

## Removal of Homogeneous Precious Metal Catalysts via Organic Solvent Nanofiltration

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In homogeneous catalysis often precious transition metal complexes are used. Ideally the used catalyst in a specific process is recovered in the downstreaming and recycled back to the reactor. In contrast to the separation of heterogeneous catalysts, the separation of homogeneous catalysts is a crucial issue: Inefficient catalyst recovery and its loss in undesired process streams may even lead to uneconomic processes. The recovery of catalytic species from these streams contributes essentially to the economic efficiency of the production process and prevents the environment from metal contaminations.

Organic solvent nanofiltration (OSN) can be applied for the separation of molecules based on differences in molecular weight and steric effects. In general smaller molecules pass through a polymeric or ceramic membrane, leaving the membrane module as permeate stream, while larger molecules are retained and leave the membrane module as retentate. The difference in concentration and the pressure difference between feed and permeate side determine the driving force for the permeation. Therefore, OSN as a pressure-driven process can be operated under mild conditions and offers economic benefits over other separation techniques, since no additional mass separating agent is introduced and no heat for evaporation has to be supplied. Industrial membrane processes also have the advantage of high packing density, resulting in a compact design, while only a pulsation free pump is required in addition to the membrane module. Based on the described concept the separation of homogeneously dissolved rhodium species from different solvents and solvent mixtures originating from hydroformylation reactions will be shown. In first experiments rejections of 97 % rhodium were achieved. Furthermore the application of the organic solvent nanofiltration as a tool for the recovery of homogeneous metal catalysts in general will be discussed.

### 1. Introduction

The application of homogeneous transition metal catalysts offers the chance to create highly efficient processes for the chemical industry. Since these tailor-made catalysts show high activity and high selectivity during the reaction, recycle streams of substrates and waste streams of side products can be reduced significantly. Often the separation and recovery of these precious catalysts is the crucial operation within a process, as the catalyst and the product are dissolved both in one single phase. Usually a homogeneously catalysed process becomes only economically feasible if an efficient catalyst recovery is achieved. (Behr und Neubert 2012) In terms of homogenous transition metal catalysis the success of the catalyst recovery strongly depends on the stability of the catalytic complex and is distinguished within this work in three types (Figure 1). In figure 1,a a scenario is shown, in which the catalyst separation but not the recycle is feasible. Here the catalyst residues can be concentrated and returned to a precious metal refiner to regain the catalyst metal. The second scenario is the application of separation techniques operating at severer conditions (e.g. higher temperatures) which lead to the recovery of the precious metal (Figure 1,b) but than a replenishment of the ligand is necessary to regain the active catalyst species. In general a separation technique which preserves the active species of the catalyst complex is the most favourable, so that the catalyst is recycled to the reactor without any further interference (Figure 1,c). (Cole-Hamilton und Tooze 2006)

In the chemical industry just a few processes exist in which the homogeneous catalyst is recycled in its active species. For processes like the Ruhrchemie/Rhône-Poulenc-process or the Wacker-Hoechst-process specific separation strategies and catalysts have been developed simultaneously (Behr und Neubert 2012). The availability of robust, efficient and universal unit operations for the recovery of homogeneous catalysts can contribute to the further increase of homogeneously catalysed processes.

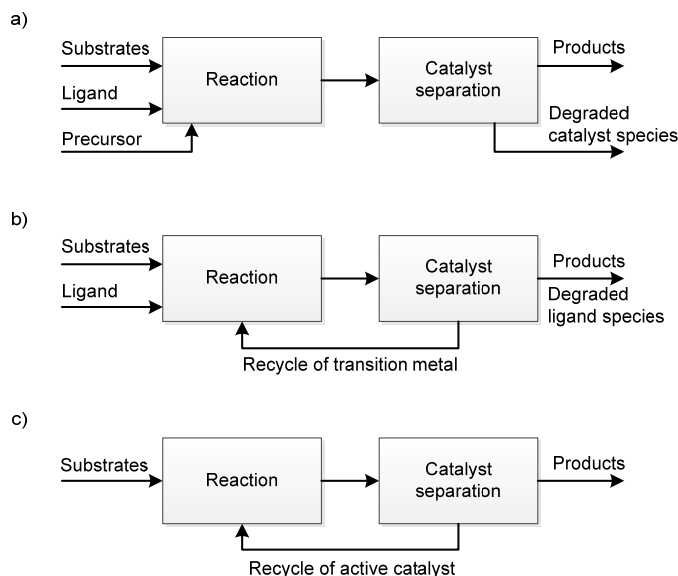


Figure 1: Catalyst recovery (a: catalyst separation without recovery; b: recovery of the transition metal and loss of the applied ligand; c: complete recovery of the active catalyst species)

A promising approach for the separation of product and catalyst is the application of organic solvent nanofiltration (OSN). Mild separation conditions and low energy demand distinguish OSN from other separation techniques e.g. distillation and crystallisation. Figure 2 shows the principle of the OSN: Here the feed stream is separated into a retentate and a permeate stream. Main objective for the recovery of transition metal catalysts is to achieve a high permeability of the product and a low permeability of the catalyst through the membrane surface (Baker 2012).

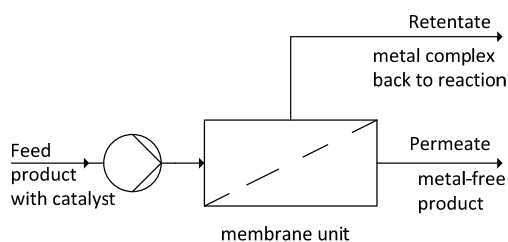


Figure 2: Organic solvent nanofiltration

Among others the flux  $J$  and the rejection  $R$  are important indicators for the characterization of membrane processes. The flux through the membrane is experimentally defined as the total volume  $V_P$  passing through the applied membrane area  $A$  during a certain time (Eq. (1)). Furthermore partial fluxes and therefore rejections can be calculated, if the composition of the permeate stream and feed stream are known (Baker 2012).

$$J = \frac{V_P}{A \cdot t} \quad (1)$$

The rejection  $R$  of a dissolved solute  $i$  is defined in Eq. (2) and depends on the concentration of the solute in the permeate  $c_{i,P}$  and the feed  $c_{i,F}$ . High rejections of rhodium and phosphorus are favourable in order to

recycle the catalyst to the reactor and low rejection of the product is necessary to overcome the separation task (Baker 2012).

$$R = 1 - \frac{C_{i,P}}{C_{i,F}} \quad (2)$$

As the separation of homogeneous transition metals and their stability always is connected to a chemical reaction, the hydroformylation is used as model reaction within this work. The hydroformylation is the most important application of homogeneous catalysts in industrial scale, with an annual production scale of  $10^7$  t. For this reaction the Ruhrchemie/Rhône-Poulenc-process (mentioned above) is one specific industrial application combining highly selective reaction and effective catalyst recycling. Within this process propene and synthesis gas ( $\text{CO}/\text{H}_2$ ) are converted to *n*-butanal. The rhodium catalyst with the surrounding triphenylphosphinetrisulfonate (TPPTS) ligands serves on the one hand for an *n*/*iso*-ratio of 96/4 and on the other a catalyst recovery is realized by the separation of two liquid phases. The catalyst is dissolved in an aqueous phase and the product is separated in an organic phase. (Dämbkes 2013; Cornils et al. 1994) As actual Rh catalysed hydroformylation processes are limited to substrates smaller  $\text{C}_5$  carbon chain, the hydroformylation of the long chain 1-dodecene is under investigation within this work. Figure 3 shows the hydroformylation to the desired *n*-tridecanal and possible side reactions during a reaction run. Internal aldehydes are lumped to the mainly occurring side product 2-methyldodecanal. Further side reactions are isomerisation to internal olefins and hydrogenation to dodecane.

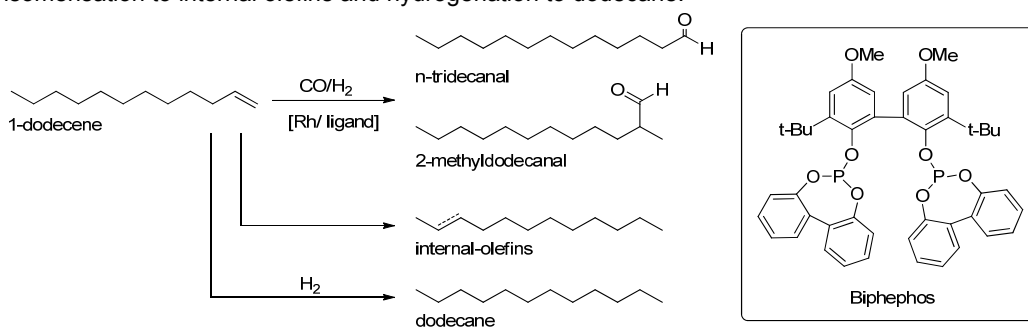


Figure 3: Hydroformylation and side reactions of 1-dodecene (left), Biphephos ligand (right)

Several investigations have been carried out on the recovery of homogeneous catalysts using organic solvent nanofiltration. Many investigations deal with the separation of homogeneous catalysts at the beginning of the process development or basic research (Scarpello et al. 2002; Schmidt et al. 2014). For example the application of bulky ligands and molecular weight enlargement in order to achieve very high catalyst rejections is under investigation (Fang et al. 2011; Guven et al. 2014; Janssen et al. 2010). Several reviews give a good summary of further applications of organic solvent nanofiltration in the separation of homogeneous catalysts (Marchetti et al. 2014; Vandezande et al. 2008). This work is focused on the separation of commercially available catalyst complexes which are rejected by commercially available membranes. Furthermore, the reaction as well as the separation task is observed at the same time.

## 2. Experimental

The chemicals used for the investigations within this work are listed in table 1. The purity was confirmed by gas chromatography analysis or inductively coupled plasma optical emission spectrometry (ICP-OES). All chemicals were used without further purification.

Table 1: Chemicals

Substance	Supplier	Purity [%]
1-dodecene	Acros Organics	95
$\text{CO}/\text{H}_2$ (1/1)	Messer Industry	99.9999
Toluene	Fisher chemical	95
Biphephos	Molisa	97
Xantphos	Sigma Aldrich	97
TPP	Acros Organics	99
$\text{Rh}(\text{acac})(\text{CO})_2$	Umicore	39.9 Rh

The hydroformylation reaction was conducted in two different pressure autoclaves (300 mL/ 800 mL). Previous to the filling with solvent and substrate the reactor was evacuated and flushed with argon subsequently (3 times). The reaction mixture was filled into the reactor using standard Schlenk technique. A composition of 75 wt.-% toluene and 25 wt.-% 1-dodecene was used. Furthermore the concentration of the Rh-precursor (Rh(acac)(CO)<sub>2</sub>) was applied at a concentration of 0.05 mol-% in respect to the used substrate and the ligand (Biphephos) was set to a concentration of 0.25 mol-% in respect to the substrate. For the investigations using the 300 mL autoclave a total liquid mass of 150 g was used. For the reaction using the 800 mL reactor a liquid mass of 500 g was used. When the reaction temperature (90 °C) was reached in the autoclave, synthesis gas (20 bar) was introduced to the reaction mixture. After 2 h the reaction was stopped by fast cooling below ambient temperature.

For the 300 mL autoclave the gas phase was removed afterwards and flushed with argon. Using Schlenk technique again the liquid was transferred into an OSN unit, which was treated with nitrogen and vacuum before. The OSN unit consists of a feed tank which holds the reaction mixture, a gear pump for the liquid feed (60 L/h) and a nanofiltration module (MET Ltd.). The membrane area in this flatsheet module is 17 cm<sup>2</sup>.

The reaction medium of the 800 mL vessel was transferred directly into the used OSN unit, without changing the gas phase. Again a feed tank for the reaction mixture is applied and a gear pump for liquid circulation. Within the nanofiltration module again a flatsheet membrane is used. The active membrane area is 30 cm<sup>2</sup>.

Both setups are operated in cross-flow at a pressure of 20 bar applying nitrogen respectively CO/H<sub>2</sub> atmosphere. An organic solvent nanofiltration Polydimethylsiloxane (PDMS) membrane purchased by GMT Membrantechnik GmbH of the GMT-ONF2 type was used. The permeate flux of pure toluene at test conditions of 30 bar and 25 °C is 60 L/m<sup>2</sup>h (Schmidt et al. 2014), while the molecular weight cut off is in a range of 250-350 Da. (Székely et al. 2011) 50 wt.-% of the reaction mixture is separated as permeate stream, here the catalyst complex is selectively retained by the membrane. Afterwards the retentate is fed to the reactor again using Schlenk technique. Substrate and solvent are added in order to reuse the catalyst in a subsequent hydroformylation reaction.

The composition of the liquid fractions are analysed by gaschromatography (Agilent Gaschromatography HP6890A), which is equipped with a capillary column (HP5, 30 m x 0.32 mm x 0.25 µm) and a flame ionization detector. The amount of Rh and P are analysed via ICP-OES (Thermo Elemental Iris Intrepid). The quantification limit of 3 ppm Rh and 5 ppm P is determined in the ICP-OES.

### 3. Results

Three different ligands (Triphenylphosphine (TPP), Biphephos and Xantphos) were tested in respect to their rejection using the GMT-oNF2 membrane and the reuse in a second reaction run. In figure 3 two consecutive reaction runs in the 300 mL Parr autoclave are presented. The left column shows the initial reaction performance for each ligand. The application of the monodentate TPP ligand leads to a yield of the *n*-tridecanal (TDC) of 60 % achieving a *n*/*iso*-ratio of 73/27. Compared to this, both bidentate ligands (Biphephos and Xantphos) are highly selective during the first reaction run. Both lead to a *n*/*iso*-ratio of 98/2, while Biphephos allows a yield of the *n*-tridecanal of 60 %. The application of the Xantphos ligand shows a decrease in the reaction speed, so that a yield of 21 % is determined. The results of the consecutive catalyst separation are shown in table 2. For all reaction mixtures a good rejection of the rhodium  $R_{Rh}$  (94 %/ 97 %) is achieved.

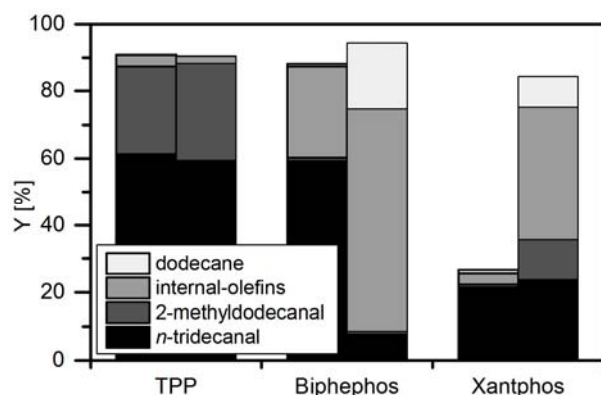


Figure 3: Catalyst recycling in a 300 mL Parr autoclave using the ligands Triphenylphosphine, Biphephos and Xantphos. (Reaction run1 left, reaction run2 right)

Furthermore the TPP ligand with a lower molecular weight of 262 Da shows low rejection  $R_p$  of 66 %. The other ligands Biphephos (787 Da) and Xantphos (579 Da) show rejections of 98 % and 95 %, according to the given molecular weight cut off (250-350 Da). The second reaction run applying the rejected catalyst complex, fresh substrate and solvent is again shown in figure 3 (right column).

The TPP ligand shows almost the same reaction performance compared to the first reaction run (yield TDC: 59 %,  $n/iso$ -ratio: 71/29), so that a desired catalyst recycling concept following figure 1,b is promising, although replenishment of the TPP ligand is necessary due to the low ligand rejection. Comparing the reactions using Biphephos and Xantphos the reaction behaviour changes from the first reaction run significantly. On the one hand the yield of  $n$ -tridecanal decreases to 8 % using the Biphephos ligand and on the other hand the  $n/iso$ -ratio decreases to 70/30 using the Xantphos ligand.

Table 2: Catalyst separation using OSN

	$R_{Rh}$ [%]	$R_p$ [%]
TPP	94	66
Biphephos	97	98
Xantphos	97	95

To overcome catalyst deactivation in the batch recycling concept using two independent units (reaction and OSN), an experimental setup was used which allows the processing of both unit operations without changing the gas phase. Furthermore a first scale up was considered, so that the reaction was conducted in a 800 mL autoclave using 500 g feed solution. As shown in figure 4, with the Rh/Biphephos catalyst again a high  $n/iso$ -ratio of 94/6 was reached in the first reaction run. Although in this scale up a yield of the TDC of 21 % is reached, a successful recovery of the catalyst complex using organic solvent nanofiltration was achieved. In the second reaction run the yield of the TDC of 26% is reached, while the  $n/iso$ -ratio of 94/6 is constantly high. This experimental setup is promising for a nearly total catalyst recycling following figure 1,c.

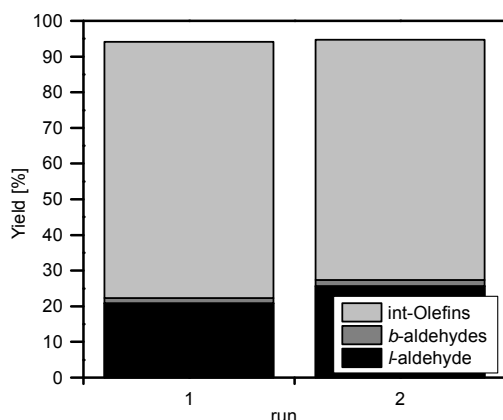


Figure 4: Consecutive hydroformylation runs with catalyst recycling via OSN ( $m_{1-dodecene}/m_{Toluene}=1/3$ ,  $m_{ges}=500$  g,  $C_{Rh(acac)(CO)_2}=0.05$  mol%,  $n_{Rh(acac)(CO)_2}/n_{Biphephos}=1/5$ ,  $T_R=90$  °C,  $p_R=20$  bar,  $t_R=2$  h)

#### 4. Conclusions

Within this work we presented a recycling concept for homogeneous transition metal catalysts with organic solvent nanofiltration. Therefore the hydroformylation with 1-dodecene was conducted using a Rh catalyst complex combined with the ligands triphenylphosphine, Biphephos and Xantphos. For the evaluation of the reaction performance two consecutive reaction runs were investigated, while the catalyst complex was recovered by the application of a PDMS Membrane by *GMT Ltd. (oNF2)*. Especially when both unit operations, the reaction and organic solvent nanofiltration, are conducted with the same synthesis gas atmosphere the recycling concept is promising for a continuous production process, as the reaction performance is equal in both reaction runs.

Based on these results further investigations will focus on the operation of a continuous miniplant process, in which the reaction is conducted in a continuously stirred tank reactor and the reaction mixture is fed to the OSN unit. In order to run this process continuously the permeate flow will be compensated by the feed of substrate and solvent in the reactor. The organic solvent nanofiltration is a sustainable unit operation, which ensures catalyst separation at low energy demands on the one hand and prevents Rh contamination of the environment on the other.

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