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Thermoregulated Liquid/Liquid Catalyst Separation and Recycling

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Abstract: Considerable effort has been done to overcome the loss of catalyst in homogeneously catalysed processes. In this contribution we describe five recycling concepts for thermoregulated catalyst separation and recycling: fluorous biphasic systems (FBS), thermoregulated phase transfer catalysis (TRPTC), soluble polymer-based catalysis, thermoregulated microemulsions and temperature-dependent multicomponent solvent systems (TMS). Each of these concepts has its own special advantages like low catalyst leaching or simple process engineering but also drawbacks like usage of expensive special solvents or complex and expensive catalysts. In this context, TMS systems exhibit most advantages of the other concepts combined with the possibility to use common and cheap solvents as well as numerous classical molecular catalysts. Therefore, TMS systems are expected to be one of the most promising thermomorphic recycling concepts for industrial scale.

Keywords: biphasic catalysis; catalyst recycling; homogeneous catalysis; phase diagrams; solvent effects; thermomorphic solvents

1 Introduction

Over the last decades homogeneous catalysis has gained more and more importance in industry. Excellent catalyst activity and selectivity as well as the ability to enable mild reaction conditions are only a few advantages of homogeneous catalysts. Nonetheless problems in recycling the mostly expensive precious metals – like rhodium, palladium and platinum, for example – and organic ligands mark the crucial drawback. Therefore considerable effort has been done to overcome this disadvantage.[1]

In some cases, like the Wacker–Hoechst or Cativa process, simple distillation is used to remove the products from the catalyst layer. But many homogeneous catalysts are sensitive towards high temperature which excludes this separation method for most processes.[2]

Another recycling principle is the so-called liquid/liquid biphasic technique and is based on dissolving the catalyst and product in different solvents[3] as is realised in the Ruhrchemie/Rhône–Poulenc process. This concept is limited by the solubility of the reaction substrates in the mostly aqueous catalyst layer and by the resulting barriers to mass transport.

In this review, concepts of catalyst recycling *via* thermomorphic effects are described. In particular, fluorous biphasic systems (FBS), thermoregulated phase transfer catalysts (TRPTC), soluble polymer-based catalysts, thermoregulated microemulsions and temperature-dependent multi-component solvent systems (TMS) are introduced. The main concept of each of these alternatives is to utilise the thermomorphic phase behaviour and distribution of catalysts in the solvents for an efficient recycling without any mass transfer limitations.

Arno Behr, born in 1952, studied chemistry at the RWTH Aachen and did his PhD in 1979. He habilitated at the institute of Technische Chemie und Petrolchemie of the RWTH with emphasis on "catalytic activation of CO_2 with transition metal complexes". From 1986 on he worked at the Henkel KGaA at the Department of Chemical Process Development. Since 1996 he holds the Chair of Technical Chemistry A at the University of Dortmund. His main focus lies on homogeneous catalysed reactions and the technical realisation in mini-plant scale.

Guido Henze, born in 1980, studied chemistry at the University of Dortmund from 1999 to 2004 and composed his diploma thesis on hydroformylation in thermomorphic solvent systems at the Chair of Chemical Process Development. The graduation under the supervision of Professor Arno Behr was carried out with an emphasis on homogeneous catalysed synthesis of new products from butadiene, CO_2 and other basic chemical compounds.

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2 Recovery Strategies for Fluorous Catalysts

The concept of fluorous chemistry is based on the development of ligands with a high affinity for perfluorinated solvents and a poor solubility in conventional organic solvents. With such ligands the immiscibility of perfluorinated (fluorous) solvents with most organic solvents at ambient temperature or below can be utilised.[4,5]

At a low temperature the catalyst is dissolved in a fluorous solvent while the substrates are dissolved in a separate organic layer (Figure 1). By heating this mixture up to the solvent-specific upper critical solution temperature (UCST), unlimited miscibility of both solvents is achieved and the reaction can be carried out under monophasic conditions. Depending on the required reaction temperature, directed fluorous/organic solvent selection with tabulated values is possible. After completion of the reaction the products can be easily removed from the catalyst by cooling the mixture again and separating the layers.[6–12]

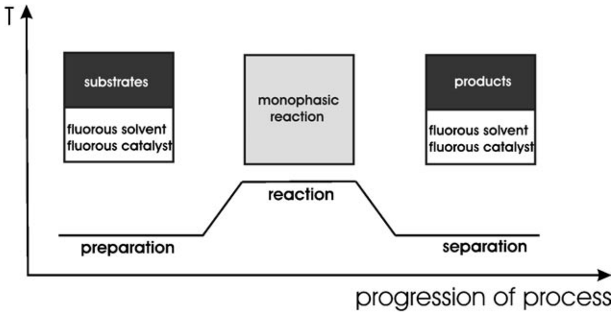

Figure 1. Catalyst recycling using fluorous biphasic conditions.

In analogy to this concept, similar work has been done using carbon dioxide partial pressures up to 6 MPa or supercritical carbon dioxide instead of increased temperatures to homogenise the fluorous and the organic phase. This homogenisation is reversible by releasing the CO_2 pressure.[13–17]

Various fluorous ligands for homogeneous catalysis were synthesised. The original aim was to modify known ligands with fluorous alkyl groups ("pony tails") to effect their immiscibility with organic solvents at low temperatures. In this regard triarylphosphines,[18] triaryl phosphites,[19] pyridines,[20] pincer ligands[21] and even chiral phosphines were modified by introduction of several fluorous alkyl groups[22] (Figure 2) and the synthesis was optimised.[23] The total affinity of these ligands to a fluorous phase depends on the number and length of the "pony tails" and is therefore adjustable.[24] As a further improve-

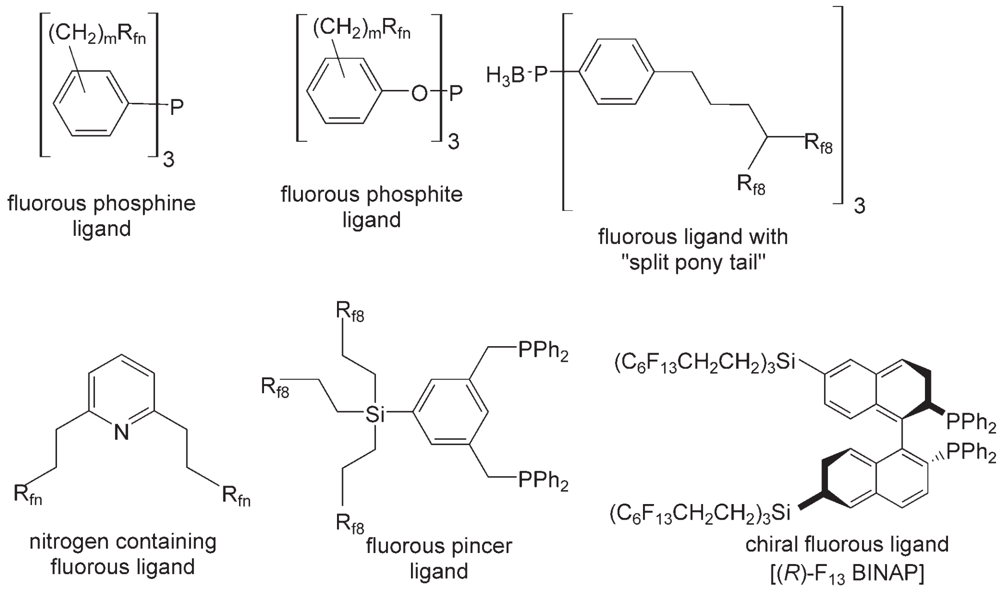

Figure 2. Various fluorous ligands.

ment, branched fluorous alkyl groups – so-called "split pony tails" – were introduced to increase the fluorous affinity while keeping the degree of substitution constant[12] (Figure 2).

Regarding the basicity as the most important attribute of a ligand for homogeneous catalysis it is obvious that fluorous substituents change this feature significantly. Therefore non-fluorous alkyl spacers are inserted between the active site and the "pony tails" to insulate the coordinative centre from electron-withdrawing effects which could decrease the catalytic activity.[25]

In this context several different reaction types were successfully performed in fluorous biphasic systems like the Heck reaction, hydroformylation, oxidations, polymerisations, enantioselective synthesis, hydrosilylations and others. In many cases the fluorous catalyst's activity is similar to its classical analogues and catalyst loss could be reduced to industrially acceptable values.[6–9,23] For example, the hydrosilylation of 2-cyclohexenone with dimethylphenylsilane constantly yields 90% of the desired products over three runs with turnover numbers (TON) of about 110 (Figure 3).[9]

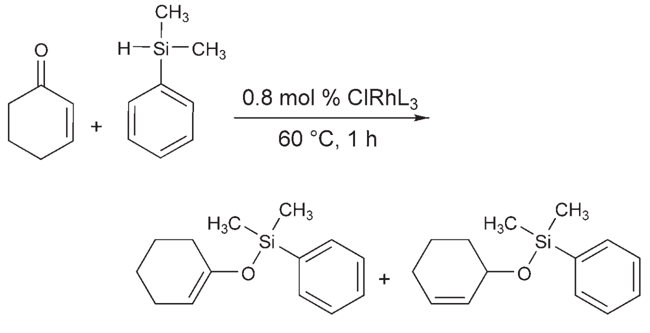

Figure 3. Hydrosilylation in thermomorphic fluorous systems.

Conversely to these undisputable laboratory-scale advantages, some drawbacks will hinder the industrial utilisation of fluorous catalysis in the near future. The expensive catalyst synthesis on the one hand combined with the ecologically questionable production of fluorinated solvents excludes a usage on a bulk scale.

3 Thermoregulated Phase-Transfer Catalysts

The idea of thermoregulated phase-transfer catalysts (TRPTC) is to induce an inverse temperature-dependent solubility in water by modifying them with hydrophilic polyalkene oxide (PAO) chains.[3,26] At ambient temperature these catalysts are well soluble in water but almost insoluble in organic solvents. By elevating the temperature the hydrogen bonds between the PAO and water cleave and an increased solubility in organic compounds can be observed (Figure 4). This point is known as the critical temperature cloud point. After completion of the reaction under biphasic conditions the product mixture is cooled down, so effecting the ligand's dissolution in the aqueous phase. Subsequent product separation and catalyst recycling can be accomplished by phase separation.[27–31]

Again as in fluorous catalysis, many ligands were developed for TRPTC based on the well known classical ligands for homogeneous catalysis. In this course

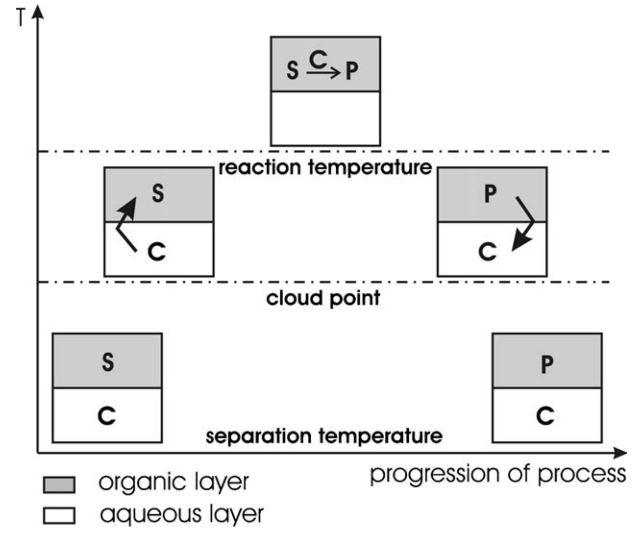

Figure 4. Catalyst recycling using thermoregulated phase transfer catalysts (TRPTC); **C** = catalyst, **S** = substrate, **P** = product.

polyether-substituted triphenylphosphines (PETPP), *N,N*-dipolyoxyethylene-substituted 4-(diphenylphosphino)-benzenesulfonamides (PEO-DPPSA), *N,N*-dipolyoxyethylene-substituted 2-(diphenylphosphino)-phenylamines (PEO-DPPPA), alkyl ethoxylated phenylphosphines (AEOPP) and *o*-phenylene alkyl polyoxyethylene glycols (OPGPP) were synthesised[31] (Figure 5).

The critical temperature cloud point – that means the temperature at which the affinity of PAO-modified ligands switches from the aqueous to the organic phase – is strongly dependent on the ratio of hydrophobic to hydrophilic functions. With increasing length and amount of PAO chains the critical temperature cloud point increases. Therefore the ligand's phase behaviour can be exactly customised depending on the required reaction temperature.[27]

So far PAO-modified ligands were basically used in hydroformylation (Figure 6) and hydrogenation reactions of higher alkenes where almost similar activities were achieved as with classical homogeneous catalysis as well as in selective reductions of nitroarenes (Figure 7).[28–31] For example a turnover frequency (TOF) of 470 h^{-1} and a yield of 94% could be achieved in the hydroformylation of styrene. Furthermore, the selective reduction of *p*-nitrobenzonitrile

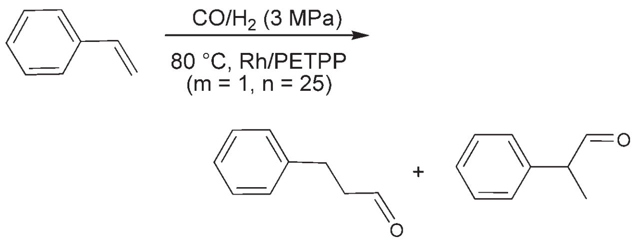

Figure 6. Hydroformylation *via* thermoregulated phase transfer catalysis.

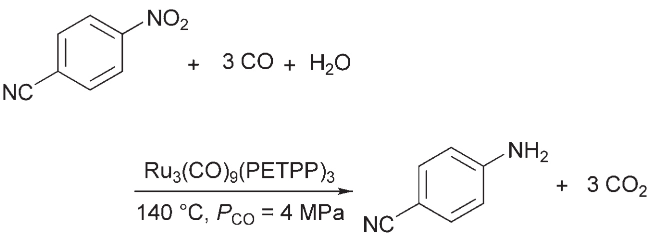

Figure 7. Selective reduction *via* thermoregulated phase-transfer catalysis.

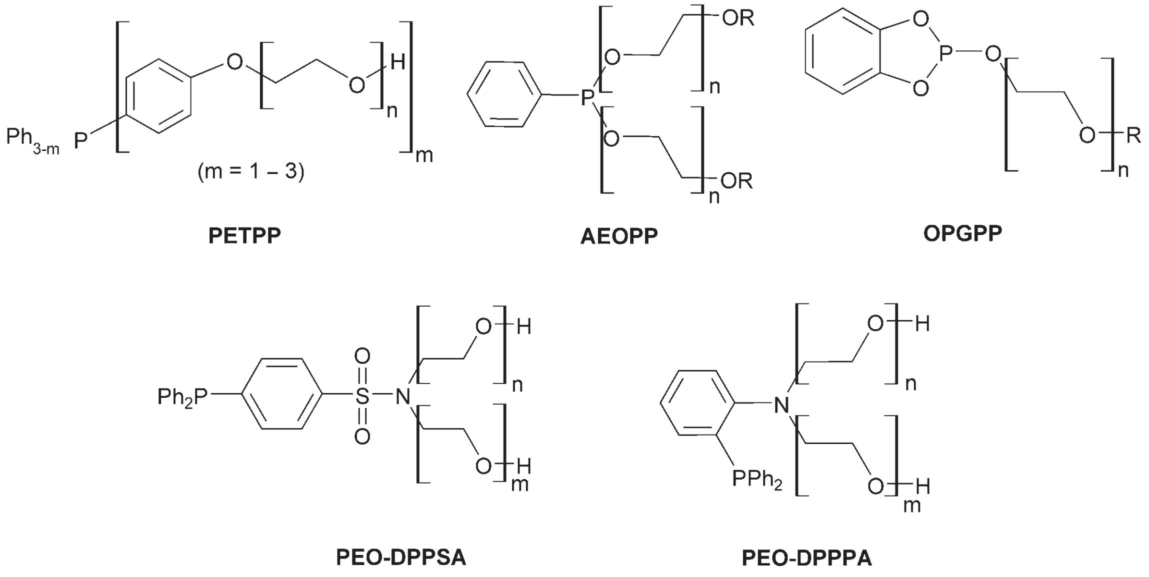

Figure 5. Selection of thermoregulated phase-transfer ligands.

yielded 97% of *p*-aminobenzonitrile with a conversion of 97%.

It is reported that catalyst recycling is possible over eight or more runs without significant loss of activity,[32] but it is also reported that at room temperature already about 30 ppm of ligand accumulate in the organic layer.[31,32]

Additionally, another problem results when using TRPTC. Recent investigations showed the formation of colloidal rhodium nanoparticles during hydroformylation of 1-octene using a thermoregulated phase-transfer catalyst. These nanoparticles tend to ripening behaviour during the recycling runs which finally leads to precipitation and deactivation of the catalyst.[33]

4 Soluble Polymer-Bound Catalysts

The concept of soluble polymer-bound catalysts is based on their phase-selectivity in a mixture of polar and non-polar thermomorphic solvents.[26,34] At ambient temperature the catalyst is soluble in the polar phase (e.g., *N,N*-dimethylformamide or a mixture of ethanol:water, 9:1) and almost immiscible in the non-polar phase (e.g., heptane). By heating up to the upper critical solution temperature (UCST) as described in Section 2 the mixture homogenises and the reaction can be carried out under monophasic conditions (Figure 8). After completion of the reaction catalyst recovery can be obtained by cooling to ambient temperature and phase separation.[35–39]

In a modification of this concept, the polymer-based catalyst is used together with water and the organic substrates. Under these conditions the catalyst is insoluble in both phases at room temperature. On heating the catalyst becomes soluble in water and forms an emulsion in which the reaction takes place. Cooling leads to precipitation of the catalyst, the formation of an aqueous phase and an organic product phase.[34,40]

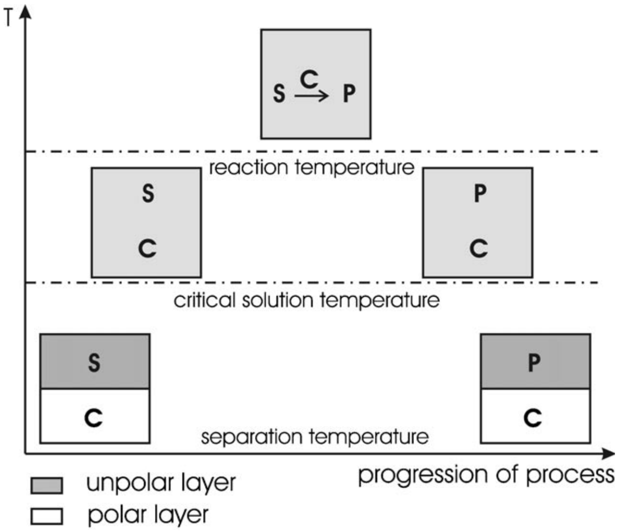

Figure 8. Recycling concept *via* soluble polymer-bound catalysts; **C** = catalyst, **S** = substrate, **P** = product.

These polymer-bound soluble catalysts are substituted poly(*N*-isopropylacrylamide)s (PNIPAM), for example[34] (Figure 9).

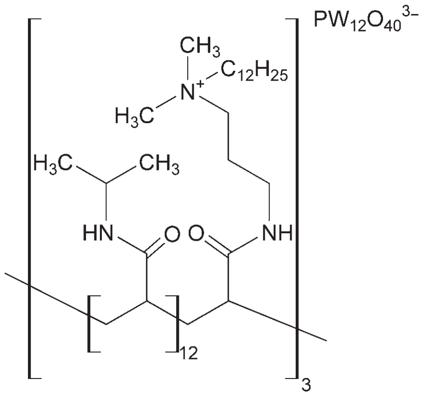

Figure 9. Poly(*N*-isopropylacrylamide)-based polymer catalysts.

Similar to the thermomorphic catalyst systems described in Sections 2 and 3 the solubility behaviour of this kind of catalyst can also be adjusted, namely by changing the length of the *N*-alkyl group. Expectedly with increasing length the *N*-alkyl group the solubility in alkanes increases.[34,41]

So far PNIPAM-based catalysts were basically used in oxidation, C–C coupling, hydrogenation and several other reactions with moderate catalytic results and satisfying catalyst leaching of far below one percent.[34–39] For example, the catalyst showed in Figure 9 catalyses the oxidation of benzyl alcohol to benzoic acid with a constant yield of about 90% over three runs (Figure 10).[40]

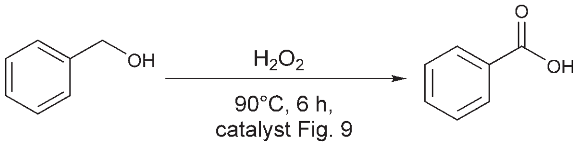

Figure 10. PNIPAM-catalysed oxidation of benzyl alcohol.

PNIPAM-based catalysts show good activities, high stability after several recycling runs and only little catalyst loss by phase separation.[38,40] On the other hand, it has to be questioned if it is reasonable to use these complicated and presumably expensive catalysts when, perhaps, classical catalysts would also operate using the concept of the UCST. This question will be discussed in Section 6.

5 Thermoregulated Microemulsions

Microemulsions are an excellent tool for the solubilisation of non-polar liquids (oil) in water (or aqueous catalyst solutions) or water in non-polar liquids.[42] Due to their ability to solubilise a broad range of substances of very different polarity, they have been used for phase-transfer catalysis,[43] enzyme catalysis[44] and for the synthesis of nanoparticles.[45] They are thermodynamically stable dispersions of the non-polar liquid, water and surfactants. Out of the range of available surfactants, the group of non-ionic surfactants is preferred for application in reaction media because of their low sensitivity to electrolyte addition. Non-ionic surfactants of the alkylpolyglycol ether-type are derived *via* ethoxylation of either isotridecanol (e.g., Marlipal O13/E_i) or a 1 to 1 mixture of dodecanol and tetradecanol (e.g., Marlipal 24/E_i). The hydrophilicity depends on the number of ether groups in the molecule, ranging from $i=5$ to 20. The phase behaviour of such a system is described in detail by the use of a Gibbs phase prism with the Gibbs triangle as base and temperature as the ordinate (Figure 11).

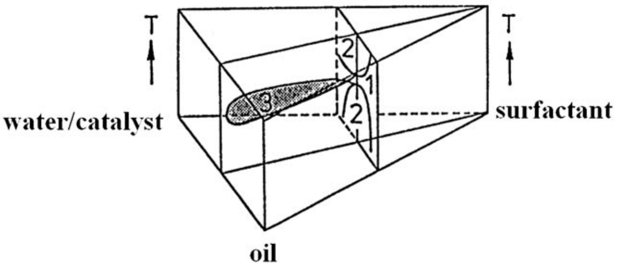

Figure 11. Gibbs phase prism for the ternary mixture of water (A), oil (B) and non-ionic surfactant (C).

The composition of the microemulsion is described by the mass fraction α of oil in the mixture of water and oil

$$\alpha = \frac{m_{oil}}{m_{oil} + m_{water}}$$

and that of the amphiphile γ in the total mixture both expressed in weight percent (wt%).

$$\gamma = \frac{m_{amphiphile}}{m_{total}}$$

The Gibbs triangle can be used to plot the compositions of microemulsion phases when temperature, pressure, type of oil and type of surfactant are fixed. If any of these variables are changed, a new Gibbs triangle must be constructed. The generic pattern of phase behaviour found upon changing variables of interest is qualitatively sketched by the three Gibbs triangles shown in Figure 12.

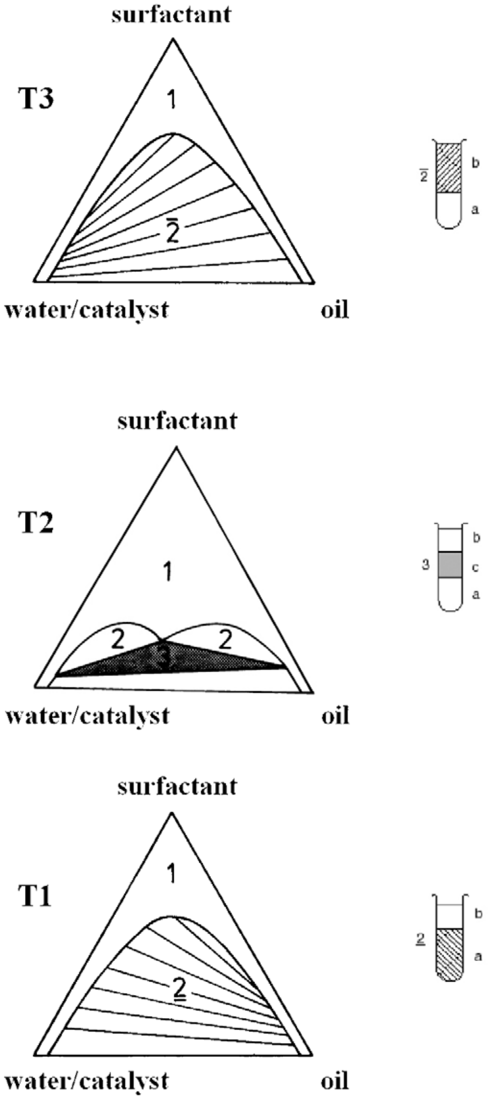

Figure 12. Schematic phase diagrams of water, oil and non-ionic surfactant mixtures, showing regions of 1, 2 and 3 phases. For a particular ternary system the sequence of patterns in the phase diagrams follows always the same temperature dependency with T1 < T2 < T3. The tie-lines connect the compositions of the phases in equilibrium.

In these diagrams, regions of 1, 2 and 3 phase coexistence are shown. Liquid crystalline phases [usually lamellar (Lα)] typically found at higher surfactant concentrations are omitted for clarity. The “1” denotes regions where the oil and water are completely mixed into a single microemulsion phase. The ends of the “tie-lines” within the two-phase region denote the compositions of the two phases in equilibrium when a sample is mixed at the overall composition located along the line. The “$\underline{2}$” denotes a two-phase sample where the majority of the surfactant, along with some oil, resides in the lower water-rich phase (an “oil-in-water” microemulsion phase), and excess oil floats on top. It also denotes a two-phase sample where the majority of the surfactant, along with some water, resides in the upper oil-rich phase (a "water-in-oil" microemulsion phase), with excess water lying underneath. Finally, "3" denotes a three-phase sample, where the middle phase, rich in oil and water (a "bicontinuous" microemulsion phase) is in equilibrium with excess water (bottom phase) and oil (top phase). The three corners of the 3-phase triangle denote the compositions of the three phases in equilibrium. At very low surfactant concentrations a region is denoted as "2," being a two-phase sample where the surfactant concentration is below the "critical microemulsion concentration" of the surfactant, where essentially no mixing of oil and water occurs, and all surfactant is dissolved as monomers in the water and oil phases.

Visual observations allow the determination of phase boundaries most precisely and reliably. Single-phase systems are usually more transparent than mixed multiphase systems which are turbid. Liquid crystalline phases, found at higher surfactant concentrations, are birefringent and easily identified by using crossed polarisers along with a strong light source. Differentiation of 2 and 3 phase regions usually requires waiting for phase separation of the samples. The relative partitioning of non-ionic surfactants between water and oil phases strongly depends upon temperature. As in the application of PEG-modified ligands, the formation of hydrogen bonds is the major factor controlling the solubility of non-ionic surfactants. With increasing temperature the hydrogen bonds break and cause a change in solubility from preferentially water soluble to preferentially oil soluble. In an intermediate temperature range solubilisation of the hydrophilic head group by water is "balanced" by the solubilisation of the hydrophobic part by the oil. In this temperature range the surfactant is able to decrease the interfacial tension between water and oil with highest efficiency. This results in the highest capacity for dispersion of water in oil or *vice versa*.

In order to better visualise the progressions shown schematically by the three triangular phase diagrams, imagine a test tube, filled with equal amounts of oil and water, with enough surfactant added to achieve some mixing of oil and water (above the 2 region), but not enough to completely mix oil and water into a single microemulsion phase (below the "1" region).

At low temperatures, non-ionic surfactants prefer water-rich phases, the test tube contains a "2" phase system (a lower "oil-in-water" microemulsion phase in equilibrium with excess oil). At intermediate temperatures, the surfactant prefers both oil and water, the test tube contains a "3" phase system (a middle "bicontinuous" microemulsion phase, in equilibrium with excess oil and water). At high temperatures, the surfactant prefers oil-rich phases, the test tube contains a "2" phase system (an upper "water-in-oil" microemulsion phase in equilibrium with excess water).

An interesting and simple principle of the patterns of phase behaviour in microemulsion systems is that the pattern of phase behaviour described above for increasing temperature (Figure 8) is also found for a number of different variables of interest. In Table 1, the direction in which the phase behaviour of non-ionic surfactants progresses is shown as a function of increasing temperature, salinity, pressure, oil "hydrophobicity", and changing the "hydrophilic/lipophilic" balance of the surfactant.

Table 1. Qualitative effects of increasing the variables listed upon phase behaviour.

Increasing parameter	2	3	2
Temperature		⟶	
Pressure		←	
Salt concentration		⟶	
Oil hydrophobicity		⟵	
Surfactant lipophilicity		⟶	
Surfactant hydrophilicity		⟵	

For example, oil "hydrophobicity" is increased by increasing the chain length of aliphatic hydrocarbons. The "hydrophilicity" of non-ionic surfactants increases upon adding mole quantities of ethylene oxide units to the surfactant (increasing *j*), which is equivalent to increasing the hydrophilic-lipophilic balance (HLB) number. The "lipophilicity" increases upon increasing the length of the aliphatic chain (increasing *i*) of the C_i E_j amphiphile, which is equivalent to decreasing the HLB number. Note that the "amphiphilicity" of ethoxylated alcohols, i.e., the strength of the "chemical dipole" between hydrophilic and lipophilic groups, is increased by increasing both *i* and *j* simultaneously.

Figure 13 shows a section of the Gibbs phase prism at constant surfactant content. A region of isotropic single-phase solutions is observed extending from the water-rich to the oil-rich side of the phase prism. At low water concentrations and higher temperatures reverse micelles are formed with diameters in the range of nanometers resulting in a large internal interfacial area.

These small droplets act as microreactors, when containing the water-soluble catalysts. For hydroformylation reactions with water-soluble Rh/TPPTS alkenes, carbon monoxide and hydrogen approach from the oil phase to the interface of the micelle, as illustrated in Figure 13. After the reaction is completed, phase separation can be achieved by changing the temperature of the reaction mixture. When the mixture is cooled down an aqueous bottom phase, containing most of the surfactant and the water-soluble

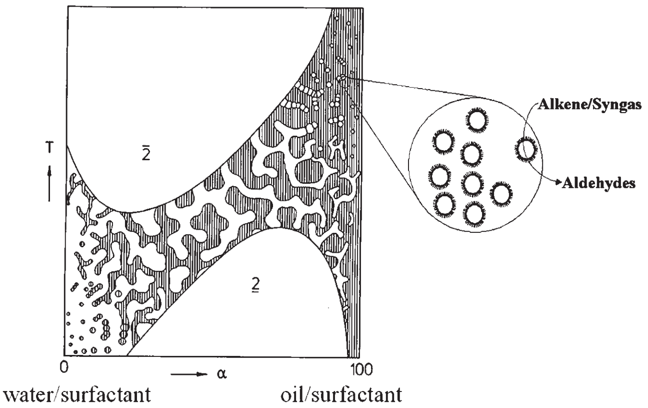

Figure 13. Section of the phase prism at constant surfactant concentration. Different structures within the one phase region are indicated by hatching.[42] In the water-rich region swollen micelles solubilise oil. In the oil-rich region the reverse micelles of nanometer size exist. Bicontinuous structures are found in the intermediate range.

catalyst separates from the organic top phase, containing the hydrophobic products and unconverted reactants. In case of incomplete catalyst recovery the micelle remaining in the product phase can be separated by means of ultrafiltration.

A first attempt at hydroformylation in a micellar system using a water-soluble rhodium catalyst (Rh-TPPTS) was made by Tinucci and Platone from Eniricherche in 1994.[46] They converted olefins with carbon numbers up to 12 in a mixture of an anionic surfactant (SDS) and butanol (as co-surfactant). It has been shown that microemulsions made of non-ionic surfactants from the alkyl-polyglycol ether type (Marlipal) are advantageous over ionic microemulsions. 1-Dodecene was hydroformylated using Rh-TPPTS at moderate temperatures and pressure (Figure 14) with almost total conversion and a turnover frequency of 440 h^{-1}.[47]

Catalyst recycling is made easy by use of an ultrafiltration unit following the phase separation. Renken reported the conversion of alkenes between C_6 and C_{16} in a micellar system using SDS in association with butanol as well.[48] Cationic surfactants were used by Fell and co-workers for the hydroformylation of unsaturated fatty acids.[49,50] Internal olefins cannot be converted to terminal aldehydes due to the highly reactive rhodium catalyst. Hydroformylation of internal double bond occurs before isomerisation towards terminal positions thus resulting in a broad product distribution.[51] Water-soluble cobalt catalysts are able to allow shifting of the internal double bond towards terminal positions before hydroformylation.[52]

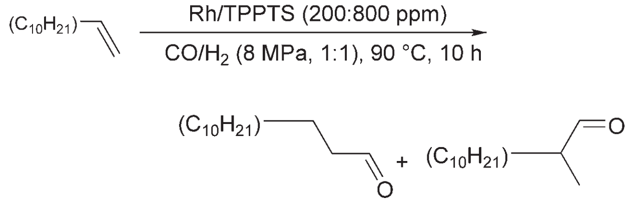

Figure 14. Hydroformylation of 1-dodecene under microemulsion conditions.

6 Temperature-Dependent Multicomponent Solvent Systems

All recycling concepts described above are based on modification of known catalysts to change their solubility behaviour. Often such modifications not only cause different solubility but also poorer catalytical activities. In contrast to these concepts, in this Section an efficient recycling method for standard non-modified homogeneous catalysts is described.

The aim of temperature-dependent multicomponent solvent systems (TMS systems) is to combine a reaction procedure without any mass transport problems as in classical homogeneous single phase catalysis with an efficient catalyst recycling concept as in liquid-liquid catalysis.

TMS usually consist of three solvents with different degrees of polarity. Solvent A (**A**) is polar in its nature and almost immiscible with the non-polar solvent B (**B**). Commonly A dissolves the catalyst while B has to be a suitable extraction agent for the reaction product. The third solvent (**C**) with a polarity in between those of A and B serves as mediator for A and B. Dependent on the composition a mixture of A, B, and C is homogeneous or heterogeneous at a certain temperature. The extent of the heterogeneous sphere of the system – the so-called miscibility gap – is temperature-dependent: usually with rising temperature the miscibility gap decreases. By carrying out the reaction at a high reaction temperature in a single phase, and separating the catalyst layer from the product layer by phase split along the tie-line at a lower temperature this effect can be used for efficient catalyst recycling (Figure 15).

6.1 Solvent Selection for Temperature-Dependent Multicomponent Solvent Systems

Solvents in industrial homogeneous catalysis have to meet various demands like chemical stability, specification in polarity, low toxicity and last but not least low price. Furthermore coordinative properties can improve or decrease the catalyst's activity which excludes certain solvents for some reactions.

For the systematic creation of TMS systems out of the almost infinite amount of organic solvents the

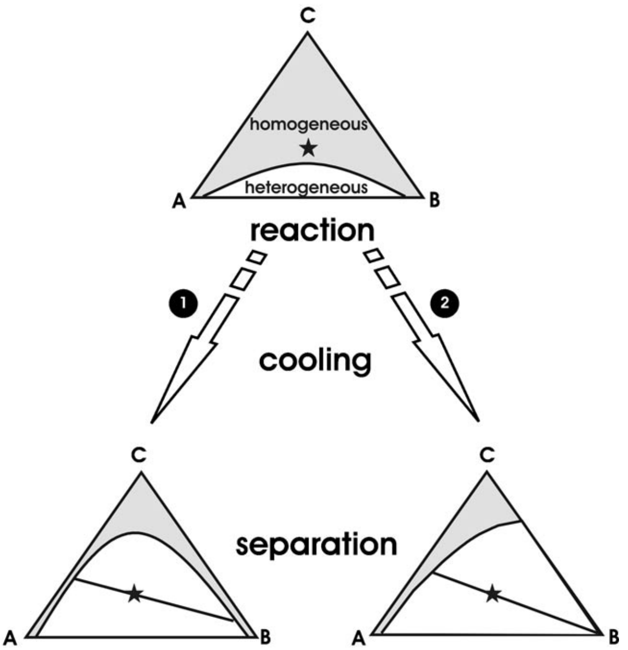

Figure 15. Principle of catalyst recycling in temperature-dependent multicomponent solvent systems; **A** = polar catalyst solvent, **B** unpolar extraction agent, **C** = semipolar mediator, **1** = separation in closed system (type I), **2** = separation in open system (type II); star = operating point.

prior demand is polarity which raises the question: what is polarity and how can it be quantified? Besides many others, the model of *Hansen solubility parameters* is quite concise and easily applicable.

The theory is derived from Hildebrand and Scott who developed the concept of the solubility parameter (δ) and defined it as the square root of the cohesive energy density:[53,54]

$$\delta = \sqrt{\frac{E}{V}}$$

where E is the energy of vaporisation of a pure solvent (reduced by the potential energy of an ideal gas) with the molar volume V. The theory postulates that the more two solvents are alike in their δ the sooner they are miscible.

Hansen's expansion of this theory was to divide the cohesive forces of liquids into three components – dispersive (**d**), polar (**p**) and hydrogen bonding (**h**) forces – and to define the three component solubility parameter δ_0 as:[55,56]

$$\delta_0 = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}.$$

It is postulated and confirmed in many cases that all substances or solvents with the same δ_0 show an optimum in solubility or rather miscibility independent of the constituent parameter's contribution. δ_0 values for many substances were determined and can be found in the literature.[56] With this tool it is possible to choose the required solvents A, B and C very easily.

For several reaction systems polar compounds like cyclic carbonates, mediators like lactams and extraction agents like saturated aliphatic hydrocarbons are suitable solvents.[57]

6.2 Different Types of Temperature-Dependent Multicomponent Solvent Systems

Classical TMS systems (type I) show a closed miscibility gap both at reaction temperature and at separation temperature (Figure 15, pathway 1, type I). That means that the catalyst layer as well as the product layer consists of all three solvents even though in different compositions. Therefore, the catalyst can be found in the product layer and the product in the catalyst layer which causes undesirable catalyst leaching.

To avoid this drawback another type of TMS was analysed. These TMS show a closed miscibility gap at reaction temperature, but an opened miscibility gap at separation temperature (Figure 15, pathway 2, type II). In this case the product layer almost exclusively consists of the extraction agent while the mediator can only be found in the catalyst layer. Hence only negligible amounts of catalyst are expected to be in the product layer.

Recent unpublished experiments deal with two component TMS systems using the concept of the UCST which has already been mentioned in previous Sections.

6.3 Examples of Use

Several homogeneously catalysed reactions like cooligomerisations,[58,59] codimerisations[60] or telomerisations[61] were conducted successfully in type I TMS. So far the successful concept of type II TMS systems

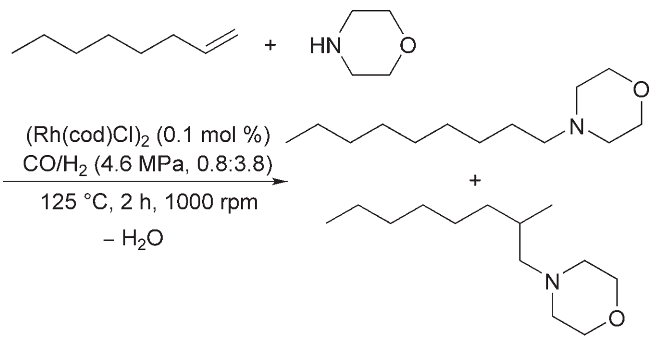

Figure 16. Hydroaminomethylation (HAM) of 1-octene in temperature-dependent multicomponent solvent systems.

was used in hydroaminomethylation (HAM, Figure 16) of 1-octene with morpholine[62] and in isomerising hydroformylation of 4-octene (Figure 17).[57,63] For both reactions a TMS system consisting of propylene carbonate, *N*-methylpyrrolidone and *n*-dodecane is suitable to suppress catalyst leaching to below 2 ppm. Total conversion with excellent yields over 80 % could be achieved after 2 h for HAM and 4 h for isomerising hydroformylation with turnover numbers (TON) of about 200 to 1000. Further reactions are under investigation.

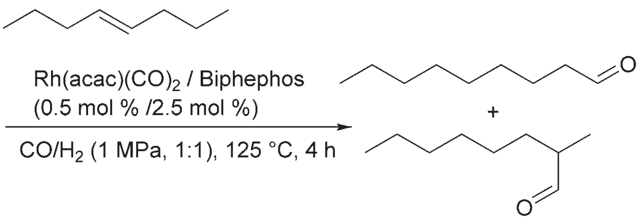

Figure 17. Hydroformylation of 4-octene in temperature-dependent multicomponent solvent systems.

7 Conclusions

Considerable effort has been done to overcome the loss of catalyst in homogeneously catalysed processes. Here we described five recycling concepts using thermomorphic effects: fluorous biphasic systems (FBS), thermoregulated phase-transfer catalysis (TRPTC), soluble polymer-based catalysis, thermoregulated microemulsions and temperature-dependent multicomponent solvent systems (TMS).

Each of the first four concepts has its own special advantages but also crucial drawbacks. FBS are characterised by very low catalyst leaching, but very expensive solvents and catalysts have to be used which are produced under ecologically critical conditions. In TRPTC water can be used as solvent, but the catalyst leaching is too high for an industrial application. Soluble polymer-based catalysts show low catalyst leaching and common solvents can be used, but complex and expensive catalysts have to be synthesised. Thermoregulated microemulsions exhibit remarkably high interfacial areas for phase transfer reactions but are still limited in application because of their time-consuming phase separation. In case of incomplete catalyst recovery an ultrafiltration step is needed as additional unit operation. In contrast, TMS systems exhibit most advantages of the other concepts combined with the possibility to use common and cheap solvents as well as numerous classical molecular catalysts. Therefore TMS systems are expected to become one of the most promising thermomorphic recycling concepts for industrial scale.

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