new catalysts having higher activity and selectivity [6]. In the last decade, the development of new and more sophisticated water-soluble phosphines has virtually exploded [11,12].

* Corresponding author. E-mail: carlaxel.andersson@inorg.lu.se

1381-1169/99/$ - see front matter
PII: S1381-1169(98)00176-9

Biphasic catalysis often suffer from low reaction rates imposed by slow phase transfer and this becomes a severe problem when trying to hydroformylate higher alkenes, which have very low, or even negligible, solubility in water. Addition of cosolvents [13] or surfactants [14,15] to the aqueous phase increase the rate of phase transfer but at the same time it hampers the separability. Application of amphiphilic phosphines, i.e., amino functionalised phosphines, which are soluble in both water and in organic solvents [16,17] is an elegant way to overcome the problem with low reaction rates. The reaction is in this case performed in a homogeneous organic phase and the catalyst is extracted into an acidic aqueous phase after the reaction. The catalyst can in this way easily be reused by neutralising the aqueous phase and back extracting the catalyst to a fresh organic phase.

The development of supported aqueous phase catalysis (SAPC), that is immobilisation of the water-soluble catalyst in a thin water film, which is adsorbed onto the surface of silica, is a new and efficient way to facilitate the hydroformylation of heavier olefins [18]. SAPC hydroformylation catalysts have been shown to be effective for both polar substrates, such as methylacrylate [19], and unpolar substrates, as oleylalchohol [20].

We have previously described the preparation of two new water-soluble phosphines using water-soluble polymers as charge carrying units [21] and rhodium complexes of these phosphines have been shown to be efficient in biphasic hydrogenations [22]. The present initial study demonstrates that phosphines bound to water-soluble polymers can be applied as ligands in rhodium catalysed hydroformylation of both gaseous and liquid olefins.

2. Experimental

All reactions were done under an inert atmosphere and water was double distilled prior to use. The ligands PAA–PNH and PEI–PNH, containing 3.2 and 2.6% phosphorus, respectively (Figs. 1 and 2), were prepared as previously described [21]. The hydroformylation of propene was done in a continuous flow reactor as described earlier [23] with a 1:1:1 mixture of $CO:H_2:C_3H_6$. The conversion to *n*- and *iso*-butanal was determined by GLC on a Shimadzu GC9-A equipped with a SCOT Squalan column. Batch hydroformylations of 1-hexene and 1-octene were carried out in a Roth stainless steel autoclave with 1:1 $CO:H_2$ mixture (AGA) using methytlnaftalene as internal standard. $[Rh(CO)_2(acac)]$ was purchased from Johnson Matthey and used as received. 1-octene and 1-hexene were supplied by Acros and distilled prior to use. Silica Sylopol 952 W (Grace) was used as carrier for the SAP catalysts. Toluene used in the SAPC autoclave hydroformylation

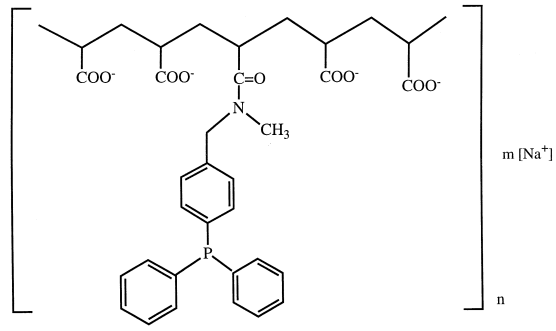

Fig. 1. The ligand PAA–PNH.

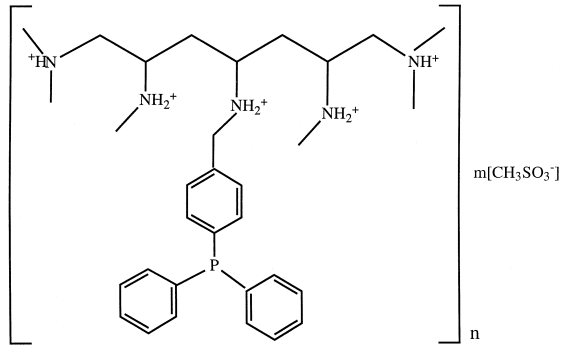

Fig. 2. The ligand PEI–PNH.

was distilled from sodium/benzophenone. Gas chromatographic analyses were carried out on a Varian 3300 using a OV 101 packed column. IR spectra were recorded on a Nicolette 20 SX FT-IR instrument using KBr tablets or Nujol-mulls. NMR spectra were recorded on a Varian XL 300 MHz instrument. TMS was used as standard for ^{1}H NMR and 85% H_3PO_4 for ^{31}P NMR, giving positive values down field. Elemental and water analyses were performed by Mikro Kemi, Uppsala Sweden.

*2.1. Preparation of trans-[Rh(L)$_2$(CO)X] (L = PAA–PNH **1**, PEI–PNH **2**)*

A Schlenk tube containing 10-ml water was charged with 500 mg of the ligand (0.52-mmol P PAA–PNH, 0.42-mmol P PEI–PNH). The solution was stirred till the ligand was completely dissolved whereafter a solution of [Rh(CO)$_2$(acac)] (PAA–PNH, 63.9 mg 0.25 mmol; PEI–PNH, 51.9 mg 0.20 mmol) in 5 ml of CH_2Cl_2 was added (Rh:P = 1:2.1). The resulting biphasic mixture was stirred for 30 min and then allowed to phase separate giving a yellow aqueous phase and a colourless organic phase. After phase separation the organic phase was discarded and the water phase washed twice with 5-ml portions of CH_2Cl_2. The water phase was evaporated till dryness giving the title compounds as orange powders.

^{31}P NMR (D_2O)**1**:29.7 broad;

^{31}P NMR (D_2O)**2**:27.1, d, $^{1}J_{Rh-P}$ 124 Hz;

IR(KBr):**1** 1979 cm^{-1}; **2** 1980 cm^{-1}.

2.2. Preparation of trans-[Rh(L)$_2$(CO)OCN] (L = PAA–PNH)

A total of 100 mg of **1** (0.049 mmol Rh) was dissolved in 5-ml water and 4-mg KOCN (s) (0.049 mmol) was added. The solution was stirred for 10 min and the solvent evaporated.

^{31}P NMR (D_2O):27.8, d, $^{1}J_{Rh-P}$ 120 Hz;

IR(KBr): 1982, 2170, 2225 cm^{-1}.

2.3. Preparation of SAPC-catalyst (SAP$_1$, SAP$_2$, SAP$_3$)

A total of 200 mg of PAA–PNH (0.206 mmol P) was dissolved in 10-ml degassed water under N_2. [Rh(CO)$_2$(acac)] (SAP_1, 23.3 mg 0.09 mmol; SAP_2, 10.7 mg 0.041 mmol; SAP_3 5.36 mg 0.021 mmol) dissolved in 4 ml of CH_2Cl_2 was added and the mixture stirred for 30 min. The organic phase was evaporated and 3.0-g dried silica was suspended in the remaining aqueous phase. The mixture was stirred for 30 min after which the water was evaporated and the silica particles dried under high vacuum. The resulting catalysts were stored under Ar(g) in a Schlenk tube.

Elemental analyses: SAP_1 0.21% P, 13.6% H_2O; SAP_2 0.19% P, 6% H_2O; SAP_3 0.21% P, 9.8% H_2O.

Rh content (calculated based on a complete uptake of Rh): SAP_1 ca 2.8 mg Rh/g catalyst; SAP_2 ca 1.3 mg Rh/g catalyst; SAP_3 ca 0.7 mg Rh/g catalyst.

2.4. Biphasic hydroformylation in the autoclave

In a typical reaction 25 mg of PAA–PNH (0.0258 mmol P) was dissolved in 2.5-ml H_2O followed by addition of 2.2 mg [Rh(CO)$_2$(acac)] (0.0086 mmol) corresponding to a Rh:P ratio of 1:3 (the amount rhodium added is dependent on the selected Rh:P ratio). 2.5 ml of toluene was added and the resulting biphasic mixture was stirred till the organic phase was colourless. 0.128 ml of 1-octene (0.86 mmol or 0.267-ml 1-hexene, 2.15 mmol) and methyl naphthalene, used as internal standard, were added and the vessel was placed in the preheated (60°C) autoclave. After pressurising and venting three times with $CO:H_2$ (1:1) the pressure was set to 40 bar and the reaction commenced by starting the stirring. After the reaction the autoclave was cooled to room temperature and depressurised. The phases were separated and the organic phase collected and immediately analysed with GC.

In the recycling experiments, the phase separation was carried out under N_2 and the aqueous phase containing the catalyst washed once with 2.5-ml toluene. The aqueous catalyst solution was then brought back to the autoclave and the reaction repeated by addition of fresh solvent (2.5-ml toluene) and 1-octene (0.128 ml) as described above. Yields and reaction times are given in Table 1.

2.5. Hydroformylation with SAP-catalyst

General procedure: The reaction vessel was charged with the selected amount of catalyst (300 mg of SAP_1; 630 mg SAP_2; 1200 mg SAP_3 (0.008 mmol Rh)), toluene (SAP_1, 2.5 ml; SAP_2, 5.25 ml; SAP_3, 10 ml), 1-octene (0.12 ml, 0.8 mmol) and internal standard. The vessel was then fitted into the preheated (60°C) autoclave, which was pressurised and vented three times with $CO:H_2$ (1:1) before the pressure was set to 40 bar and the reaction started. After the selected reaction time the autoclave was allowed to reach room temperature and the catalyst filtered and washed with 2-ml toluene. The combined organic phases were analysed with GC.

In the recycling experiments, the catalyst was allowed to sediment, the liquid phase decanted and the catalyst washed twice with degassed toluene (2 ml). A second run was started by addition of toluene and 1-octene following the same procedures as for the first run. Yields and reaction times are given in Table 1.

2.6. Continuous gas phase hydroformylation of propene

The selected amount of the SAP-catalyst (53.8 mg SAP_1, 112 mg SAP_2, 228 mg SAP_3 (0.0014 mmol Rh)) was placed in a stainless steel tubular reactor. The pressure was set to 5.0 bar and $CO:H_2$ was flushed through the system for 30 min whereafter the reactor was placed in a preheated (100°C) oil bath. The gas flow was adjusted to maintain a conversion of propene of approximately 1% (approximately 25 ml/min). This allowed calculation of the turn over frequency (TOF) for *n*- and *iso*-butanal formation as F[aldehyde]$/W_{Rh}$ where F is the gas flow in ml/s from the reactor, [aldehyde] is the concentration of *n*- or *iso*-butanal (mol/ml) in the product stream and W_{Rh} is the weight of rhodium in the reactor. The amount of *n*- and *iso*-butanal were determined by GLC analysis of the outlet gas, which was periodically injected on the column by a sample loop and a splitter valve.

Table 1
Hydroformylation of 1-hexene and 1-octene using rhodium complexes of PAA–PNH

Substrate (entry)	Rh:olefine	Rh:P	Yield (time/h)	Percentage of *n*-isomer	Remarks
1-octene (1)	1:100	1:2.3	100 (20)	67	SAP 1
1-octene (2)	1:100	1:5	100 (20)	65	SAP 2
1-octene (3)	1:100	1:5	100 (20)	58	Recycled
1-hexene (4)	1:250	1:2.5	24 (15)	74	
1-hexene (5)	1:250	1:8.5	2.5 (20)	85	
1-hexene (6)	1:250	1:4.5	100 (20)	69	25-mM SDS
1-octene (7)	1:100	1:7	10 (22)	84	
1-octene (8)	1:100	1:7	9 (22)	80	Recycled
1-octene (9)	1:100	1:3	25 (15)	73	
1-octene (10)	1:100	1:3	3 (15)	87	27-mM $NaClO_4$
1-octene (11)	1:100	1:3.1	54 (15)	72	20% MeOH
1-octene (12)	1:100	1:3	100 (6)	69	10-mM SDS

40 bar, $CO:H_2$ 1:1, 60°C.

3. Results and discussion

3.1. Complex formation

The preparation of the water-soluble phosphines (PAA–PNH, PEI–PNH see Figs. 1 and 2) have been described earlier [21]. The feasibility of the ligands in hydrogenation of olefins under biphasic conditions using cationic rhodium complexes have also been demonstrated [22] but no account for their use in hydroformylation reactions have been given before.

It is well documented that $[Rh(CO)_2(acac)]$ and phosphines (L) in a 1:1 ratio react and give the complex [Rh(CO)L(acac)]. For L = PPh_3 this complex exhibit a doublet at 48.7 ppm with a Rh–P coupling constant of 175 Hz in its ^{31}P NMR spectrum [24]. The reaction of the ligand PAA–PNH with $[Rh(CO)_2(acac)]$ in a 1:1 Rh:P molar ratio under biphasic conditions (H_2O/CH_2Cl_2) do not, however, follow the expected pattern. The organic phase is not fully decolourised indicating that the Rh-precursor is not fully consumed. Furthermore, the ^{31}P NMR spectrum of the isolated product shows one resonance at 29.7 ppm, so broad that not even the Rh–P coupling constant can be seen [1] and, importantly, the resonances around 48 ppm expected for the [Rh(CO)L(acac)] complex is not present. The IR shows one peak in the CO stretching region at 1979 cm^{-1} but no peaks at 1580 and 1520 cm^{-1} for coordinated acac. When the same reaction is run at a rhodium phosphine ratio of 1:2 the organic phase is completely decolourised and the ^{31}P NMR spectrum as well as the IR-spectrum of the isolated product are identical to those obtained at the 1:1 stochiometry thus confirming that the same product is formed, independent of the stochiometry.

Complexes of the general formula *trans*-$[Rh(CO)(PPh_3)_2X]$ (where X is an anion or a solvate molecule) exhibit a doublet in their ^{31}P NMR spectra around 30 ppm and CO stretching frequencies around 1980 cm^{-1} [25]. Furthermore, reaction of $[Rh(CO)_2(acac)]$ with excess TPPTS gave *trans*-$[Rh(CO)(OH)(TPPTS)_2]$ exhibiting a doublet at 31.8 ppm ($^1J_{Rh-P} = 129$ Hz) [8]. Accordingly, we conclude that $[Rh(CO)(L)_2X]$ (L = PAA–PNH, X = carboxylate group or H_2O) is formed independently of Rh:P ratio.

Double substitution in the precursor complex can be explained taking the concentration gradient over the phase boundary and rates of substitution into account. The solubility of $[Rh(CO)_2(acac)]$ in water is very low and the rate of diffusion of rhodium into the aqueous phase is thus determined by the rate of the initial CO–phosphine exchange reaction. Once the mono-substituted product is formed it will be contained in the aqueous phase, where an excess of phosphine and carboxylate groups will be present thus promoting the second acac-phosphine substitution reaction.

The ^{31}P NMR shift and CO stretching frequencies of complexes **1** and **2** are almost identical and this indicates that the same type of complex is formed independent of polymer type. The situation with respect to phosphine and anion excess is the same for both ligands except that the anion in the PAA–PNH case is carboxylate groups from the polymer and in the PEI–PNH case $CH_3SO_3^-$ anions. The two complexes differ, however, with respect to the line width in the ^{31}P NMR, the line-width for the PAA–PNH ligand being considerably larger. For both polymers part of the line broadening can be explained by slow tumbling of the large polymeric aggregates but dynamic processes at the complex can of course also contribute. Having different X groups (COO^- and $CH_3SO_3^-$) in the two complexes the extra broadening in complex **1** can be caused by a dynamic process involving the anionic group and this hypothesis can be tested by exchanging the anionic group.

[1] The dipole–dipole contribution to the T_1 relaxation time for small molecules is low. The slow tumbling of macromolecular aggregates do however not average the dipole–dipole contribution to the T_1 relaxation thus causing broad NMR resonances.

Addition of 1 equivalent isocyanate OCN^-, which forms strong complexes with Rh(I) [26] to complex **1** results in a new complex which we formulate as $[Rh(L)_2(CO)(OCN)]$. This complex displays a ^{31}P NMR resonance at 27.8 ppm with a Rh–P coupling constant of 120 Hz, typical for trans phosphines. The IR spectrum displays three characteristic vibrations one at 1982 cm^{-1} for the carbonyl and two at 2170 and 2225 cm^{-1} for coordinated OCN^-. The observed decrease in line-width as OCN^- is added shows that the *X* ligand in **1** partitions in an exchange process. The well resolved doublet in **2** indicates that the exchange rate of *X* is fast while the extra broadening observed for **1** indicates a rate of exchange comparable to the NMR time scale. Thus, it is possible to suggest that *X* in **1** is $-COO^-$ since it is expected to exchange slower than the labile ligand $CH_3SO_3^-$.

3.2. SAP catalysts

In supported aqueous phase catalysis (SAPC) the heterogenisation relies on interaction between surface hydroxyl groups on the carrier particle, the thin layer of water and the hydrophilic groups on the catalyst. The thin layer of water makes the complex fairly mobile and its mobility resembles that of a homogeneous catalyst in solution.

Controlled pore glasses CPG-240 and CPG-350 with slight variations in their surface area, 67.5 and 77.5 m^2/g, respectively, were applied as carriers in the first SAPC applications but no difference in activity depending on surface area [20] was observed for these two carriers. Furthermore, it has been shown that ordinary silicas can be used as SAP carriers with very good results and mesoporous materials with a narrow pore distribution is not a prerequisite to obtain a good catalyst [27].

The three different SAP catalyst investigated in the present study are all based on Sylopol 952 W Silica as carrier, with a surface area of 307 m^2/g and a pore volume of 1.58 ml/g. However, the catalysts prepared differ with respect to their Rh:P ratio and consequently to their rhodium content. Their Rh:P ratio, rhodium and water content varies as follows: SAP_1 1:2.3, 2.7 mg Rh/g catalyst and 13.6% water; SAP_2 1:5, 1.3 mg/g catalyst and 6.0% water; SAP_3 1:10, 0.7 mg Rh/g catalyst and 9.8% water. The rhodium contents given has been calculated from the amount rhodium added and are thus only approximate.

Attempts to characterise the catalyst by IR spectroscopy have failed the CO stretching frequency of the complex is obscured by strong absorbtions of the carrier around 1900 cm^{-1}.

4. Catalysis

4.1. SAP catalysts

4.1.1. Gas phase hydroformylation of propene

The variations in activity and regioselectivity with time on stream using SAP_1 and SAP_2 as catalysts in gas phase hydroformylation of propene are shown in Figs. 3 and 4. The initial total TOF of 3.29 mmol/(s gRh) for catalyst SAP_1 is high but it decreases rapidly and a constant TOF of 1.40 mmol/(s gRh) is reached after 100 min on stream. The regioselectivity behaves slightly different it increases at first but after having reached a maximum of 2.9 after 50 min it decreases and reaches a constant value of 2.1. No induction period is observed for catalyst

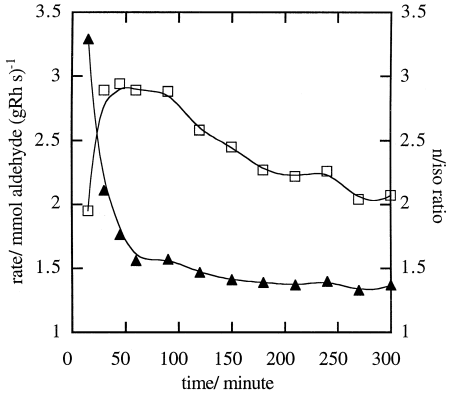

Fig. 3. Hydroformylation of propene with SAP_1. 100°C, 5 bar $CO:H_2$:propen 1:1:1. □ = *n*/*iso* ratio, ▲ = rate.

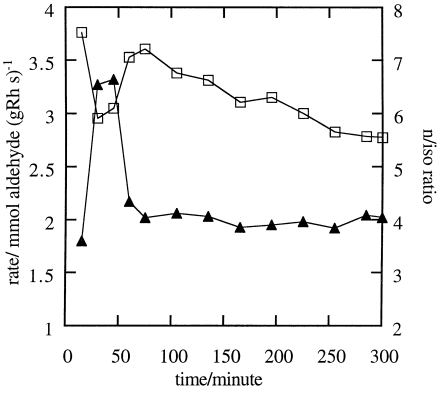

Fig. 4. Hydroformylation of propene with SAP_2. 100°C, 5 bar CO:H_2:propen 1:1:1. □ = *n / iso* ratio, ▲ = rate.

SAP_1 and this is probably due to that the catalytically active complexes, $[HRh(CO)(L)_2]$ and $[HRh(CO)_2(L)]$, are easily formed when the P:Rh ratio is low.

The behaviour of catalyst SAP_2 (Fig. 4) is in many respects rather similar to that of SAP_1, i.e., a rapid decrease in the initial activity followed by a constant TOF after about 50 min on stream and an initial increase followed by a slow decrease in the regioselectivity. The longer activation period for SAP_2 and the somewhat higher constant TOF of 2 and the higher regioselectivity of 6 are the main differences between SAP_1 and SAP_2.

The characteristics features of catalyst SAP_3 (Fig. 5) are similar to that of catalyst SAP_2 but in both the total TOF and the regioselectivity are continuously decreasing over the period studied (6 h) and no constant TOF is reached.

It is well documented that the regioselectivity of the parent organo-soluble complex $[HRh(CO)(PPh_3)_3]$ increases by increasing the P:Rh ratio in the reaction mixture but that it becomes independent at a P:Rh ratios over 10 [28]. It is thus pleasing to note that the present ligand system resembles its triphenylphosphine counterpart in this respect. However, the upper limit at which the phosphine excess does not increase the regioselectivity is lower (P:Rh = 5) than that of triphenylphosphine (P:Rh = 10).

The initial activation period for SAP_2 and SAP_3, but not for SAP_1, are not surprising since the higher P:Rh ratio favours the formation of the complex $[RhH(CO)(L)_3]$ and dissociation of one of the phosphine ligands from that complex is a prerequisite for the formation of the catalytically active hydroformylation complex.

The initial light yellow catalysts are slightly brownish after use and this might indicate decomposition and formation of inactive complexes. Two type of deactivation mechanisms have been suggested for Wilkinson type hydroformylation catalysts namely formation of phosphido bridged dimers and orthometalation of one of the phenyl rings [29,30]. The formation of phosphido bridged dimers has been shown to be the major deactivation pathway. It is impossible to draw any definite conclusions from the activity vs. water content but it is interesting to note that SAP_2, with lowest water content, has the highest activity and the best stability.

SAP catalysts based on the PEI–PNH ligand are considerably less active than those based on the PAA–PNH ligand and they deactivate very fast and within 3 h low or no activity is observed. It has previously been shown that amino functionalised phosphines give very low activity in acidic aqueous solutions due to acid promoted decomposition of the hydrido rhodium phosphine complex responsible for the catalytic activity [16]. We suggest that the same mechanism is the cause of the low stability and activity observed for the PEI–PNH based SAP-catalysts.

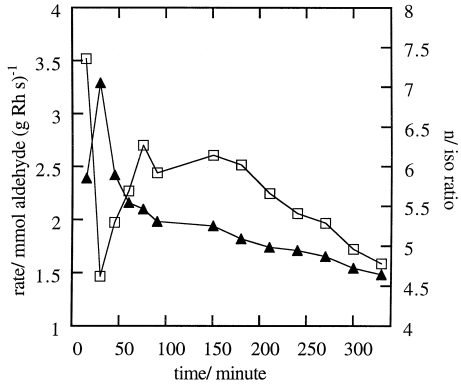

Fig. 5. Hydroformylation of propene with SAP_3. 100°C, 5 bar CO:H_2:propen 1:1:1. □ = *n / iso* ratio, ▲ = rate.

4.1.2. Liquid phase hydroformylation of 1-octene

To demonstrate the applicability of our SAP catalysts for heavier olefins hydroformylation of 1-octene have been performed. The autoclave we are having access to is not equipped with a sampling device and all runs were therefore conducted setting a fixed (20 h) reaction time. Both SAP_1 and SAP_2 behaves very similar giving 100% conversion and a regio-selectivity of 67% *n*-isomer. The conversion is maintained upon recycling of the catalyst a second time but the regioselectivity drops to 58% *n*-isomer. Visually the catalysts seem to be rather stable, the organic phase remains uncoloured and the catalyst maintains its original light yellow colour.

*4.2. Biphasic hydroformylation using PAA–PNH (**1**) based catalysts*

4.2.1. 1-hexene and 1-octene as substrates

The low solubility of heavier olefins in water and the accompanying slow rates is one of the drawbacks with biphasic hydroformylation. This is also a general trend for the PAA–PNH ligand system and clearly born out for both substrates studied (entry 4 and 7; Table 1). Is the low rate observed merely an effect of the very low solubility of the olefin in water or are there other causes? A report describing the effect of carboxylic acids on the yield and selectivity of the hydroformylation of 1-hexene catalysed by Rh/PPh_3 complexes has appeared [31]. The presence of carboxylic acid has a inhibiting effect, which was suggested to be due to the formation of carboxylate complexes. We cannot rule out that coordination of the carboxylate groups to the rhodium centre also contribute to the low rates observed but the experiments displayed in Table 1 clearly shows that the low solubility of the olefin is the main cause.

For instance, addition of sodiumdodecyl sulphate (SDS), which increases the solubility of unpolar substrates in water, increases the conversion for both substrates substantially (compare entries 4 and 6 or 9 and 12, Table 1). The 100% conversion obtained in these cases are a clear indication that low conversion is not related to poor performance of the catalyst itself but to the low solubility of the olefin. Co-solvents can also enhance the solubility, e.g., addition of EtOH to a solution of a Rh/TPPTS catalyst in water increases the rate of hydroformylation of 1-octene dramatically [13]. A higher conversion as a result of performing the reaction with 20% methanol in the aqueous phase was consistently observed (entries 9 and 11) also in the present study.

Addition of salt have been shown to increase the rate of hydroformylation using complexes of surface active phosphines, because higher salt concentration facilitates the formation of structured aggregates [32]. An increased salt concentration, however, also increases the polarity of the aqueous phase and hence decreases the olefin solubility. The second aspect of an increased ionic strength is the prevailing one for the present ligand system since addition of $NaClO_4$ significantly reduces the conversion (entries 9 and 10). A lower conversion as the ionic strength is increased also explains the effect of an increase in the P:Rh ratio (entries 4 and 5 or 9 and 7). The ligand PAA–PNH is a poly-electrolyte and an increase in PAA–PNH concentration increases the ionic strength thus lowering the olefin solubility in analogy with $NaClO_4$ addition. The effects of recycling of the catalysts are very small, the conversion remains the same while there is a small decrease in regioselectivity (entries 7 and 8), as also observed for the SAP catalyst. A more general comparison of the regioselectivity in the different runs displayed in Table 1 cannot be made because the variations in conversion is large and a variation in regioselectivity with conversion cannot be ruled out.

*4.3. Biphasic hydroformylation using PEI–PNH (**2**) as ligand*

The pH of an aqueous solution of catalyst **2** is approximately 3 and a low pH is necessary for keeping the polymer protonated and thereby

soluble in water. Aforementioned, low pH affects the stability of the active rhodium hydride complex and performing hydroformylations in acidic aqueous solution is thus not suitable. Biphasic hydroformylation of 1-octene using **2** as catalyst give after 4 and 17 h **2** and 100% conversion, respectively. The 100% conversion observed is somewhat surprising, but the remain after evaporating the organic phase was slightly yellow in the 17 h reaction while the remain was colourless in the 4-h reaction. Accordingly, we conclude that the catalyst degrades over time under the rough conditions applied leaking phosphine and rhodium to the organic phase. The conversion observed is therefore not the result of biphasic catalysis but the outcome of a homogeneous reaction in the organic phase.

5. Conclusion

For heavy olefins the rate of hydroformylation is largely controlled by the rate of olefin diffusion into the aqueous phase irrespective of the ligand applied and the polymer back-bone of our ligands do not improve the performance of catalyst based on these ligands relative that of catalysts based on the TPPTS ligand. The polymer based ligands are, however, well worth further studies in SAPC applications for both light and heavy olefins and the PAA–PNH is for reasons of stability the most interesting of the ones described in this paper.

References

[1] R. Selke, K. Häukpe, H.W. Krauss, J. Mol. Catal. 56 (1989) 315, and references therein.
[2] W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem. Int. Ed. Engl. 32 (1993) 1524.
[3] P. Kalck, F. Monteil, Adv. Organomet. Chem. 34 (1992) 219.
[4] H. Bahrmann, H. Bach, Phosphorus and Sulfur 30 (1987) 611.
[5] E.G. Kuntz, Chemtech. (1987) 570.
[6] B. Cornils, E.G. Kuntz, J. Organomet. Chem. 502 (1995) 177.
[7] T. Bartik, B. Bartik, B.E. Hanson, T. Glass, W. Bebout, Inorg. Chem. 31 (1992) 2667.
[8] W.A. Herrmann, J.A. Kulpe, W. Konkol, H. Bahrmann, J. Organomet. Chem. 389 (1990) 85.
[9] S. Ahrland, J. Chatt, N.R. Davies, A.A. Williams, J. Chem. Soc., 1958, p. 1403.
[10] A.F. Borowski, D.J. Cole-Hamilton, G. Wilkinson, Nouv. J. Chem. 2 (1977) 137.
[11] H. Ding, B.E. Hanson, T. Bartik, B. Bartik, Organometallics 13 (1994) 3761.
[12] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger, H. Bahrmann, H. Kottmann, J. Mol. Catal. A: Chem. 97 (1995) 65.
[13] P. Purwanto, H. Delmas, Catalysis Today 24 (1995) 135.
[14] R.G. Nuzzo, S.L. Haynie, M.E. Wilson, G.M. Whitesides, J. Org. Chem. 46 (1981) 2861.
[15] H. Bahrmann, B. Cornils, W. Konkol, W. Lipps. German. Patent. 3,412,335 (1985).
[16] A. Buhling, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Mol. Catal. A: Chem. 98 (1995) 69.
[17] A. Buhling, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.W. Elgersma, K. Goubitz, J. Fraanje, Organometallics 16 (1997) 3027.
[18] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, Nature 339 (1989) 454.
[19] G. Fremy, E. Monflier, J.-F. Carpentier, Y. Castanet, A. Mortreux, J. Catal. 162 (1996) 339.
[20] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, J. Catal. 121 (1990) 327.
[21] T. Malmström, H. Weigl, C. Andersson, Organometallics 34 (1995) 2593.
[22] T. Malmström, C. Andersson, J. Mol. Catal. A: Chem. 116 (1997) 237.
[23] B. Heinrich, Y. Chen, J. Hjortkaer, J. Mol. Catal. 80 (1993) 365.
[24] F.R. Hartley, S.G. Murray, P.N. Nicholson, J. Mol. Catal. 16 (1982) 36325.
[25] D.M. Barlex, M.J. Hacker, R.D.N. Kemmitt, J. Organomet. Chem. 43 (1972) 425.
[26] F. Araghizadeh, D.M. Branan, N.W. Hoffman, J.H. Jones, E.A. McElroy, N.C. Miller, D.L. Ramage, A.B. Salazar, S.H. Young, Inorg. Chem. 27 (1988) 3752.
[27] M.J. Naughton, R.S. Drago, J. Catal. 155 (1995) 383.
[28] K.L. Olivier, F.B. Booth, Hydrocarbon Process 49 (1970) 112.
[29] R.M. Deshpande, S.S. Divekar, R.V. Gholap, R.V. Chaudhari, J. Mol. Catal. 67 (1991) 333.
[30] A.G. Abatjoglou, E. Billig, D.R. Bryant, Organometallics 3 (1984) 923.
[31] E. Mieczynska, A.M. Trzeciak, J.J. Ziolkowski, J. Mol. Catal. 80 (1993) 189.
[32] H. Ding, B.E. Hanson, J. Chem. Soc. Chem. Commun. (1994) 2747.