A stable and recyclable supported aqueous phase catalyst for highly selective hydroformylation of higher olefins†

Albertus J. Sandee, Vincent F. Slagt, Joost N. H. Reek, Paul C. J. Kamer and Piet W. N. M. van Leeuwen*

Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands. E-mail: pwnm@anorg.chem.uva.nl

A highly regioselective supported aqueous phase hydroformylation catalyst is presented that is completely and conveniently separated from the products and reused in numerous consecutive catalytic cycles.

Hydroformylation is one of the mildest and cleanest methods to produce aldehydes and is therefore widely applied in the petrochemical industry. The cleanest and most important industrial hydroformylation process is the aqueous biphasic process, developed by Ruhrchemie, affording a straightforward separation of the organic products from the catalyst. The applicability of this system, however, is strictly limited to substrates that are slightly water soluble, such as propene and but-1-ene.[1] The industrial hydroformylation of higher olefins is carried out in a single, organic phase and the catalyst is separated by distillation, which may result in catalyst decomposition. Distillation techniques are not suitable for the production of heavier products or fine chemicals because of the high boiling points of the products.

An interesting novel concept of catalyst immobilisation is the supported aqueous phase catalyst (SAPC).[2] In this system the catalyst is immobilised in a thin water layer adhered within the pores of a high-surface-area silicate.[3] Using this system higher alkenes can be converted at a relatively high rate without metal leaching. The regioselectivity, however, towards the linear aldehyde of the reported systems thus far is very low and surprisingly little has been reported on the recyclability and stability of these systems.[4] Virtually all SAP hydroformylation catalysts described in literature are based on rhodium, cobalt or platinum/nickel complexes with TPPTS as the ligand.[5,6] Only in a single case were sulfonated diphosphines examined.[7] Diphosphines with a large P–M–P bite angle have a beneficial influence on the regioselectivity of homogeneous hydroformylation catalysts.[8,9] We recently reported on the synthesis of a water-soluble ligand with a large bite angle: the disodium salt of 2,7-bissulfonate-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Sulfoxantphos) (**A**) and its use in biphasic hydroformylation reactions.[10] The high regioselectivity obtained with this ligand stimulated us to investigate its performance as an SAPC.

It was shown that the rhodium hydride HRh(**A**)(CO)$_2$ (**1**), the precursor to the active species in hydroformylation reactions, was formed quantitatively under a CO–H$_2$ (1:1) atmosphere in DMSO-d$_6$.[10] When **1** is exposed to 1 bar of CO it completely transforms to the rhodium dimer [Rh(**A**)(CO)(μ-CO)]$_2$ (**2**) (Scheme 1), which was isolated and characterised by means of NMR, FT-IR and FAB-MS.[11] The ^{31}P NMR spectrum of **2** is consistent with an AA′BB′XX′ spin system ($^1J_{RhP}$ = 129, 135, 155 and 164 Hz, $^2J_{RhP}$ = 8 Hz, $^1J_{PP}$ = 18 Hz, $^3J_{PP}$ = 2 and 5 Hz, see Fig. 1). The equilibrium between **1** and **2** can be forced completely to either side by changing the hydrogen pressure.[12] A similar experiment in D$_2$O revealed that the formation of both **1** and **2** is much slower under aqueous conditions. The *in situ* formation of **2** on CPG-240 was, however, clearly observed using NMR techniques.‡
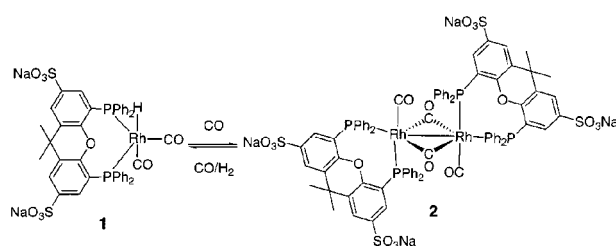
Scheme 1 Equilibrium between rhodium hydride and carbonyl-bridged dimeric species.

Both the novel Rh(**A**)/SAPC and the known Rh(TPPTS)/SAPC were studied in the hydroformylation of oct-1-ene.§ Rh(**A**)/SAPC is very selective towards the linear aldehyde; a linear to branched aldehyde ratio of 40:1 was obtained. This is an increase in regioselectivity, compared to Rh(TPPTS)/SAPC, of a factor of at least 10 (Table 1, entries 1 and 11). This proves that **A** plays a key role in the regulation of the regioselectivity in the hydroformylation of immobilised homogeneous catalysts.

The rate of hydroformylation of oct-1-ene using Rh(**A**)/SAPC at 80 °C in toluene as the co-solvent was found to be low (*ca.* 1 turnover per hour; Table 1, entries 1 and 2). When the catalysis was performed in pure oct-1-ene, however, the rate increased to a turnover rate of 15 per hour (Table 1, entry 1 and 3). Interestingly, this large concentration dependence was not found for Rh(TPPTS)/SAPC (Table 1, entries 11 and 12). We also found a 5-fold increase on performing the catalysis at 100 °C (turnover rates of 55 and 160 per hour, entries 9 and 13). Under optimised conditions the activities of Rh(**A**)/SAPC and Rh(TPPTS)/SAPC are competitive while the high selectivity of the former catalyst is retained.
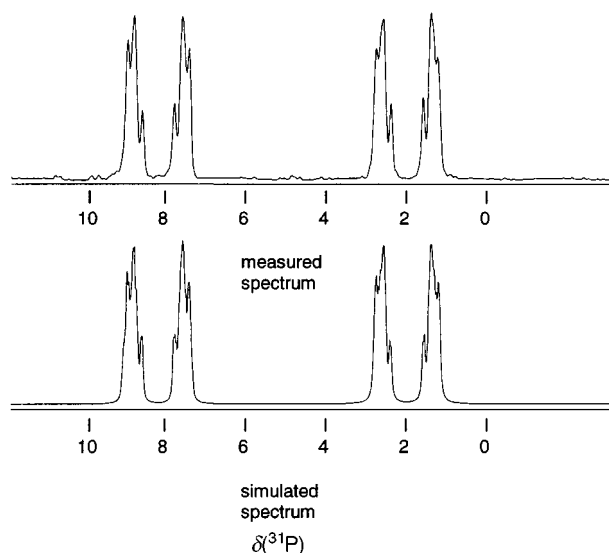
Fig. 1 Observed and calculated ^{31}P NMR spectrum of [Rh(Sulfoxantphos)(μ-CO)(CO)]$_2$ **2**.

Table 1 Results from the hydroformylation of oct-1-ene at 80–100 °C and 50 bar CO–H_2 (1:1).

Entry	Catalyst [cycle][a]	Conversion after 24 h (%)	TOF[b]	Linear to branched ratio[c]	Alkene isomerisation[c] (%)	Linear aldehyde[c] (%)
1	Rh(**A**) [1]	7	1	38	1.9	95.6
2	Rh(**A**) [2]	28[d]	1	44	5.7	92.2
3	Rh(**A**) [3][e]	14	15	46	5.0	93.0
4	Rh(**A**) [4][e]	14	14	42	8.7	89.2
5	Rh(**A**) [5][e]	12	14	40	8.5	89.3
6	Rh(**A**) [6][e]	10	13	40	7.7	90.0
7	Rh(**A**) [7][e]	24[f]	10	39	7.3	90.3
8	Rh(**A**) [8][g]	37	44	31	7.0	90.1
9	Rh(**A**) [9][g]	46	55	31	4.1	92.9
10	Rh(**A**) [10][g]	48	55	27	5.8	90.7
11	Rh(TPPTS) [1]	20	15	3	7.4	67.2
12	Rh(TPPTS) [2][e]	3	30	3	12.3	67.2
13	Rh(TPPTS) [3][g]	17	160	3	7.3	70.5
14	Rh(TPPTS) [4][g]	90[f]	146	2	52.6	33.9

[a] Ligand to rhodium ratio is 10 for Rh(**A**) and 20 for Rh(TPPTS), catalysis performed at 80 °C and 50 bar CO–H_2 in 15 ml toluene as a co-solvent using 1 ml of oct-1-ene. [b] Average turnover frequencies were calculated as (mol aldehyde/mol catalyst)$^{-1}$ h^{-1}. [c] Determined by means of GC analysis using decane as an internal standard. [d] Conversion after 96 h. [e] Catalysis performed in 15 ml oct-1-ene at 80 °C. [f] Conversion after 72 h. [g] Catalysis performed in 15 ml oct-1-ene at 100 °C.

The product/catalyst separation efficiency of the SAPCs was examined on performing recycling experiments (Table 1). Rh(**A**)/SAPC could be recycled numerous times without deterioration of the catalyst performance (entries 1–10). The selectivity towards the linear aldehyde remained high during all experiments and the decrease in rate of hydroformylation was very small (at 100 °C we even observed a small increase in rate in successive runs).¶ This indicates that ligand **A** retains the rhodium quantitatively on the support which is confirmed by rhodium analysis on the product by means of ICP-AES. No traces of rhodium were detected in the product phase of any of the SAPC experiments (detection limit 1 ppm). In contrast, Rh(TPPTS)/SAPC showed a drop in catalyst performance after three catalytic runs (Table 1, entries 11–14). In the fourth cycle, over 50% of the oct-1-ene isomerised and the linear-to-branched ratio decreased to 2. The Rh(**A**)/SAPC is thus far more robust then the TPPTS based SAPC; Rh(**A**)/SAPC could be recycled over at least three weeks, showing no deterioration of the catalyst performance whereas under similar conditions Rh(TPPTS)/SAPC showed a strong reduction in hydroformylation performance after three days.

Importantly, Rh(**A**)/SAPC is stable in the absence of substrate as it can be transformed into the dimer [Rh(**A**)(μ-CO)(CO)]$_2$ which is stable over weeks when properly stored under 1 bar of CO. The reversible switching between the catalytically active species **1** and the stable dimeric species **2** did not influence the catalytic performance in at least four consecutive runs.‖

We can conclude that the introduction of rigid bidentate diphosphines with a large 'natural' bite angle in the supported aqueous phase catalysis improves the regioselectivity towards the linear aldehyde enormously compared to the SAPCs known thus far. Moreover, the application of Sulfoxantphos in SAP catalysed hydroformylation gives rise to a significant improvement of the sustainability of the system. To the best of our knowledge this supported aqueous phase catalyst is the first example of an immobilised homogeneous catalyst that is highly selective and robust and shows no metal leaching in numerous consecutive catalytic runs.

Notes and references

‡ For more experimental details see Electronic Supplementary Information (ESI).

§ The recycling experiments were performed as follows. A stainless steel 50 ml autoclave, equipped with a mechanical stirrer, a substrate vessel, a cooling spiral and a sample outlet, was charged with 1 g of SAPC containing (1) 1×10^{-4} mol **A**; (2) 1×10^{-5} mol Rh(acac)(CO)$_2$ and (3) 4% (m/m) water on CGP-240 in 10 ml toluene. The suspension was incubated for 1 h at 80 °C under 20 bar CO–H_2 (1:1). A mixture of 1 ml oct-1-ene and 1 ml decane in 3 ml toluene was added and the CO–H_2 pressure was brought to 50 bar. The mixture was stirred for 24 h. The autoclave was cooled to 15 °C and the pressure was reduced to 2 bar. With the small overpressure the liquid was slowly removed from the catalyst with a 1.2 mm syringe. After the catalyst was washed with 5 ml toluene, 10 ml of toluene was added and the pressure was brought to 20 bar. Finally the mixture was heated to 80 °C and the next cycle was performed.

¶ We also observed this increase in rate of hydroformylation in successive catalytic runs in the biphasic Rh(**A**) system (ref. 10). We suggest that at this temperature the remaining catalytically inactive species are slowly transformed into the active form (the inactive species is most probably the carbonyl bridged rhodium dimer).

‖ The procedure described above is extended as follows. After a catalytic run was performed the reaction medium was cooled to 90 °C the CO–H_2 (1:1) pressure was removed and 20 bar of CO was introduced. The mixture was slowly cooled to 20 °C and stirred for 4 h. The liquid was subsequently removed from the catalyst by means of a syringe. The catalyst was washed with CO-saturated toluene and the next cycle proceeded after the reaction mixture was pressurised with 50 bar of CO–H_2.

1 E. G. Kuntz, *Chemtech*, 1987, 570.
2 J. P. Arhancet, M. E. Davis, J. S. Merola and B. E. Hanson, *Nature*, 1989, **339**, 454.
3 M. E. Davis, *Chemtech*, 1992, 498.
4 J. P. Arhanchet, M. E. Davis and B. E. Hanson, *J. Catal.*, 1991, **129**, 100.
5 W. A. Herrmann and C. W. Kohlpainter, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1524.
6 M. S. Anson, M. P. Leese, L. Tonks and J. M. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1998, 3529.
7 I. Tóth, I. Guo and B. E. Hanson, *J. Mol. Catal.*, 1997, **116**, 217.
8 C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavey and D. R. Powell, *J. Am. Chem. Soc.*, 1992, **114**, 5535.
9 M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz and J. Fraanje, *Organometallics*, 1995, **14**, 3081; L. A. van der Veen, M. D. K. Boele, F. R. Bregman, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk and C. Bo, *J. Am. Chem. Soc.*, 1998, **120**, 11 616.
10 M. Schreuder Goedheijt, P. C. J. Kamer and P. W. N. M. van Leeuwen, *J. Mol. Catal.*, 1998, **134**, 243.
11 B. R. James, D. Mahajan, S. J. Rettig and G. M. Williams, *Organometallics*, 1983, **2**, 1452.
12 A. Castellanos-Paéz, S. Castillón, C. Claver, P. W. N. M. van Leeuwen and W. G. J. de Lange, *Organometallics*, 1998, **17**, 2543.

Communication 9/03916C