Rh-Catalyzed Reductive Amination of Undecanal in an Aqueous Microemulsion System Using a Non-Ionic Surfactant

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Abstract: The homogeneously catalyzed reductive amination of the long-chain aldehyde undecanal with diethylamine was performed in an aqueous microemulsion system using the non-ionic surfactant Marlophen NP8. The experiments showed that the used water-soluble rhodium/SulfoXantphos catalyst system is suitable for this reaction. The Rh-catalyzed formation of the alcohol by-product can be completely suppressed by the use of carbon monoxide with its stabilizing effect of the catalyst system. In addition to pressure and temperature, the most important parameters for the reaction performance of the reductive amination are the concentrations of reactants. Especially, the initial concentration of the aldehyde has a strong impact on the chemoselectivity, and the formation of aldol by-product due to the fact that both, the enamine condensation and the aldol condensation are equilibrium reactions.

Keywords: homogeneous catalysis; microemulsion; rhodium; reductive amination

1. Introduction

Currently, the concept of Green Chemistry is of great interest in research as well as industrial applications. Therefore, the “12 principles of Green Chemistry” by Paul Anastas and John C. Warner are a well-known concept for researchers in that field. One of these principles describes the use of metal-catalyzed reactions instead of stoichiometric ones [1]. For example, for the production of fatty amines (approx. 800,000 t in 2011 [2]) different synthesis routes are known. In addition to the option of stoichiometric reducing agents such as NaBH₄ [3] also catalytic hydrogenation reactions can be applied, and their importance is steadily increasing. The most common production route for amines is the heterogeneously catalyzed hydrogenation of nitriles with low-priced metal catalysts (Ru/C, Pd/C, or Pt/Al₂O₃) [4]. In addition to nitriles, aldehydes can also be converted into amines via reductive amination. In these processes, the aldehyde reacts with an amine to an imine/enamine, which can subsequently be hydrogenated with a heterogeneous catalyst e.g., Pd/C or Raney nickel [5]. In general, heterogeneous catalysts have a lot of advantages, like low costs and an easy removability. The biggest disadvantage is their low chemoselectivity, depending on involved functional groups and the complexity of the substrate. The described heterogeneous methods for the synthesis of aliphatic amines show low selectivity in the hydrogenation, resulting in a mixture of primary, secondary and tertiary amines, and further side products.

Referring to the 12 principles of Green Chemistry, chemical reactions should be performed as selective as possible, which can be accomplished by the application of homogeneous catalysts. For the homogeneously catalyzed reductive amination of aldehydes with amines, transition metals like Rh, Ir or Ru are frequently used for the hydrogenation of the imine/enamine intermediate [6,7]. Undeniably, the separation of the dissolved catalyst from the products is the biggest challenge for homogeneous catalysis. There are several approaches available for the separation and reuse of the homogeneous catalyst, e.g., a simple biphasic system [8] or so-called switchable solvent systems, like switchable-hydrophilicity...
solvents (SHS [9,10]), thermomorphic systems (TMS [11,12]), and microemulsion systems (MES [13,14]). The homogeneously catalyzed reductive amination of aldehydes using aqueous media has also been described in the literature [15–17]. Reductive amination becomes particularly important when it is coupled with a hydroformylation the so-called hydroaminomethylation (HAM). Ideally, the HAM is carried out as a one-pot synthesis in which both reactions take place under the same reaction conditions. For this purpose, it is necessary to examine both reactions carefully for the identification of a mutual optimum of the reaction conditions. Even for this complex tandem reaction, multicomponent solvent systems like TMS, ionic liquids, or supercritical fluids were demonstrated to be favorable in comparison to conventional single solvents [18].

In this work, we studied the reductive amination of undecanal with diethylamine (Figure 1) in an aqueous microemulsion system with the objective to couple it later with the hydroformylation to a one-pot hydroaminomethylation. The investigated reaction network consists of two consecutive reactions, first the condensation of an aldehyde with diethylamine to give an enamine, and second the Rh-catalyzed hydrogenation of the enamine to produce the final product the fatty amine (N,N-diethylundecylamine). Side reactions like the self-aldol condensation (via enamine mediated organocatalysis) and the hydrogenation of the aldehyde resulting in the alcohol were observed. The applied microemulsion system consists of an aqueous catalyst phase containing the metal (Rh-precursor, 1) and the bidentate phosphine ligand SulfoXantphos (SX, 2). The aldehyde, enamine, and product/by-products are located in the organic phase. Depending on the surfactant type, concentration, and temperature different types of microemulsions are formed. The non-ionic surfactant Marlophen NP8 (3) is illustrated in Figure 1. For a detailed description of its phase behavior, a reference is made to our published literatures [19,20]. The focus of this study is set on the influence of reaction conditions (pressure/temperature) and initial concentrations of reactants, catalyst, and surfactants on the reaction performance.

![Figure 1. Reaction scheme of the Rh-catalyzed reductive amination of undecanal with diethylamine to give the fatty amine N,N-diethylundecylamine; the grey highlighted side reactions of undecanal: the Rh-catalyzed alcohol reduction and the enamine-catalyzed self condensation of undecanal; the used Rh-precursor 1, the bidentate phospine ligand SulfoXantphos (SX, 2). The aldehyde, enamine, and product/by-products are located in the organic phase. Depending on the surfactant type, concentration, and temperature different types of microemulsions are formed. The non-ionic surfactant Marlophen NP8 (3) is illustrated in Figure 1. For a detailed description of its phase behavior, a reference is made to our published literatures [19,20]. The focus of this study is set on the influence of reaction conditions (pressure/temperature) and initial concentrations of reactants, catalyst, and surfactants on the reaction performance.](image-url)

2. Materials and Methods

2.1. Chemicals

The reactant undecanal (97%) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and the diethylamine (>99.5%) was obtained from Carl Roth (Karlsruhe, Germany). To prepare the catalyst solution the used rhodium precursor acetylacetonato-1,5-cyclooctadienylrhodium(I) (Rh(acac)(cod), 98%) was acquired from abcr (Karlsruhe, Germany). The company Molisa (Magdeburg, Germany) synthesized the water-soluble ligand 2,7-bissulfonate-4,5-bis(diphenylphosphino)-9,9-dimethylxanthen (SulfoXantphos (SX), technical grade). For the application of the microemulsion system the used organic solvent
n-dodecane (>99%) was purchased from abcr, the polar solvent water (ultrapure) was provided by the water treatment system Synergy UV from Merck (Darmstadt, Germany), and the salt sodium sulfate (>99%, anhydrous) was obtained from Carl Roth. The non-ionic surfactants of the Marlophen series with a specific chain length distribution and a technical grade were contributed by Sasol Germany (Hamburg, Germany). The external GC-standard n-nonane (>99%) was received from Carl Roth and the GC-solvent 2-Propanol (>99.8%) was purchased from VWR (Radnor, PA, USA). The reaction gases hydrogen and synthesis gas (1:1 mixture of hydrogen and carbon monoxide) were obtained from Air Liquide (Paris, France). The used acids for the ICP-OES preparation HCl (37%), H₂SO₄ (96%), and HNO₃ (67%) were all purchased from Carl Roth (Karlsruhe, Germany). The Rh- and P-standards for ICP-OES were obtained from Fluka Analytical (St. Louis, MO, USA). All chemicals were used as received without further purification.

2.2. Preparation of the Catalyst Solution

The aqueous catalyst solution was prepared overnight by weighing 15.5 mg (0.05 mmol, 1 eq.) of rhodium precursor Rh(acac)(cod) and 156.9 mg (0.20 mmol, 4 eq.) of ligand SX in a Schlenk tube. After evacuating and flushing the tube with argon, 4 g of degassed water was added to the Schlenk tube. The dark red catalyst solution was received after stirring (800 rpm) at room temperature overnight.

2.3. Experimental Setup and Procedure for the Reductive Amination Experiments

All experiments were performed in a 100 mL stainless steel autoclave (produced by Halmosi GmbH, Heilbronn, Germany) which is shown in the Figure 2. For the addition of substrates under reaction conditions, a pressurized storage vessel (13) is installed. In a typical reductive amination experiment, water, the co-solvent (dodecane), the surfactant, and the sodium sulfate were weighed into the autoclave. The addition of salt ensures the phase separation due to the fact that the surface active and ionic catalyst complex has a strong impact on the phase separation, as already described in our previous work [13]. After evacuation for exactly five minutes and flushing with nitrogen, the prepared catalyst solution was injected with a syringe under nitrogen counterflow via valve 14. In order to reduce the loss of DEA the nitrogen counterflow was closed and the DEA was injected with a syringe into the reactor. The mixture was heated up to the reaction temperature and pressurized with the reaction gas at a stirring speed of 300 rpm. Undecanal was added to the storage vessel and flushed with the reaction gas. After reaching the reaction conditions (temperature and pressure) the reaction was started by increasing the stirring speed up to 1200 rpm and adding the undecanal. Several samples were taken at defined times, the external standard (nonane) and GC-solvent (2-propanol) were added and analyzed by gas chromatography (Shimadzu GC2010 Plus, 30 m × 0.25 mm × 0.25 µm Restek RTX5-MS column, flame ionization detector).

For the catalyst recycling experiments, the reaction mixture was prepared as described above. After the first run, the mixture was cooled down to 50 °C, the reaction gas was released and the reactor was flushed with nitrogen. Via valve 14 the whole mixture was transferred into an argon-flushed graduated cylinder (with an argon-flushed syringe) and tempered in a water bath at 80 °C for phase separation. After a complete separation into an organic and an aqueous phase, the aqueous catalyst phase was transferred back into the reactor with a syringe. Fresh diethylamine and co-solvent were added and the reaction mixture was heated up and pressurized with reaction gas. Undecanal was added via the storage vessel and another run started.
2.4. Determination of Catalyst Leaching via ICP-OES

The loss of rhodium and phosphorus during recycling experiments can be determined by an inductively coupled plasma optical emission spectroscopy (ICP-OES). Therefore, the organic phase as well the aqueous phase were analyzed. The organic phase was distilled under reduced pressure (25 mbar) to remove the organic components and treated with 1 mL H₂SO₄, 1 mL HNO₃ and 3 mL HCl. To determine the concentration of Rh and P in the aqueous phase 500 µL of the sample were treated with the same amount of acids as described above. After dilution with distilled water, all samples were measured with a Varian 714 ES.

2.5. Used Parameters

In addition to yields and conversions, the decisive factors for evaluating the performance are effective reaction rates and the turn-over-frequency (TOF), which is used as a parameter for the catalyst activity irrespective of the used solvent system. For the sake of simplicity the effective reaction rate is here called initial reaction rate \( r_0 \) and is determined from the concentration profiles \( \Delta c \) over time \( \Delta t \) of the desired fatty amine at the linear area for the reaction rate (Equation (1)). The TOF was determined using Equation (2), and includes the initial amount of undecanal \( n_0 \) multiplied with the yield of desired fatty amine based on the amount of rhodium within a specific period of time \( \Delta t \). The parameters \( \alpha \) (mass fraction of oil) and \( \gamma \) (surfactant concentration) characterize the microemulsion system and are calculated from the mass fraction of their components according to the following Equations (3) and (4).

\[
\begin{align*}
  r_0 &= \frac{\Delta c}{\Delta t} \\
  \text{TOF} &= \frac{n_0(\text{undecanal}) \cdot \Delta Y(\text{fatty amine})}{n(\text{Rh}) \cdot \Delta t} \\
  \alpha &= \frac{m(\text{organic phase})}{m(\text{organic phase}) + m(\text{aqueous phase})} \\
  \gamma &= \frac{m(\text{surfactant})}{m(\text{organic phase}) + m(\text{aqueous phase}) + m(\text{surfactant})}
\end{align*}
\]
3. Results and Discussion

3.1. Influence of Pressure, Temperature and Stirring Speed

As already described in Section 1 and shown in Figure 1, molecular hydrogen is used as a hydrogen resource. The concentration of it has a considerable influence on the reaction performance as it is shown in Table 1. Surprisingly, the higher the pressure of hydrogen, the more alcohol is observed as a by-product (entry 1–3), while the amount of desired fatty amine is negligibly small.

With regard to the already mentioned tandem reaction (HAM) and our knowledge about the hydroformylation, which much less alcohol production as a consecutive reaction [21], we used synthesis gas with different compositions to enhance the reductive amination (entry 4–6). In the presence of carbon monoxide the alcohol formation can be completely suppressed and the amount of fatty amine increases up to about 20%. The exact quantity of CO is not decisive, since the resulting amounts of fatty amine and aldol remain constant. The role of CO as a ligand in the rhodium complex seems to be very important here. This changes the electronic structure of the Rh-catalyst and prevents the catalytic alcohol formation.

With increasing pressure of synthesis gas (entry 6–10) the conversion of undecanal increases and the amount of fatty amine can be improved from 13% up to ∼20%. There is no noticeable impact on the aldol condensation.

Table 1. Effect of reaction gas composition and pressure on the reductive amination of undecanal with diethylamine a.

| Entry | Pressure [bar] Total (H₂/CO) | Amount b [mol%] Fatty Amine | Aldol | Undecanol | X b (UCHO) [mol%] |
|-------|-----------------------------|----------------------------|-------|-----------|------------------|
| 1     | 10 (10/-)                  | 0                          | 12.1  | 30.6      | 56.0             |
| 2     | 20 (20/-)                  | 3.9                        | 8.5   | 46.0      | 68.6             |
| 3     | 30 (30/-)                  | 6.0                        | 5.8   | 50.5      | 71.8             |
| 4     | 30 (27.5/2.5)             | 19.7                       | 10.4  | 0.9       | 45.0             |
| 5     | 30 (20/10)                | 19.4                       | 10.6  | 0         | 44.9             |
| 6     | 30 (15/15)                | 19.5                       | 11.6  | 0         | 46.3             |
| 7     | 10 (5/5)                  | 13.1                       | 11.6  | 0         | 40.1             |
| 8     | 15 (7.5/7.5)              | 16.7                       | 12.7  | 0         | 46.2             |
| 9     | 20 (10/10)                | 20.3                       | 12.7  | 0         | 49.6             |
| 10    | 25 (12.5/12.5)            | 20.8                       | 12.0  | 0         | 47.9             |

a Reaction conditions: T = 100 °C, 0.28 mol% Rh, 1.12 mol% SX, 17.6 mmol undecanal, 9 g dodecane (co-solvent), 12 g water, α = 0.5, γ = 0.08 Marlophen NP8, 1 wt% Na₂SO₄, 1200 rpm, t = 4 h. b Determined after 4 h with GC, nonane as external standard, X = conversion of undecanal.

A further important impact on the reaction performance is the temperature, which affects the kinetic and in our case also the phase behavior of the microemulsion. Figure 3 shows the influence of the reaction temperature on the results of the reductive amination reaction and its side reactions. The amount of aldol by-product remains constant at about 10%, so the much smaller impact of the temperature on the aldol condensation can be used for an optimization at a higher temperature. As already mentioned above, with the use of synthesis gas the alcohol formation can be completely suppressed. It is not surprising that with increasing temperature the reaction rate and the amount of fatty amine increases; however, the strong increase of the initial reaction rate between 100 and 110 °C can be caused by a switch within the phase behavior of the microemulsion leading to a higher interfacial area and higher reaction rates. Due to this observation, the Arrhenius diagram for the investigated temperature interval shows two different ranges for the activation energy. The reductive amination at lower temperatures (80–100 °C) has an activation energy of 76.2 kJ/mol and 48.8 kJ/mol for higher temperatures (110–130 °C). This indicates an impact of mass transport. This can be, for example, film diffusion within the liquid phases or also film diffusion between the gas and the liquid phase. The influence of stirring speed on the reductive amination was also investigated. At a constant temperature of 100 °C the
stirrer speed was varied from 600 to 1500 rpm. No difference was observed in reaction rates, yields or conversion of undecanal. This also indicates that mass transport limitations occur only at higher temperatures above 100 °C.

Figure 3. (a) Effect of the reaction temperature on the reductive amination of undecanal with diethylamine. (b) Arrhenius diagram with determined activation energies for the Rh-catalyzed reductive amination. Reaction conditions: p = 30 bar, 0.28 mol% Rh, 1.12 mol% SX, 17.6 mmol undecanal, 9 g dodecane (co-solvent), 12 g water, α = 0.5, γ = 0.08 Marlophen NP8, 1 wt% Na₂SO₄, 1200 rpm, t = 4 h.

3.2. Influence of Reactant Concentrations

Of particular importance for the reaction performance are the initial concentrations of the reactants, in our case the initial concentrations of undecanal (UCHO) and diethylamine (DEA). In Table 2, the variation of undecanal (represent as initial concentration per kg reaction mass, entry 1–5) and the variation of diethylamine (represent as equivalents referring to undecanal, entry 2, 6–9) are shown. With increasing initial concentration c₀ of undecanal, its conversion increases, but the yield of the desired fatty amine drops from ∼30% to half; however, the actual produced concentration of fatty amine increases from 0.07 mol/kg to 0.42 mol/kg of fatty amine. As can be seen in entries 3, 4, and 5, the final concentration of fatty amine is nearly constant (∼0.4 mol/kg) and cannot be enhanced. Crucial for this is that the ratio of catalyst molecules to substrate molecules differs with different initial concentrations.

Table 2. Variation of the educt concentration (c₀) and effect of it on the reductive amination of undecanal with diethylamine.

| Entry | c₀ (UCHO) [mol/kg] | eq. DEA | Ratio Rh:UCHO | Yield [mol%] | c (Fatty Amine) [mol/kg] | X [%] | TOF [h⁻¹] |
|-------|-------------------|---------|---------------|--------------|-------------------------|-------|----------|
| 1     | 0.23              | 1       | 1:118         | 29.6         | 11.1                    | 0.07  | 41.7     | 8.4      |
| 2     | 0.68              | 1       | 1:352         | 27.1         | 23.3                    | 0.18  | 53.2     | 24.6     |
| 3     | 1.35              | 1       | 1:704         | 26.8         | 51.0                    | 0.36  | 80.4     | 66.3     |
| 4     | 2.03              | 1       | 1:1058        | 19.7         | 59.0                    | 0.40  | 82.4     | 102.9    |
| 5 e   | 2.70              | 1       | 1:1410        | 15.6         | 66.8                    | 0.42  | 85.5     | 97.7     |
| 6     | 0.68              | 0.5     | 1:352         | 26.6         | 21.2                    | 0.18  | 49.4     | 16.1     |
| 7     | 0.68              | 1.5     | 1:352         | 23.3         | 25.1                    | 0.16  | 51.8     | 20.4     |
| 8     | 0.68              | 2       | 1:352         | 20.1         | 25.0                    | 0.13  | 48.6     | 21.1     |
| 9     | 0.68              | 3       | 1:352         | 16.6         | 26.4                    | 0.11  | 48.5     | 17.1     |

a Reaction conditions: T = 100 °C, p = 30 bar synthesis gas, 0.28 mol% Rh, 1.12 mol% SX, 17.6 mmol undecanal, 12 g organic phase (undecanal + co-solvent), 12 g water, α = 0.5, γ = 0.08 Marlophen NP8, 1 wt% Na₂SO₄, 1200 rpm, t = 4 h. b Based on the total mass of the reaction mixture. c Determined after 4 h with GC, nonane as external standard. d Determined at a reaction time of 30 min. e Organic phase: 12 g undecanal, no co-solvent.
For example, the ratio of Rh:undecanal for the lowest concentration is 1:118. The ratio for the highest concentration of undecanal is 1:1410. This also explains an enormous increase in the turn-over-frequency (TOF) by a factor of 12. The highest catalyst activity (103 h⁻¹) is observed with an initial concentration of 2.03 mol/kg undecanal. This corresponds to an organic phase, consisting of 75 wt-% undecanal and 25 wt-% co-solvent dodecane. The results with an organic phase consisting of 100 wt-% reactant undecanal are shown in entry 5, but no improvement of catalyst activity can be observed. The production of the aldol by-product increases rapidly with increasing concentration of undecanal from 11% up to over 66%. This can be explained by the two equilibrium reactions of both condensation steps as shown in the following equations.

\[
\text{undecanal} + \text{diethylamine} \rightleftharpoons \text{enamine} + \text{water} \tag{5}
\]

\[
\text{undecanal} + \text{enamine} \rightleftharpoons \text{aldol} + \text{diethylamine} \tag{6}
\]

Therefore, with increasing concentration of undecanal both equilibria are shifted to the aldol product (see Equation (6)). The condensation of undecanal with diethylamine to the enamine is also an equilibrium reaction (Equation (5)). Consequently, a higher enamine concentration also leads to a shift of the equilibrium to the aldol.

An excess of diethylamine causes a negative influence on the reaction performance of the reductive amination of undecanal. The yield of the desired fatty amine decreases from ~27% to ~17%, while the yield of the aldol by-products remains constant. It is conceivable that the increasing pH causes this effect or the high concentration of DEA inhibits the catalyst by shifting the catalyst equilibrium towards inactive species. The results of the TOF do not give any clear indications as they are in a very similar range. A change in the phase behavior is also imaginable. As is known from our published hydroformylation experiments [20,21], an increasing concentration of aldehyde leads to a shift of the three-phase area to lower temperatures while polar components, such as diethylamine, leads to a shift to higher temperatures (as shown in Figure 4).

![Figure 4. Schematical phase diagram of a ternary mixture of oil, water, and a non-ionic surfactant with illustrated shifts of the three-phase area (3) depending on added components, $\alpha = 0.5$, adapted from [13].](image)

3.3. Influence of Catalyst and Surfactant Concentration

In addition to the already discussed parameters and their influence on the reductive amination, the concentration of rhodium catalyst is decisive for the economic viability of the catalytic process on industrial scale. Therefore different Rh-concentrations were investigated with a constant Rh-SX ratios of 1:4. As expected, an increasing concentration of catalyst leads to an increasing reaction rate of reductive amination (quadrupled) and higher amounts of the desired fatty amine (from ~11% up to ~32%) as it is shown in Figure 5. During the catalytic reaction, there is an equilibrium between the Rh precursor, inactive Rh species and catalytically active species. As the concentration of Rh increases, the equilib-
rium shifts towards the active species and more of the undecanal can be converted per time. This observation is based on the known catalyst preequilibria, which are already described in the literature for a comparable Rh/SX system for the hydroformylation of 1-dodecene in an aqueous microemulsion system [22].

The most important component for generating the microemulsion system as reaction medium for this reaction is the surfactant, for which an appropriate concentration needs to be chosen. The choice of the surfactant concentration has to be a compromise between the generation of a high interfacial area for an acceleration of the reaction and the stabilization of the reaction mixture against separation in the catalyst recycling operation. The study is performed with the non-ionic surfactant Marlophen based on nonoxynols (polyethylene glycol nonyl phenyl ether). This class of surfactant is well-known and was chosen because of its wide three-phase area. As can be seen in Figure 5, the reaction rate and the amount of desired fatty amine are very low without the use of a surfactant due to the low interfacial area between the aqueous catalyst phase and the organic reactant phase. With increasing surfactant concentration to 4 wt% the interfacial area increases due to micelle formation, resulting in an increase of desired fatty amine formation and reaction rate. A further increase to 12 wt% leads to a further increase in yield after 4 h, while the initial reaction rates stay constant. A surfactant concentration of 16 wt% improves the amount of fatty amine and, in addition, a strong increase in the reaction rate. This indicates a switch in the phase system.

3.4. Catalyst Recycling

As described in Section 1, the big advantage of microemulsion systems as reaction media is the efficient recycling of the catalyst system and the easy reuse of it. Therefore, catalyst recycling is the most important parameter for the evaluation of a suitable microemulsion system for this example of a reductive amination. In Table 3, the results for three consecutive runs with successful catalyst recycling are illustrated. The first and second runs are very similar with respect to the amount of fatty amine and side product aldol. The third run showed an increase in the amount for both products, which was not expected. Furthermore, the separation temperature for a fast and complete phase separation into the aqueous catalyst and organic phase changed in this run. This indicates a complex separation dynamics which cannot be easily handled on lab-scale in a small batch process. In addition, the implementation of multi-phase separation cannot be carried out under optimal conditions and is therefore not constant. The establishment of the catalyst
equilibrium depends on parameters such as metal and ligand concentration, temperature, and pressure, causing different concentrations of active catalyst species. Nevertheless, this lab scale experiment is very useful for a scale up to a continuous miniplant operation, as it is already described for the hydroformylation in a microemulsion system [23]. Based on the quite stable performance of the reductive amination and the low leaching of catalyst into the organic phase, this reaction is suggested for further investigations in a continuously operated miniplant. The higher leaching values after the first run (2 ppm Rh) are in accordance with our previous work and can be explained by the different existing catalyst species. In addition to the numerous water-soluble species of the catalyst complex, small amounts of oil-soluble species can also be formed, which are preferably located in the oil phase.

Table 3. Catalyst recycling for the reductive amination of undecanal with diethylamine.

| Run | Amount [mol%] | Separation Temperature [°C] | Leaching [ppm] |
|-----|---------------|----------------------------|----------------|
|     | Fatty Amine   | Aldol                      | Rh | P      |
| 1   | 8.9           | 5.5                        | -  | 2.3    | <0.1 |
| 2   | 8.6           | 4.4                        | 80 | 0.12   | <0.1 |
| 3   | 14.7          | 7.0                        | 90 | 0.11   | <0.1 |

*a Reaction conditions: T = 100 °C, 0.28 mol% Rh, 1.12 mol% SX, 17.6 mmol undecanal, 9 g dodecane (co-solvent), 12 g water, α = 0.5, γ = 0.08 Marlophen NP8, 1 wt% Na₂SO₄, 1200 rpm, t = 4 h. b Determined after 4 h with GC, nonane as external standard. c Loss of catalyst into the organic phase.

4. Conclusions

Based on the illustrated results, much of the previous general research results on catalytic reactions in microemulsion systems can be confirmed. Here, too, it can be concluded that the active catalyst species is located in the interfacial area and the reductive amination takes place at this interface. In addition, similar influences of temperature and surfactant concentration were observed as before for the hydroformylation of long-chain olefins. In this case, the chemical environment of the catalyst plays an even more important role in the reductive amination. Especially, the use of carbon monoxide as a ligand stabilizes the catalyst species and suppresses the formation of alcohol as a side product. In addition, water plays a decisive role for the reaction performance, since it is not only a solvent but also involved in the reaction and thus has an influence on various equilibria. These findings are particularly important when coupling hydroformylation with reductive amination to a hydroaminomethylation in an aqueous microemulsion system. The most important points of this work, with regard to the realization of the HAM as a tandem reaction, are:

1. The use of synthesis gas suppresses the alcohol formation. Because synthesis gas is used for the hydroformylation reaction, the alcohol formation should be occurring in the HAM;
2. High concentrations of aldehyde favor the aldol condensation as a side reaction of the reductive amination. For the HAM it is necessary to reduce the accumulation of the aldehyde, produced by the hydroformylation step by adjusting the hydroformylation rate to that of the reductive amination;

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Abbreviations

The following abbreviations are used in this manuscript:

DEA       diethylamine  
HAM       hydroaminomethylation  
MES       microemulsion system  
SHS       switchable hydrophilicity solvent  
SX        SulfoXantphos  
TMS       thermomorphic system  
TOF       turn-over-frequency  
UCHO      undecanal

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