DOI: 10.1002/anie.201007164

Hydroformylation

Rhodium–Phosphite SILP Catalysis for the Highly Selective Hydroformylation of Mixed C_4 Feedstocks**

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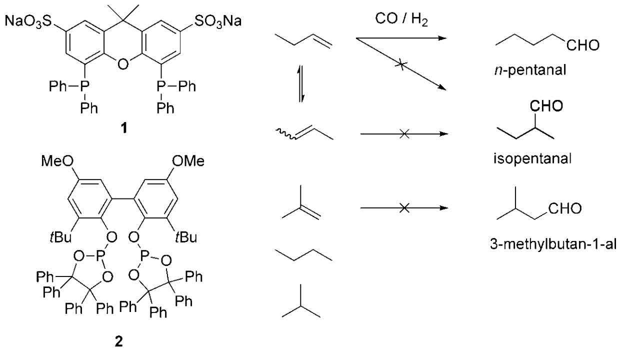
The hydroformylation of alkenes catalyzed by dissolved rhodium complexes is not only one of the largest applications of homogeneous catalysis in industry,[1] but also an established benchmark reaction for testing immobilization concepts for homogeneous catalysts.[2] In recent years, ionic liquids (ILs) as non-aqueous solvents for liquid–liquid biphasic hydroformylation catalysis have been the subject of intensive study.[3] Important features of ILs compared to the industrial aqueous–organic biphasic catalysis (Ruhrchemie–Rhône–Poulenc process[4]), are their much better solubility for higher alkenes[5] and their compatibility with phosphite ligands, which readily decompose by hydrolysis in water.[6]

Despite these attractive features, we know of no large-scale industrial application of ionic liquids in biphasic hydroformylation catalysis to date. Two important drawbacks of the biphasic ionic liquid systems are the relatively high amounts of expensive IL that are required and its intrinsically high viscosity, which leads to slow mass transport between the two liquid phases.

To overcome these limitations, we, among others,[7] have in recent years developed the supported ionic liquid phase (SILP) concept. SILP materials are prepared by dispersing a solution of the catalyst complex in an ionic liquid as a thin, physisorbed film on the large internal surface area of a porous solid material.[8] Since the film thickness of the ionic liquid is within the nanometer range, diffusion problems are minimized by the extremely small diffusion distances. Excellent ionic liquid utilization is achieved; that is, the same catalytic performance can be achieved with a much smaller total IL amount compared to liquid–liquid biphasic systems. Because ionic liquids typically have extremely low vapor pressures,[9] catalysis with SILP materials is particularly attractive in continuous gas-phase contact. During catalysis the immobilized catalytic ionic liquid film comes into contact solely with gaseous reactants and products. For the continuous gas-phase hydroformylation of pure 1-alkene feedstock, such as, propene and 1-butene, this concept has been demonstrated quite successfully with good catalytic activity (turnover frequencies (TOFs) up to 500 h^{-1} in the case of propene[10] and 564 h^{-1} in the case of 1-butene[11]) and excellent catalyst stability (up to 200 h time-on-stream in the case of propene[10] and 120 h in the case of 1-butene[12]) as was demonstrated using a Rh-SILP catalyst modified with the sulfonated phosphine ligand sulfoxantphos (**1**). The sulfoxantphos–rhodium catalyst is, however, unable to react with internal alkenes such as 2-butenes in either hydroformylation or isomerization. Thus, to convert 1-butene and 2-butenes from a mixed technical C_4 feedstock from steam-cracker into the desired linear pentanal, a different catalyst system is required. Rhodium–phosphite complexes are known to be capable of selective isomerization/hydroformylation activity, which converts internal alkenes in a classical monophase homogeneous catalysis into linear aldehydes with good to excellent selectivity.[13] Most of these ligands, however, are highly air- and moisture-sensitive, making it difficult to handle and use them in large quantities and a real challenge to recycle rhodium–phosphite systems.[14]

Herein, we show how the new diphosphite ligand **2** in form of a SILP catalyst system is applied in the continuous gas-phase hydroformylation of an industrial mixed C_4 feedstock as illustrated in Scheme 1. Synthesizing **2** and using it in



Scheme 1. Left: sulfoxantphos (**1**) and the novel diphosphite (**2**) ligands. Right: possible reaction pathways for hydroformylation of mixed C_4 feed to yield predominantly *n*-pentanal.

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[**] A.S., S.W., M.H., and P.W. thank the German Science Foundation for infrastructural support through the Erlangen Cluster of Excellence "Engineering of Advanced Materials". SILP = Supported ionic liquid phase.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201007164.

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homogeneous-catalyzed hydroformylation in organic solvents has been recently described by Börner's group.[15]

The industrial feedstock (raffinate 1 by Evonik Oxeno GmbH) used contained isobutene (43.1 %), 1-butene (25.6 %), *trans*-2-butene (9.1 %), *cis*-2-butene (7.0 %), non-reactive butanes (14.9 %), and 1,3-butadiene (0.3 %). To selectively obtain the desired linear product *n*-pentanal, hydroformylation of isobutene must be avoided and both 2-butenes have to be isomerized prior to hydroformylation.

We modified a procedure in the literature to prepare the Rh-**2**-SILP catalyst (see Experimental Section). 2 g of the catalyst were placed in a fixed bed reactor. A gas mixing unit supplied the gaseous reactant stream (the industrial C_4 feed/syngas (H_2/CO)). Online GC was used to analyze all reaction products. The continuous reactor setup has been previously described[10] and further details can be found in the Supporting Information.

In a first set of experiments, the Rh-**2**-SILP catalyst was tested at different temperatures while the conversion and selectivity were measured over time as shown in Figure 1.

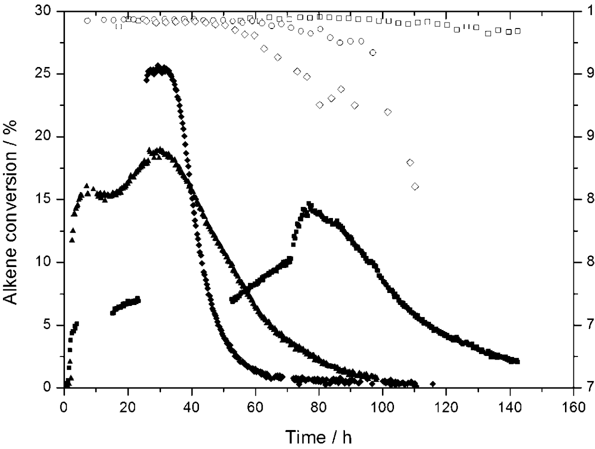

Figure 1. Hydroformylation of an industrial C_4 mixture (raffinate 1, 500 ppm H_2O) in the presence of Rh-**2**-SILP catalyst. $p_{total} = 10$ bar, $p_{raffinate1} = 2$ bar, $p_{H_2} = p_{CO} = 4$ bar. Total volume flow = 13.8 mL min^{-1}, residence time = 29 s, $m_{SILP} = 3$ g, $w_{Rh} = 0.2$ wt %, **2**/Rh = 10:1, ionic liquid loading = 10 vol % [EMIM][NTf$_2$] relative to total pore volume. Conversion (■, ▲, ◆) and selectivity (□, ○, ◇) plotted over time at 80 (■, □), 90 (▲, ○), and 100 °C (◆, ◇). EMIM = 1-ethyl-3-methylimidazolium, NTf_2 = bis(trifluoromethanesulfonyl)imide

At temperatures of 80, 90, and 100 °C, the system showed an exceptionally high regioselectivity toward *n*-pentanal of up to 99.5 %. Despite the high isobutene content of 43.1 % in the feedstock used, we observed no formation of 3-methyl butan-1-al, and the 2-butenes were hydroformylated only after isomerization, finally producing *n*-pentanal.

The Rh-**2**-SILP catalyst exhibited good activity (20 % conversion corresponds in these experiments to a TOF of 330 h^{-1}.) but low catalyst stability. After an initial activation phase, the catalyst deactivated rapidly with increasing temperature. The increasing activity in the beginning of the experiment is a typical sign of slow ligand decomposition over time as a decreasing L/Rh ratio results in more active hydroformylation catalysts.[16] Once all the ligand has decomposed (note that the L/Rh ratio in the IL film was 10:1 in the freshly prepared SILP materials), the homogeneously dissolved nature of Rh cannot be maintained and inactive Rh clusters form under the reaction conditions.[17] Our experiments indicate that this process is temperature dependent and results in an irreversible loss of activity.

Given the notorious susceptibility to hydrolysis of the phosphite ligand it was clear that its decomposition is attributable to traces of water present in the gaseous feedstock mix. For this reason, dried raffinate 1 from Evonik Oxeno was used (water content less than 16 ppm) in subsequent continuous hydroformylation experiments. As ligand decomposition leads to the formation of phosphoric acid, the latter being a catalyst for further ligand decomposition, we decided to add an acid scavenger to the ionic liquid film in addition to all the other measures to eliminate traces of water in the system. Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (**3**; BTPS, from Evonik Oxeno GmbH) was found to be a suitable acid scavenger that does not interact or react with the active catalytic species. When BTPS was added in a molar ratio **3**/**2** = 4:1 to the ionic liquid catalyst solution, the stability of the system could be improved significantly. Figure 2 shows an example of a long-term catalytic experiment at 100 °C applying these optimized conditions for ligand preservation.

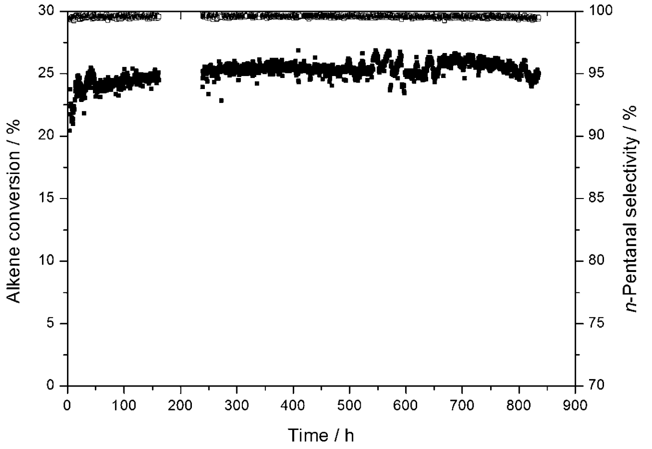

Figure 2. Hydroformylation of an industrial C_4 mixture (raffinate 1, less than 16 ppm H_2O) in the presence of Rh-**2**-SILP catalyst. $T = 100$ °C, $p_{total} = 10$ bar, $p_{raffinate1} = 2$ bar, $p_{H_2} = p_{CO} = 4$ bar. Total volume flow = 29.2 mL min^{-1}, residence time = 15 s, $m_{SILP} = 3$ g, $w_{Rh} = 0.2$ wt %, **2**/Rh = 10:1, **3**/**2** = 4:1, ionic liquid loading = 10 vol % [EMIM][NTf$_2$] relative to total pore volume. Conversion (■) and selectivity (□) plotted over time.

Remarkably, with these modifications the initial conversion of 25 % could be retained for more than 800 h on stream without loss of the high selectivity. The average activity of the Rh-**2**-SILP system was 410 h^{-1} which resulted in an accumulated turnover number (TON) of more than 350 000. The success of this stability test confirms that the phosphite ligand **2** can indeed be applied as a SILP catalyst through a combination of drying procedures and acid scavenging without adversely affecting the ligand or complex stability, thus achieving a highly selective and active SILP catalyst system.

Kinetic investigations revealed a first order dependence on substrate partial pressure in the temperature range between 70 and 100 °C. Varying the partial pressures of hydrogen and carbon monoxide showed that H_2 has a slightly positive and CO a slightly negative influence on the reaction rate. These observations are in accordance with the well accepted Wilkinson mechanism for ligand-modified rhodium catalysis.[18] In the temperature range under investigation, the Rh-**2**-SILP catalyst had an activation energy of $E_A = 41\,\mathrm{kJ\,mol^{-1}}$.

The performance of the new Rh-**2**-SILP catalyst system could be further optimized by increasing the temperature to 120 °C and the total pressure to 25 bar. Under these conditions, the TOF reached $3600\,\mathrm{h^{-1}}$ which corresponds to a space–time yield (STY) of 850 kg *n*-pentanal per cubic meter per hour. This is—to our knowledge—the highest STY reported for a SILP catalyst and a value that clearly outperforms most industrially realized, homogeneously catalyzed processes. Under these harsher conditions, the selectivity toward *n*-pentanal always remained above 99 %. Note that this ligand-induced, homogeneous catalyst performance was achieved with a material that macroscopically has the appearance of a dry solid and by using a highly diluted (43 % inert isobutene) industrial feedstock. Inductively coupled plasma atomic emission spectrometry (ICP–AES) analysis of aldehyde product condensate did not reveal any Rh in the product (detection limit ca. 100 ppb). Increasing the temperature to boost catalytic productivity even further was unfeasible because the thermal instability of the phosphite ligand.

Our catalytic studies were accompanied by ^{31}P NMR spectroscopic investigations to learn more about the nature and stability of the Rh-**2**-SILP catalyst. A fresh solution of the $[Rh(acac)(CO)_2]$ precursor (acac = acetylacetonato) together with a tenfold excess of **2** in the ionic liquid $[EMIM][NTf_2]$ was measured (Figure 3 a). A strong signal at $\delta = 145.3$ ppm corresponding to the free ligand can be seen together with a doublet centered at $\delta = 147.5$ ppm ($J_{\text{Rh-P}} = 296$ Hz) resulting from the rhodium–phosphite species.[19] In a comparative experiment, a freshly prepared Rh-**2**-SILP material was washed with dried dichloromethane to remove the ionic liquid catalyst solution from the silica support and this washing solution was analyzed by NMR spectroscopy. As expected the same signals at $\delta = 145.3$ and 147.5 ppm were found (Figure 3 b) indicating that contact with the support material during the SILP synthesis does not change the catalyst complex or the free ligand. Even a SILP catalyst that had been stored in the glovebox for 10 months showed still the same ^{31}P NMR spectrum after the material was washed with CH_2Cl_2 (Figure 3 c). Weak signals in the range between $\delta = 5$ and 8 ppm, however, correspond to formation of a small amount of oxidized ligand species.[20] This result indicates that the rhodium–phosphite SILP catalysts can be stored in the complete absence of air and water for prolonged times.

We also performed spectroscopic investigations on SILP catalyst material that had been in catalytic use for more than 800 h (see Figure 2). The sample was taken from the reactor, washed with CH_2Cl_2 and the washings analyzed by NMR spectroscopy (Figure 3 d). In this case, a slightly different peak pattern is observed with additional signals appearing at $\delta \approx 172$ ppm and 152 ppm and in the range between $\delta = -2$ and 8 ppm. Signals for the intact ligand and the rhodium complex ligand are also present. For technical reasons, it was unavoidable that the SILP material should briefly come into contact with air and moisture during removal from the reactor. However, a reference sample of the Rh-**2** complex that was placed in H_2O_2 solution for 10 min showed no significant sign of decomposition or oxidation products. It can therefore be assumed that the decomposition products were formed during catalysis without affecting the selectivity of the system over 800 h. The nature of these decomposition products and their role in the Rh-**2** catalyzed hydroformylation under the given conditions is not yet clear. Note that additional ^{1}H NMR experiments with the same SILP washing solution revealed very intense signals arising from the ionic liquid, demonstrating the presence of the supporting film still after 800 h time-on-stream.

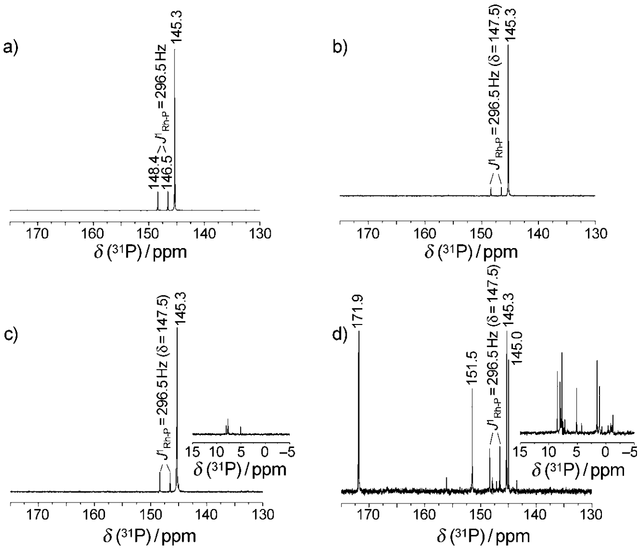

Figure 3. ^{31}P NMR solution spectra of Rh-**2** hydroformylation catalysts. a) Rh-**2** in $[EMIM][NTf_2]$, dissolved in CH_2Cl_2; b) fresh Rh-**2**-SILP, washed with CH_2Cl_2, c) Rh-**2**-SILP, stored for 10 months under Ar, washed with CH_2Cl_2; d) used Rh-**2**-SILP, 800 h on stream, washed with CH_2Cl_2.

In conclusion, we have demonstrated the applicability of the sophisticated diphosphite ligand **2** in the continuous gas-phase hydroformylation of a diluted C_4 olefin mixture using the SILP approach. Given the complex composition of the industrial feedstock, the obtained selectivity of more than 99 % *n*-pentanal under all the applied conditions is remarkable. It indicates that the Rh-**2**-SILP material is a highly active isomerization catalyst that selectively adds CO/H_2 to 1-butene and leaves 2-butenes and the large amount of isobutene (43.1 % of the feedstock mixture) completely untouched with respect to direct hydroformylation. Furthermore, it is noteworthy that the neutral ligand **2** can be applied efficiently in a continuous gas-phase SILP process. In an ionic liquid–organic biphasic operation, the same ligand would leach quickly into the product phase and structural modification (e.g., attachment of ionic groups) would be necessary to immobilize it in the ionic liquid. Compared to former SILP hydroformylation work where ionic ligands with ionic immobilizing groups were always used (such as e.g. in sulfoxantphos, **1**) this important new finding will certainly pave the way for the application of a much broader range of non-ionic ligand systems in future SILP catalysis studies.

As expected, **2** was found to be sensitive to hydrolysis. If, however, a dried feed gas is used and an acid scavenger added to the immobilized ionic liquid on support, the catalyst stability can be extended to more than 30 days time-on-stream. During this operation time a total turnover number of more than 350000 was achieved. Under slightly harsher reaction conditions (120 °C, 25 bar total pressure) the performance of Rh-**2**-SILP can be increased with the same highly diluted feed to a TOF of 3600 h^{-1} and a space–time yield of 850 $kg_{n\text{-pentanal}}\,m^{-3}\,h^{-1}$. This productivity level can be maintained for at least 10 h time-on-stream without visible deactivation or loss in selectivity.

Our work demonstrates that SILP catalysis is suitable for performing homogeneous catalysis with complex, sensitive, and expensive ligand systems in a highly productive manner using simple fixed-bed technology. In this particular case where rhodium–diphosphite SILP systems were investigated, significant space–time yield and excellent selectivity could be achieved in a highly substrate-specific isomerization/hydroformylation reaction sequence. This result makes these systems relevant for a future industrial use.

Experimental Section

All syntheses have been carried out under inert atmosphere in a glovebox. Details of the experimental setup have been reported elsewhere and can be found in the Supporting Information. The pre and post analysis of the SILP catalyst was carried out using a 400 MHz Jeol NMR spectrometer. Further details can be obtained in the Supporting Information.

Both the ligand **2** and stabilizer **3** were obtained from Evonik Oxeno GmbH. $[Rh(CO)_2(acac)]$ (Aldrich) was dissolved in water-free CH_2Cl_2 and stirred for 5 min. Ligand **2**, dissolved in CH_2Cl_2, was added in a tenfold excess (**2**/Rh = 10:1), and the resulting yellow solution was stirred for another 5 min. For stabilizer addition, a fourfold excess (**3**/**2** = 4:1) in CH_2Cl_2 was added. Afterward, the ionic liquid $[EMIM][NTf_2]$ (Merck KGaA) was added to the solution. After 5 min stirring, the appropriate amount (see Supporting Information) of calcinated silica (Merck KGaA) was added and the suspension was stirred for 15 min. The CH_2Cl_2 was removed in vacuo, and a pale yellow powder was obtained (for details see Supporting Information). The SILP catalyst was stored under argon until further use.

Received: November 15, 2010

Published online: April 8, 2011

Keywords: butene · hydroformylation · isomerization · phosphates · supported ionic liquid phase

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[20] ^{31}P NMR shifts for possible degradation and oxidation products have been calculated using ACD Labs NMR predictor software.

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