Homogeneous Catalysis

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Carbon Dioxide Induced Phase Switching for Homogeneous-Catalyst Recycling**

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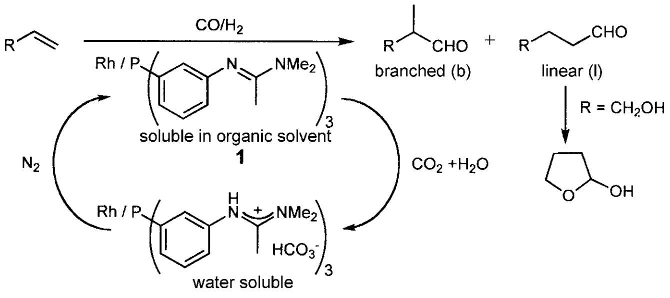
Homogeneous catalysts typically display high activity, high selectivity, and can be tailored through ligand modification. However, because they are dissolved in the reaction medium, their separation from the products and subsequent reuse can be complicated, hindering their widespread use for commercial applications. Herein we report a new approach to solve the product–catalyst separation problem involving carrying out the reaction in a single phase and switching the catalyst into a separate phase by bubbling with or removal of CO_2 (Scheme 1).



Scheme 1. Hydroformylation of alkenes ($R = C_6H_{13}$ (1-octene) or CH_2OH (allyl alcohol)) using a catalyst that can be switched between an organic phase and water by bubbling with CO_2 or N_2.

Several methods have been developed, aimed at efficient ways of recycling homogeneous catalysts.[1,2] An aqueous biphasic system is currently used in industry for the hydroformylation of propene and butene.[3] In this process, the catalyst is dissolved in an aqueous phase by the use of sulfonated ligands, whereas the starting material and products form a separate phase. This method allows fast and efficient separation of the product from the catalyst by simple decantation. The aqueous phase containing the catalyst can then be reused for further operation.

Although the introduction of a second phase ensures efficient catalyst separation and recycling, it induces mass-transfer limitations that reduce the reaction rate. For higher alkenes ($> C_5$), which display poor solubility in water, mass-transport limitations render the reaction rate too low to be economically viable, greatly limiting the scope of this elegant technology.

An interesting approach for a general solution to this limitation is to carry out the reaction in a single phase and to transfer the catalyst into the second phase once the reaction is complete. Heat has been used to trigger such phase transitions.[4] At the reaction temperature (≥ 70 °C) a rhodium complex catalyst bearing polyoxoethylene moieties is soluble in the organic phase, whereas upon cooling hydrogen bonds form between the polyether chains and water rendering the catalyst soluble in water. The phenomenon is reversible and this strategy has been used for the hydroformylation of higher alkenes, allowing the catalyst to be recycled eight times without noticeable loss in activity.

Variation of pH value has also been used to alter catalyst solubility.[5] By incorporating amine groups onto the ligand, the catalyst can be extracted from an organic phase into an acidic aqueous solution. Deprotonation of the ammonium group by addition of base allows re-extraction into a fresh organic phase for catalyst reuse. This approach, however, results in the formation of significant quantities of salt by-products. CO_2 has also been described for such recycling, when using $P\{(CH_2)_3NEt_2\}_3$, with the CO_2 being removed by boiling to reverse the extraction. Rhodium leaching in the organic phase was found to be < 1 ppm.[6,7] Herein we report catalysts for which the solubility in organic and aqueous phase can be reversibly switched upon addition or removal of carbon dioxide (1 bar).

Jessop and co-workers have described CO_2 phase-switchable surfactants.[8] They demonstrated that hydrophobic long-chain alkyl amidines could be protonated and become water-soluble surfactants upon addition of CO_2. The amidinium ion could then be deprotonated and returned to the organic phase by removing the CO_2 using N_2, a process similar to the catalyst recycling shown in Scheme 1 but with the phenyl phosphine being replaced by an alkyl chain. This approach allowed the reversible formation and breaking of water–oil emulsions stabilized by the amidine-based surfactants. We reasoned that by introducing amidine moieties onto phosphorus ligands we could make catalysts for which the solubility could be switched using CO_2 as a trigger.

We prepared and characterized ligand **1** based on PPh_3 bearing three amidine groups and tested it for the hydroformylation of 1-octene (Scheme 1, $R = C_6H_{13}$). The catalyst was prepared in situ by heating **1** together with [Rh-

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(acac)(CO)$_2$] (**1**/Rh = 50, acac = 2,4-pentanedione; acetylacetone))[*] in toluene under a syngas (CO/H$_2$) atmosphere yielding a bright yellow solution. Coordination of the ligand to the rhodium center was confirmed by ^{31}P{^{1}H}-NMR spectroscopy. This catalytic solution was used for the homogeneous hydroformylation of 1-octene under a constant pressure of syngas (20 bar) at 100 °C. The progress of the reaction was monitored at constant pressure by recording the pressure drop from a ballast vessel from which gas was continuously fed to the reactor (Figure 1 a, cycle 1a). Another reaction was carried out with a freshly prepared catalytic solution to ensure reproducibility (Figure 1 a, cycle 1b). The catalytic system was found to be very active; impressive initial turnover frequencies (TOF$_0$) of 11 046 h^{-1} and 9996 h^{-1} were observed. The gas uptake profiles recorded were very similar (Figure 1 a, cycles 1a and b).

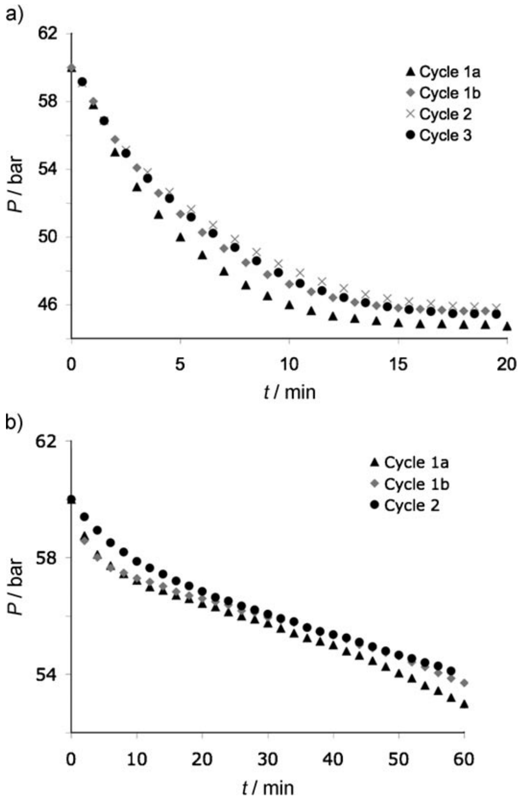

Figure 1. Gas uptake curves from a ballast vessel obtained for the hydroformylation of a) 1-octene and b) allyl alcohol.

The crude product solutions from the two cycle 1 reactions were combined and water was added (Figure 2, image 1a). This biphasic system was stirred for 10 min and left to settle. Visual observation did not show any change in coloration of either phase. This result indicates that the catalyst does not transfer significantly to the aqueous phase in the absence of CO$_2$. After 10 min stirring with CO$_2$ bubbling gently through the solution, the upper organic phase had completely decolorized while the aqueous phase turned yellow indicating transfer of the catalyst to the aqueous phase (Figure 2, image 1b). Bubbling of CO$_2$ was continued for a total of 1.5 h to ensure complete transfer of the catalyst to the aqueous phase. The upper colorless organic phase was separated and analyzed by GC-FID for organics (92.8 % aldehyde yield) and by ICP-MS for rhodium (1.9 ppm, 0.5 % of initial rhodium charged; Table 1, entry 1).

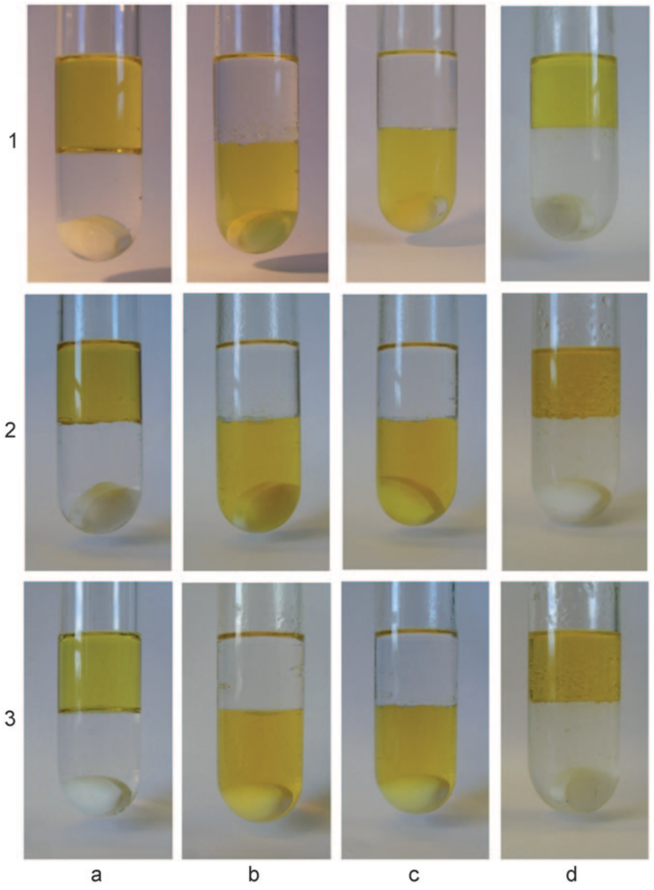

Figure 2. Photographs obtained during the catalyst recycling process. a) the crude product from cycle n (number on left of row) with added water; b) after 10 min of stirring and CO$_2$ bubbling; c) after 1.5 h of stirring and CO$_2$ bubbling, separation of the organic phase and addition of fresh toluene; d) after 30 min of stirring at 60 °C and N$_2$ bubbling.

After separation of the two layers, fresh toluene was added to the remaining aqueous phase (Figure 2, image 1c) and the biphasic system was stirred for 10 min. There was no change in the color of either phase. Stirring was continued for 10 min with N$_2$ bubbling gently through the system. A pale yellow color developed in the upper organic phase indicating some transfer of the metal complex from the aqueous phase. The system was heated to 60 °C, and stirring and N$_2$ bubbling was continued for 30 min, during which time the aqueous phase completely decolorized and the organic phase turned yellow (Figure 2, image 1d). Stirring and N$_2$ bubbling at 60 °C were continued for a total of 1.5 h. The upper organic yellow phase was separated and fresh toluene was added to

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[*] Although the catalyst conserves the same level of activity upon recycling when using **1**:Rh = 10, the rhodium leaching into the organic phase was found to be higher (18 ppm) than with **1**:Rh = 50.

Table 1: Hydroformylation of 1-octene using amidine derivatized catalysts.[a]

Entry	Catalyst	Aldehydes [%]	l/b	TOF_0 [h^{-1}]	$[Rh]_{org}$ [ppm]	$[Rh]_{aq}$ [ppm]
1	cycle 1a	92.8	2.86	11 046	1.9	0.4
2	cycle 1b			9996		
3	cycle 2	94.4	2.78	9660	0.7	0.3
4	cycle 3	90.9	2.81	9555	0.4	0.5

[a] The crude product arising from cycles 1a and 1b were combined and subjected together to the recycling procedure.

compensate for that lost by evaporation. The aqueous phase was analyzed for the rhodium content by ICP-OES (OES = optical emission spectroscopy; 0.4 ppm; Table 1, entry 1). A sample of the remaining organic phase (same volume as that used for each initial run) was used to carry out another hydroformylation reaction with fresh 1-octene, whereas the remainder of the organic phase (solution A) was kept to one side. The gas uptake profile of the reaction was found to be almost identical to the ones obtained with fresh catalyst (Figure 1 a and Table 1, cycle 2).

The crude product from cycle 2 was combined with solution A and the mixture subjected to the same treatment with water and CO_2, phase separation, and treatment of the aqueous phase with fresh toluene and N_2 at 60 °C (Figure 2, images 2a–2d). After addition of toluene to compensate for evaporation, a sample of the toluene phase (same volume as for the initial run) was again used for a catalytic reaction with fresh alkene. Once again, the gas uptake curve was very similar to those of the other runs (Figure 1 a).

The phase transfer was carried out to ensure that the rhodium was not being leached into the organic phase. (Figure 2, images 3a–3d). Very low levels of rhodium were detected in the organic and in the aqueous phases (Table 1, cycle 3).

$^{31}P\{^1H\}$-NMR analysis of the catalyst solution at the end of the process described above showed the presence of free and coordinated ligand ($\delta = 39.98$ ppm, $J_{Rh\text{-}P} = 153.5$ Hz.) as well as a small amount of phosphine oxide (< 5 %). This result indicates that the integrity of the catalyst is conserved throughout the recycling procedure and that oxidation of the ligand is not a serious issue.

To test whether the catalyst recycling could be carried out for a reaction in water and extracting the product into an organic solvent, the hydroformylation of allyl alcohol was carried out in water using the same catalyst system (Rh/**1**) in the presence of CO_2 (1 bar; Scheme 1, $R = CH_2OH$). Gas uptake curves, shown in Figure 1 b, indicate that the reactions are slower than for 1-octene and do not proceed to completion in 60 min. The curves also have an unusual shape, but are reproducible. The recycling of the catalyst was carried out as described above, but starting by adding toluene and bubbling N_2 for 1.5 h at 60 °C. The results of two initial reactions and one reaction using recycled catalyst are shown in Figure 1 b, with photographs of the process provided in the Supporting Information. Once again, the gas uptake profile using the recycled catalyst is very similar to those obtained with the initial fresh catalyst solutions. There is slightly higher rhodium loss (12.9 ppm in the combined first two runs and 9.9 pp in the run using recycled catalyst) in the recovered aqueous solutions of the product (mainly 2-hydroxytrihydrofuran, the cyclic hemiacetal from 4-hydroxybutanal, see Scheme 1) which may be due to the lower excess of phosphine used (P/Rh = 50 for hydroformylation of octene and P/Rh = 10 for hydroformylation of allyl alcohol). Rhodium leaching in the organic phase is again low (0.8 and 0.3 ppm).

In conclusion, we report a new method for the separation of the products from the catalyst in homogeneous catalytic reactions. It involves using ligands which can be protonated by carbonic acid (aqueous solutions of CO_2), thereby switching the catalyst from being organic soluble to water soluble. The catalyst, which has a very high activity for alkene hydroformylation, can be switched back into the organic phase by flushing the CO_2 from the solution with N_2 at 60 °C. No residues accumulate during the process. The system can be used effectively with low catalyst losses for substrates and products that are hydrophobic or hydrophilic.

Experimental Section

Full details of the synthesis of the ligand, for carrying out the catalytic reactions, and for the recycling appear in the Supporting Information.

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