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Catalyst Recycling

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Temperature-Controlled Catalyst Recycling in Homogeneous Transition-Metal Catalysis: Minimization of Catalyst Leaching**

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Catalysis is a key technology in the chemical industry and has a significant impact on value creation. However, less than 10% of all chemical processes are based on homogeneously catalyzed reactions where the catalyst and the product are in the same phase after reaction.[1] The advantages of the homogeneous operation mode are often mild reaction conditions and high selectivities. However, the technological challenge of homogeneous catalysis is the efficient separation of the catalyst from the product as well as the recycling of the metal catalyst.[2]

The first industrial-scale application of homogeneous transition-metal catalysts in the chemical industry was hydroformylation. More than 8 million tons of aldehydes and alcohols are produced worldwide each year by the hydroformylation of alkenes. These intermediates are used for the production of detergents and plasticizers. The most important technical hydroformylation is the conversation of the short-chain alkene propene, which is catalyzed by rhodium. In one important process alternative, the Ruhrchemie/Rhône–Poulenc process, catalyst recycling is accomplished by aqueous–organic liquid–liquid two-phase extraction.[3]

In the hydroformylation of long-chain alkenes this two-phase extraction technique is not appropriate for catalyst recycling. Long-chain alkenes are only poorly soluble in the aqueous catalyst phase; consequently, mass transfer is limited, reaction times are long, and conversions are low. In the chemical industry the hydroformylation of long-chain alkenes to aldehydes with subsequent hydrogenation to alcohols is possible by the thermal separation of the long-chain products under reduced pressure. However, owing to the high boiling points of the long-chain products and thereby thermal stress for the temperature-sensitive catalyst system, the catalyst slowly decomposes under these conditions.[3]

Consequently an effective catalyst recycling concept is required for the hydroformylation of long-chain alkenes with the highly active but expensive rhodium catalyst. Therefore we applied the concept of the temperature-controlled (or thermomorphic) multicomponent solvent systems (TMS systems), which was developed in our group in 1999 (Figure 1).[4]

The principle of TMS systems is based on temperature-dependent phase behavior. During reaction a TMS system is single phase, thus homogeneous, so that no mass transport limitation occurs. After the temperature is reduced the TMS system possesses a miscibility gap and separates into two liquid phases, a polar and apolar phase. The catalyst is dissolved in the polar phase, while the apolar phase contains the organic product. The different solubility properties of the catalyst and the product in the phases make their separation possible. After reaction and phase separation the apolar product phase can be purified in a down-streaming process, while the polar catalyst phase can be recycled. If the catalyst is dissolved in the product phase, a loss of the catalyst (catalyst leaching) takes place.[5]

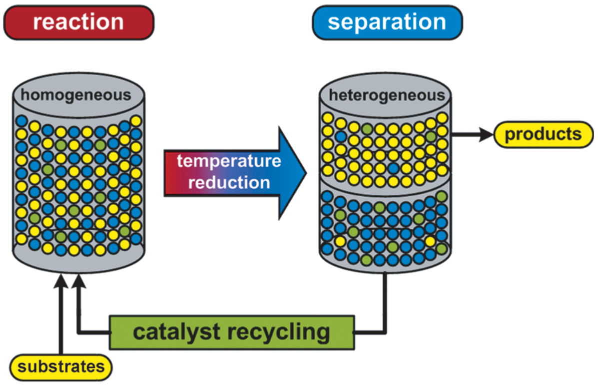

Figure 1. The TMS catalyst recycling concept.

The model reaction in our work was the homogeneously catalyzed hydroformylation of the long-chain 1-dodecene to the linear *n*-tridecanal with the highly selective catalyst system $[Rh(acac)(CO)_2]$/Biphephos (Scheme 1, acac = acetylacetonato). Our results concerning the hydroformylation in TMS systems are contributing to an interdisciplinary process development project.[6] During hydroformylation isomeric alkenes and dodecane are formed. According to the literature, the use of the bidentate phosphite ligand Biphephos provides the aldehydes with very high *n*/*iso* ratios of up to 97:3.[7]

Previous studies of the rhodium-catalyzed hydroformylation of 1-dodecene predominantly dealt with the use of the liquid–liquid two-phase technique for the development of a catalyst recycling method.[8] Furthermore, the application of microemulsions and micellar solvent systems (MLS) have also

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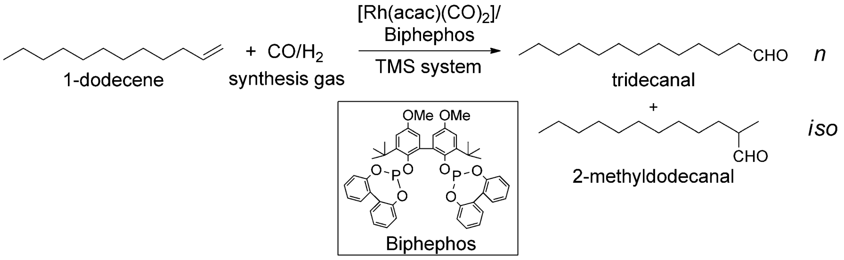

Scheme 1. The hydroformylation of 1-dodecene.

been described.[9] The TMS catalyst recycling concept has already been applied successfully for many homogeneously catalyzed reactions.[10] The use of thermomorphic solvent systems has also been described for the hydroformylation of long-chain alkenes.[11] The hydroformylation of 1-dodecene has been studied in the organic two-phase system poly(ethylene glycol)-400/1,4-dioxane/*n*-heptane, which is heterogeneous under reaction conditions. Under optimal reaction conditions a conversion of 96 % was achieved with a moderate *n*/*iso* ratio of 1:1. Catalyst recycling was accomplished in 23 recycling cycles with an average catalyst leaching of 1 %.[12] In our interdisciplinary studies the TMS system dimethylformamide (DMF)/decane was examined.[13] The thermodynamic basics and the temperature-dependent phase behavior of the pure substances were determined. For the hydroformylation of 1-dodecene, catalyst recycling with eight recycling cycles was already demonstrated with the TMS system DMF/decane.[13a]

Now for the first time we have focused on the systematic investigation of the catalyst separation in the context of integral process development. Nearly complete recovery of the catalyst is absolutely necessary for an economically viable process with expensive rhodium catalysts. Therefore knowing the factors that influence catalyst leaching is essential for the chemical process development of homogeneous catalyzed reactions. This work deals with the question of how catalyst leaching can be minimized effectively. To evaluate the efficiency of catalyst recycling, the separation of the product and catalyst was investigated and the catalyst leaching determined.

First, three different TMS systems were tested for catalyst recycling. In the TMS system propylene carbonate/decane (entry 1 in Table 1) as well as in the TMS systems acetonitrile/decane (entry 2) and DMF/decane (entry 3) high conversions of 99 % were achieved with *n*/*iso* ratios of 99:1. However, the catalyst leaching with the propylene carbonate/decane system into the product phase (35 %) was five times higher than that with the DMF/decane system. Nearly half of the rhodium catalyst was dissolved in the "wrong" phase in the acetonitrile/decane system. Therefore the TMS system DMF/decane, which has the lowest catalyst leaching, was considered for ongoing investigations.

We then determined what parameters influence catalyst leaching and how it can be minimized effectively. Based on the investigation of the phase behavior, the substrate concentration was varied between 10–30 wt % (Table 2, entries 1–5).[13a] In all hydroformylation experiments aldehyde yields higher than 80 % were obtained. Thus the product concentration increases along with the substrate concentration. At higher substrate or product concentrations the catalyst leaching also increases. Up to a concentration of 25 wt % substrate, phase separation could be achieved at a separation temperature of 25 °C. At 30 wt % a lower separation temperature of 10 °C was necessary for phase separation. Furthermore, we found that the solubilizing product influences the catalyst leaching: it is favorable to run the hydroformylation reaction with lower product concentrations for effective separation of the catalyst and therefore minimization of the catalyst leaching.[13a] We also found that the leaching of the rhodium catalyst is equimolar to the leaching of the phosphite ligand, which indicates that a rhodium–ligand complex is dissolved in the product phase.

Table 1: Hydroformylation results and catalyst leaching upon variation of the TMS system.[a]

Entry	Polar TMS component	*X* [%][b]	*Y* [%][c]	*n*/*iso*	Rh [%][d]	P [%][e]
1	propylene carbonate	99	79	99:1	35	36
2	acetonitrile	99	79	99:1	43	34
3	dimethylformamide	99	80	99:1	7	9

[a] $T = 100$ °C, $p = 20$ bar, 30 mL solvent: polar TMS solvent component/decane 50:50 (wt %), $t = 1$ h. [b] Conversion *X* of 1-dodecene. [c] Yield of aldehyde *Y*. [d] Rhodium leaching. [e] Ligand leaching.

Table 2: Hydroformylation results and catalyst leaching upon variation of the amount of substrate and the separation temperature T_{Sep}.[a]

Entry	C[b]	T_{Sep} [°C]	*X* [%][c]	*Y* [%][d]	*n*/*iso*	Rh [%][e]	P [%][f]
1	10	25	99	80	99:1	3	5
2	15	25	99	80	99:1	7	9
3	20	25	99	81	99:1	19	21
4	25	25	99	81	99:1	45	46
5	30	10	99	81	99:1	61	61
6	15	35	99	81	99:1	10	13
7	15	25	99	81	99:1	5	6
8	15	15	99	81	99:1	5	4
9	15	5	99	81	99:1	4	3
10	15	0	99	81	99:1	1	2
11	15	−9	99	81	99:1	0	2

[a] $T = 100$ °C, $p = 20$ bar, 30 mL solvent: DMF/decane 50:50 (wt %), $t = 1$ h. [b] Mass fraction of the substrate 1-dodecene in wt % (entries 1–5) or separation temperature T_{Sep} in °C (entries 6–11). [c] Conversion *X* of 1-dodecene. [d] Yield of aldehyde *Y*. [e] Rhodium leaching. [f] Ligand leaching.

We also investigated the influence of the separation temperature T_{sep} on the catalyst leaching (Table 2, entries 6–11). We found that catalyst leaching into the product phase can be minimized effectively by reducing the separation temperature. At the same time the solubility of the polar solvent in the product phase is reduced at lower temperatures. If the loss of polar solvent is reduced, then the catalyst leaching is reduced. At a separation temperature of 35 °C the catalyst leaching is 10 %, while no catalyst loss can be detected at a separation temperature of −9 °C with ICP-OES analysis.

To check whether the catalyst concentration has a significant influence on catalyst leaching, the substrate/metal molar ratio was varied between 100:1 and 5000:1 (Table 3). With increasing catalyst concentration, the aldehyde yield increases to 89 %. However, the greater the catalyst loading, the higher the level of catalyst leaching. At a substrate/metal ratio of 5000:1 only 1 % of the rhodium catalyst is dissolved in the product phase. Our results demonstrate that a low catalyst concentration is preferable to minimize the catalyst leaching.

Table 3: Hydroformylation results and catalyst leaching upon variation of the substrate/metal ratio.[a]

Entry	Substrate/metal	*X* [%][b]	*Y* [%][c]	*n*/*iso*	Rh [%][d]	P [%][e]
1	100:1	99	89	98:2	11	14
2	1000:1	99	81	99:1	6	7
3	5000:1[f]	97	82	98:2	1	3

[a] 0.026 mol substrate, $T = 100$ °C, $p = 20$ bar, 30 mL solvent: DMF/decane 50:50 (wt %), $t = 1$ h. [b] Conversion *X* of 1-dodecene. [c] Yield of aldehyde *Y*. [d] Rhodium leaching. [e] Ligand leaching. [f] Reaction time $t = 5$ h.

An important factor in the selection of solvents for a TMS system is the polarity. Therefore the length of the carbon chain of the apolar TMS component was varied (Table 4, entries 1–6). With increasing chain length of the apolar alkane, the polarity difference to the polar solvent DMF is raised. The chain length of the apolar solvent component had no influence on the hydroformylation reaction. In all experiments high conversions, yields, and *n*/*iso* ratios were obtained. By increasing the chain length of the apolar TMS component the catalyst leaching could be reduced effectively. When hexane (C_6) was used, 25 % of the rhodium was carried into the product phase, while with hexadecane (C_{16}) the rhodium leaching was only 2 %.

Table 4: Hydroformylation results and catalyst leaching upon variation of the apolar TMS component and the chain length of the 1-alkene.[a]

Entry	U[b]	V[c]	*X* [%][d]	*Y* [%][e]	*n*/*iso*	Rh [%][f]	P [%][g]
1	C_6	C_{12}	99	81	99:1	25	29
2	C_8	C_{12}	99	81	99:1	21	24
3	C_{10}	C_{12}	99	81	99:1	6	7
4	C_{12}	C_{12}	99	81	99:1	6	7
5	C_{14}	C_{12}	99	81	99:1	4	4
6	C_{16}	C_{12}	99	82	99:1	2	4
7	C_{10}	C_6	97	75	99:1	1	2
8	C_{10}	C_8	99	82	98:2	2	4
9	C_{10}	C_{10}	99	81	99:1	4	6
10	C_{10}	C_{12}	99	81	99:1	5	2
11	C_{10}	C_{14}	99	81	98:2	11	4
12	C_{10}	C_{16}	99	81	97:3	10	7
13	C_{10}	C_{18}	99	79	97:3	13	5

[a] $T = 100$ °C, $p = 20$ bar, 30 mL solvent: DMF/decane 50:50 (wt %), $t = 1$ h. [b] Chain length of the apolar TMS component. [c] Chain length of the 1-alkene. [d] Conversion *X* of 1-dodecene. [e] Yield of aldehyde *Y*. [f] Rhodium leaching. [g] Ligand leaching.

We also checked the effect of the chain length of the substrate and thus the chain length of the product on the catalyst leaching (Table 4, entries 7–13). With long-chain substrates and products, up to 13 % of the rhodium catalyst was dissolved in the product phase. This is because the solubility of the polar DMF in the product phase increases with increasing chain length and therefore also catalyst leaching. With increasing chain lengths, both substrates and products were better dissolved in the product phase. The shorter the chain length of the substrate or product, the lower the undesirable leaching of the rhodium catalyst.

The efficiency of the optimized TMS concept was verified in recycling experiments, in which the catalyst phase was separated after reaction and recycled for the next experiment (Figure 2). The hydroformylation of 1-dodecene was carried out in the TMS system DMF/decane and the phase separation was conducted at −10 °C after each reaction. For the first reaction cycle a substrate/metal ratio of 1000:1 was selected and a reaction time of only one hour was sufficient for complete conversion.[13a]

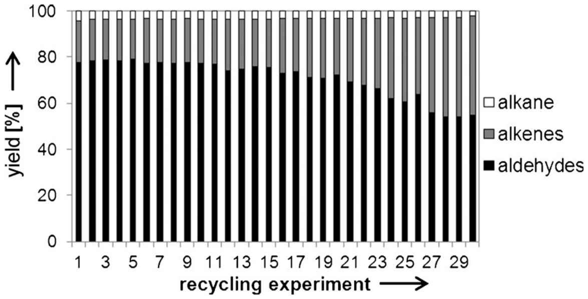

Figure 2. Catalyst recycling in the hydroformylation of 1-dodecene in 30 consecutive experiments.

Catalyst recycling was carried out for a total of 30 consecutive experiments. Aldehyde yields of nearly 80 % were obtained as well as *n*/*iso* ratios of 99:1. In recycling experiment 13 it turned out that the reaction time of one hour was not sufficient for complete conversion; this was apparent from the decreasing aldehyde yields and increasing alkene yields. By extending the reaction time the conversion could be increased. It is supposed that a small amount of the catalyst is removed with the product phase in each recycling cycle. For this reason we investigated the product phase from recycling experiment 30, which showed a rhodium content of 1.7 ppm (1 %) and a phosphorus ligand content of 14 ppm (1 %). The reduction of the catalyst concentration resulted in longer reaction times. This hypothesis was additionally proved by recording the reaction progress of recycling experiment 30 (see the Supporting Information). After 6 h a high aldehyde yield of nearly 80 % was obtained with an *n*/*iso* ratio of 99:1.

Our work shows that the TMS concept can be a valuable tool for the recycling of homogeneous catalysts under mild conditions and therefore it provides economic potential for the technical application of homogeneous transition-metal catalysis. This was the first systematic investigation that focused on whether catalyst leaching can be influenced and which influencing factors are significant. It was shown that the product has an unfavorable influence on catalyst leaching. Furthermore we demonstrated that catalyst leaching can be minimized effectively by reducing the separation temperature and the catalyst concentration and by increasing of the polarity difference between the TMS solvent components. The TMS catalyst recycling concept offers the possibility for the development and realization of industrial processes of homogeneous catalyzed reactions.

Experimental Section

In a typical hydroformylation reaction the catalyst precursor [Rh(acac)$(CO)_2$] and the ligand Biphephos (ratio 1:5) were dissolved in the solvents (30 mL DMF/decane 50:50 (wt %)). After the addition of 1-alkene (0.026 mol) the reaction mixture was transferred under argon atmosphere into a 300 mL steel Parr autoclave. The autoclave was adjusted with 20 bar of synthesis gas (CO/H_2 1:1). The autoclave was heated to 100 °C and the reaction time of 1 h started at the onset of heating. Samples were removed with a capillary and the reaction progress was recorded. The reaction was stopped by cooling with an ice-water bath. After removal of the synthesis gas, the reaction mixture was tempered to the required separation temperature in a double-walled 50 mL separating funnel with a cooling circulation thermostat (HAAKE K40, Thermo Electron Corporation HAAKE DC50, internal temperature regulation, tempering medium: ethylene glycol/water 1:1). After phase separation samples from both the product and catalyst phase were analyzed by gas chromatography and emission spectrometry.

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