Advances in thermomorphic liquid/liquid recycling of homogeneous transition metal catalysts

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Abstract

One decisive disadvantage of homogeneous transition metal catalysis is the loss of the transition metal during the work-up of the product mixture. Especially when precious metals are involved the catalytic process is no more economic. Therefore considerable effort has been done with various concepts to overcome the loss of the homogeneous catalyst. In recent years several reports have been published on an integrated downstream processing for catalyst recycling using temperature dependent multi-component solvent systems. In the present contribution this concept has been improved and extended by optimisation of solvent selection and simplification. Potential solvent combinations have been found by using the upper critical solution temperature as selection criterion in addition to the concept of HANSEN solubility parameters. Furthermore a new type of temperature dependent solvent systems consisting of only two solvents has been investigated.
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1. Introduction

Over the last decades homogeneous transition metal 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 with different success [1,2].

In recent years we published several reports on an integrated downstream processing for catalyst recycling using temperature dependent multi-component solvent systems [3–9]. This concept has now been improved and extended recently by optimisation of solvent selection and simplification.

1.1. Temperature dependent multi-component solvent systems (TMS systems)

The concept of temperature-dependent multi-component solvent systems (TMS systems) is based on the idea

- to maintain homogeneous conditions without any mass transport problems during the reaction and
- to enable an efficient catalyst recycling by phase split and decantation after completed reaction like in liquid–liquid biphasic catalysis.

Classical TMS systems consist of three solvents with different polarities. 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 serves as extracting agent for the products. The semi-polar third solvent (C) is used as solubility mediator for the components A and B. Depending on the composition a mixture of A, B and C is homogeneous or heterogeneous at certain temperatures. The extent of the heterogeneous sphere of the system – the 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

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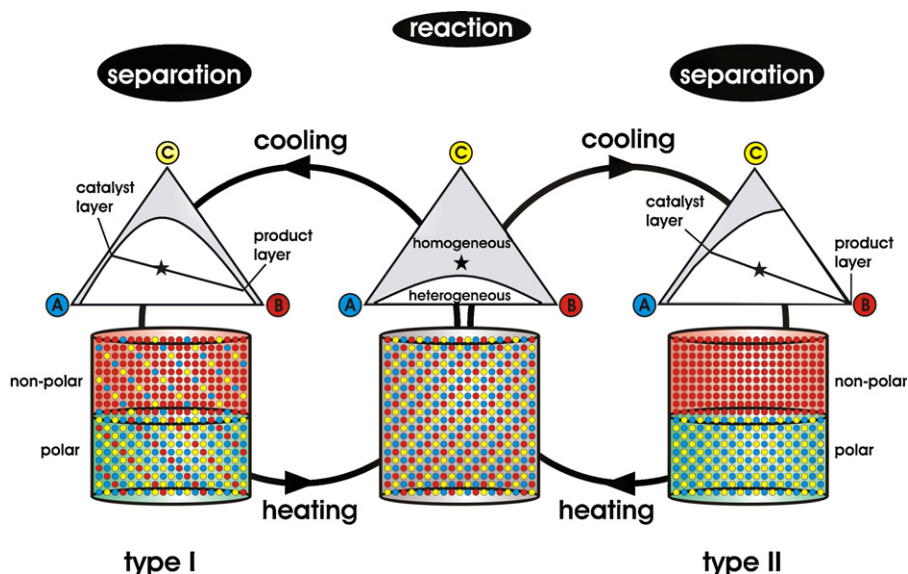 *E-mail address:* behr@bci.uni-dortmund.de (A. Behr).

Fig. 1. Principle of catalyst recycling in temperature-dependent multi-component solvent systems: A = polar catalyst solvent; B = non-polar extraction agent; C = semi-polar mediator; type I = separation in closed system; type II = separation in opened system; star = operating point.

layer by phase split along the tie-line at a lower temperature this effect can be used for efficient catalyst recycling (Fig. 1).

1.2. Solvent selection for TMS 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 systematic creation of TMS systems out of the almost infinite amount of organic solvents the 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 [10,11]:

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

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 value 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 [12,13]:

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

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 literature [13]. With this tool it is possible to choose the required solvents A, B and C very easily.

1.3. Different types of TMS systems

Type I TMS systems show a closed miscibility gap both at reaction temperature and at separation temperature (Fig. 1, type I). As a consequence both layers consist of all three solvents even though in different compositions after cooling. Therefore the catalyst is not totally immobilised in the polar layer but can also be found in certain amounts in the non-polar product layer. This effect causes undesirable catalyst leaching.

This drawback does not exist in type II TMS systems. These TMS systems have a closed miscibility gap at an elevated reaction temperature, but an open miscibility gap at separation temperature (Fig. 1, type II). That means that the product layer consists almost exclusively of the extraction agent B while the semi-polar mediator C can only be found in the catalyst layer. Hence only negligible amounts of catalyst are expected to be in the product layer.

For chemical processing it is desirable to handle simple reaction systems. Thus a novel type of TMS systems (type III) with only two solvents – a polar catalyst solvent and a non-polar extraction agent – was considered which will be presented in detail in the following sections.

2. Experimental

2.1. Reagents

N,N-Dimethylformamide (p.a.), *N,N′*-dimethyl propylene urea (97%), *N*-methylpyrrolidone (99%), 1-butanol (99%), propylene carbonate (99.5%), methanol (p.a.), ethanol (p.a.), isopropyl alcohol (p.a.), 1-butanol (p.a.), acetonitrile (p.a.),

dimethylsulfoxide (p.a.), sulfolane (99+%), toluene (p.a.), morpholine (99+%), methyl-*tert*-butylether (99%), cyclohexane (99+%), *n*-octane (99+%), *n*-decane (99+%), *n*-dodecane (99%), 1-octene (99%) and Wilkinson's catalyst (99.99%) were purchased from Acros Organics and used without further purification. 1-Dodecene (95%) was obtained from Aldrich, butylene carbonate (99%) from Huntsman, Rh(acac)(CO)$_2$ (39.90 wt.% Rh) from Umicore and triphenylphosphin trisulfonate-sodium (Na-TPPTS) from EOXO.

2.2. Analytics

Water contents were determined by Karl-Fischer titration on a 652-KF-Coulometer (Metrohm Herisau, Switzerland). Precious metal and phosphorous content were measured by inductively coupled plasma spectrometry with an IRIS Intrepid ICP-OES spectrometer (Thermo Elemental). Routine gas chromatographic analyses were done on a HP 6890 instrument (Hewlett-Packard GmbH, Waldbronn, Germany) equipped with a FI-detector and a HP-INNOWax capillary column (30 m, coating polyethylene glycol, diameter 0.25 mm, film thickness 0.25 μm) in connection with an autosampler.

2.3. Determination of type I and II TMS systems

All experiments for TMS systems were carried out by cloud titration. 1 g of a mixture of a polar catalyst solvent and a nonpolar extraction agent (5:1, 3:1, 1:1, 1:3, 1:5 wt. ratio) was transferred into a 5 mL centrifuge glass and warmed in a silicone oil bath under intense stirring. After having reached the desired temperature the mediator was added drop by drop by a syringe to the cloudy mixture until a homogeneous phase was formed.

2.4. Determination of type III TMS systems

1 g mixtures of different compositions of the catalyst solvent and the extraction agent were transferred into a 5 mL centrifuge glass and were intensely stirred in a silicone oil bath giving cloudy emulsions. Gradual warming led to homogenisation of the several mixtures while the temperature was noted.

2.5. Catalyst leaching

2.5.1. Phase separation at room temperature

5 g mixtures of catalyst solvent, mediator and extraction agent (*x*:*y*:60 wt.%) for type I and II TMS systems and of catalyst solvent and extraction agent (40:60 wt.%) for type III TMS systems, respectively were transferred into a centrifuge glass followed by addition of 1×10^{-5} mol rhodium acetylacetonatobiscarbonyl (Rh(acac)(CO)$_2$) and 4×10^{-5} mol triphenylphosphine (PPh$_3$). The mixtures were warmed up to their homogenisation temperature under intense stirring followed by cooling to room temperature. The upper layer was separated and analysed via ICP-OES.

2.5.2. Temperature dependent phase separation

262.0 mg (1 mmol) PPh$_3$ and 64.7 mg (0.25 mmol) Rh(acac)(CO)$_2$ were dissolved in 100 g mixtures of catalyst solvent and extraction agent (50:50 wt.%). The mixtures were placed in a silicone oil bath and heated under intense stirring until a homogeneous phase was obtained. Then the solutions were tempered at the desired temperature, the stirring stopped and phase separation was awaited. After 30 min the extract layer was analysed by ICP-OES.

2.6. Hydrogenation experiments

All hydrogenation experiments were carried out in 300 mL laboratory reactors from Parr Instrument Company (USA). The reaction mixture was transferred into the reactor using standard Schlenk technique to prevent oxidation of the catalyst precursors.

In a typical experiment 1.0×10^{-2} mol alkene and 1×10^{-4} mol Wilkinsons's catalyst were dissolved in 60 mL of a solvent mixture and transferred into the evacuated stainless steel autoclave. After heating the vessel up to the reaction temperature it was pressurised with hydrogen. The reaction time was taken after accelerating the stirrer to 500 rpm. The reaction was ended by stopping the hydrogen influx, reducing the stirring velocity and rapidly cooling down to room temperature with an ice bath. After venting the hydrogen the reaction mixture was separated at 0 °C. A sample of both the catalyst phase and the product phase were taken and analysed by gas chromatography with *n*-heptane as internal standard and isopropanol as solvent. The catalyst leaching was analysed by ICP-OES.

2.7. Recycling experiments

After separation of the product layer from the catalyst layer the latter was reused by adding new substrate and fresh extraction agent analogous to the original experiment. This reaction mixture then was treated as it is described in Section 2.6. A sample of both the catalyst phase and the product phase were taken and analysed by gas chromatography with *n*-heptane as internal standard and isopropanol as solvent. The catalyst leaching was analysed by ICP-OES.

3. Results and discussion

3.1. Type I temperature dependent three component solvent systems

Some new solvent systems of type I are listed in Table 1 and are displayed in Fig. 2 for ambient temperature.

Obviously morpholine acts as an efficient mediator. Acetonitrile/alkane systems as well as *N,N*-dimethylformamide/alkane systems exclusively form a closed miscibility gap with morpholine at ambient temperature. Also alcohols like isopropyl alcohol or *n*-butanol are efficient mediators which easily close the miscibility gap between the polar butylene carbonate and the non-polar *n*-decane. The most potent mediators which form merely a small miscibility gap between methanol – which is one
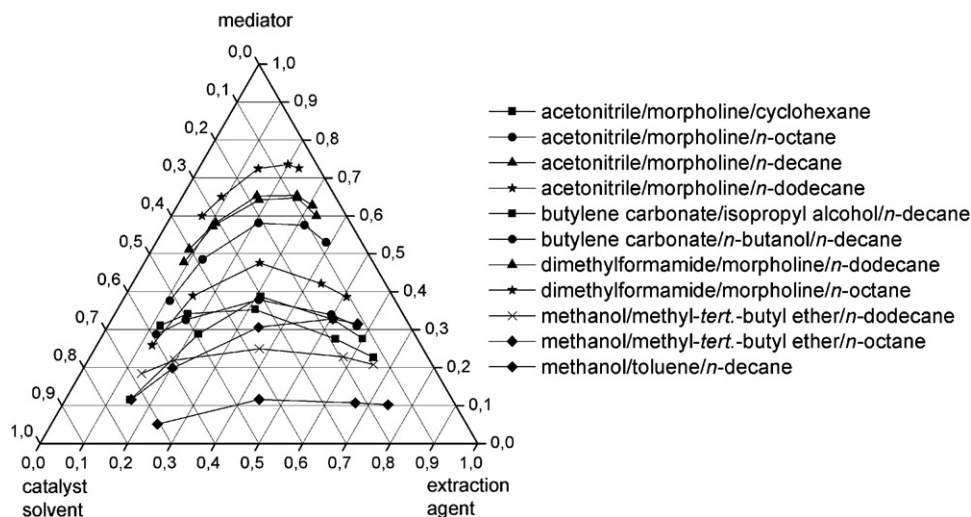
Fig. 2. TMS systems with a closed miscibility gap at ambient temperature.

of the most polar organic solvents – and alkanes are toluene and methyl-*tert*-butylether.

With acetonitrile as catalyst solvent and morpholine as mediator the miscibility gap strongly increases with growing chain length of the non-polar extraction agent. The same trend can be observed with *N,N*-dimethylformamide as catalyst solvent.

For a low catalyst leaching a large miscibility gap at ambient temperature is desired. Type I TMS systems consisting of acetonitrile or *N,N*-dimethylformamide with long chain alkanes and morpholine as mediator therefore seem to be the most promising combinations.

3.2. Type II temperature dependent three component solvent systems

Former results showed that cyclic carbonates like ethylene carbonate, propylene carbonate and butylene carbonate together with long chain alkanes form type II TMS systems together with *N*-methylpyrrolidone as mediator [8]. Regarding this we found new solvent systems with similar behaviour utilising HANSEN solubility parameters. These systems are listed in Table 2 and displayed in Fig. 3 for room temperature.

From Fig. 3 it can be seen that the run of all binodal curves at ambient temperature is almost parallel to the left blade of the phase diagram which demonstrates a constant low solubility of the catalyst solvent/mediator mixtures in the extraction agent. It can be assumed that besides these type II TMS systems also other combinations of acetonitrile, *N,N*-dimethylformamide, methanol, *N*-methylpyrrolidone, *N,N'*-dimethyl propylene urea and alkanes show similar behaviour.

The temperature dependency of some selected type II TMS systems is shown in Figs. 4–6.

It can clearly be seen that with increasing temperature the miscibility gap decreases and that there is a certain temperature in all three cases where the miscibility gap closes. Noticeable this temperature is almost equal for the TMS systems *N,N*-dimethylformamide/*N,N'*-dimethyl propylene urea/*n*-decane and methanol/*N,N'*-dimethyl propylene urea/*n*-decane (about 55–60 °C, Figs. 4 and 6). The miscibility gap of the system *N,N*-dimethylformamide/*N*-methylpyrrolidone/*n*-decane gets closed above about 65–70 °C (Fig. 5). An explanation for this effect will be given after analysis of the type III TMS systems.

All type II TMS systems described above are suitable for efficient catalyst recycling in homogeneous catalysis when the reaction temperature is higher than 60 °C for *N,N'*-dimethyl propylene urea as mediator and 70 °C for *N*-methylpyrrolidone, respectively.

Table 1
New type I TMS systems

Catalyst solvent	Mediator	Extraction agent
Acetonitrile	Morpholine	Cyclohexane
Acetonitrile	Morpholine	*n*-Octane
Acetonitrile	Morpholine	*n*-Decane
Acetonitrile	Morpholine	*n*-Dodecane
Butylene carbonate	Isopropyl alcohol	*n*-Decane
Butylene carbonate	1-Butanol	*n*-Decane
N,N-Dimethylformamide	Morpholine	*n*-Dodecane
N,N-Dimethylformamide	Morpholine	*n*-Octane
Methanol	Methyl-*tert*-butylether	*n*-Dodecane
Methanol	Methyl-*tert*-butylether	*n*-Octane
Methanol	Toluene	*n*-Decane

Table 2
New type II TMS systems

| Catalyst solvent	Mediator	Extraction agent
Acetonitrile	*N*-Methylpyrrolidone	*n*-Decane
Acetonitrile	*N*-Methylpyrrolidone	*n*-Octane
N,N-Dimethylformamide	*N,N'*-Dimethyl propylene urea	*n*-Decane
N,N-Dimethylformamide	*N*-Methylpyrrolidone	*n*-Decane
N,N-Dimethylformamide	*N*-Methylpyrrolidone	*n*-Octane
Methanol	*N*-Methylpyrrolidone	*n*-Decane
Methanol	*N*-Methylpyrrolidone	*n*-Octane
Methanol	*N,N'*-Dimethyl propylene urea	*n*-Decane
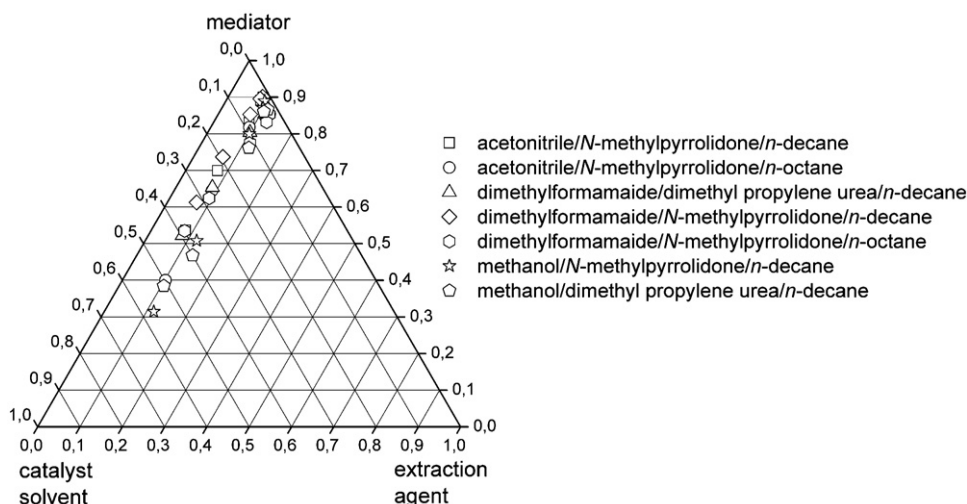
Fig. 3. Type II TMS systems at ambient temperature.

3.3. Type III temperature dependent two component solvent systems

The drawback of type I TMS systems is that the product- as well as the catalyst-layer consist of all three solvents. This problem could be solved by usage of type II TMS systems. If the mediator's polarity resembles the polarity of the catalyst solvent like in type II TMS systems it is suggested to work without the mediator and to examine TMS systems of only two components (type III).

Type III TMS systems have to be divided into those which only show an elevated miscibility at reaction temperature (type IIIa) and those with infinite miscibility above a certain temperature (type IIIb). For this concept a strong temperature dependency of the catalyst solvent's solubility in the extraction

agent is essential. Many values for binary liquid/liquid equilibriums are available in literature [14], but nonetheless many potential combinations are still unknown. Therefore we measured the solubility of several polar solvents in non-polar alkanes as a function of temperature. The results are given in Table 3.

Obviously sulfolane and propylene carbonate show a poor temperature dependency of miscibility with n-decane while methanol, acetonitrile, butylene carbonate and at certain extent also dimethylsulfoxide show a significant increase of miscibility with n-decane.

The limitation of this concept is that the amount of catalyst solvent which is necessary to solve the catalyst at room temperature has to be able to be homogenised in the extraction agent at reaction temperature.
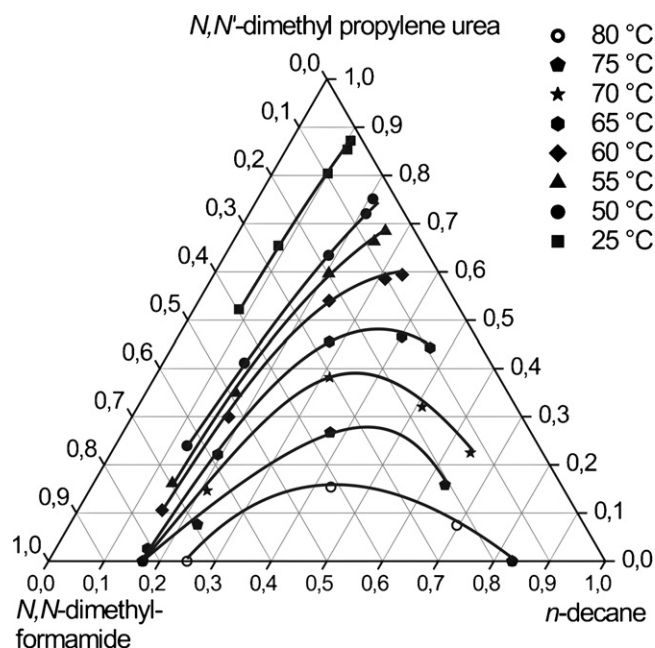

Fig. 4. Temperature behaviour of N,N-dimethylformamide/N,N′-dimethyl propylene urea/n-decane between 25 and 80 °C.

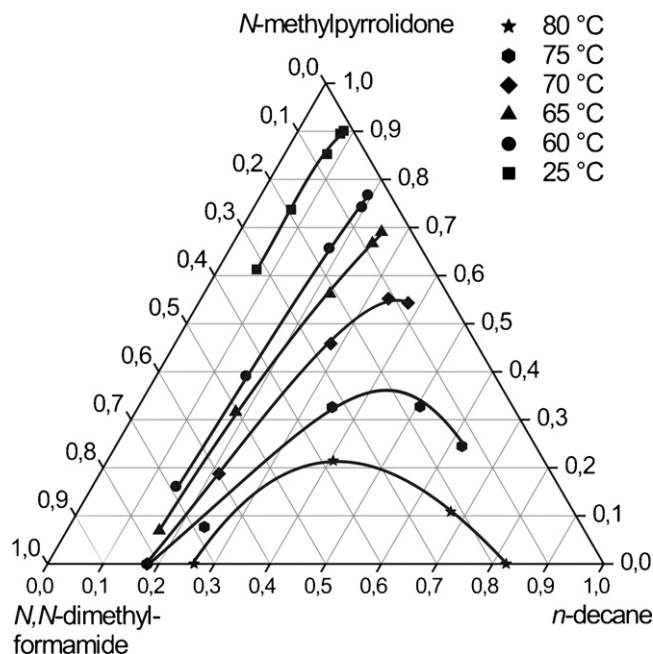

Fig. 5. Temperature behaviour of N,N-dimethylformamide/N-methylpyrrolidone/n-decane between 25 and 80 °C.

Table 3
Type IIIa TMS systems with *n*-decane as extraction agent; b.b.p. = beyond boiling point

Component A	wt.% A; 25 °C	wt.% A; 50 °C	wt.% A; 80 °C	wt.% A; 100 °C
Methanol	0.4	5.2	b.b.p.	b.b.p.
Acetonitrile	1.4	2.9	b.b.p.	b.b.p.
Sulfolane	0.7	1.0	1.5	2.6
Dimethylsulfoxide	0.8	1.7	3.3	4.6
Propylene carbonate	2.7	3.1	3.6	5.2
Butylene carbonate	2.7	3.9	6.2	8.8

Besides these TMS systems with limited miscibility even at elevated temperature there are some solvent systems which show an unlimited miscibility beyond a certain temperature (type IIIb). This temperature is known as *upper critical solution temperature* (*UCST*) and is already utilised for organic/fluorinated solvent systems and soluble polymer-bound catalysts [9]. For many solvent mixtures this UCST is higher than the reaction temperatures in common homogeneous catalysis. For this reason we investigated the phase behaviour of several potential polar catalyst solvents with *n*-decane as extraction agent and found that nitrogen containing solvents basically have UCST below 100 °C. Table 4 shows the miscibility of three nitrogen containing solvents with *n*-decane at room temperature as well as their UCST. The appropriate liquid/liquid phase diagrams are displayed in Fig. 7.

It can be seen that the miscibility of *N,N*-dimethylformamide, *N*-methylpyrrolidone and *N,N′*-dimethyl propylene urea in *n*-decane is poor at low temperatures and is exponentially rising with increasing temperatures up to unlimited miscibility at 85, 69 and 60 °C, respectively.

There are also some aqueous/organic solvent mixtures with an UCST at applicable range for homogeneous catalysis, i.e. water/1-butanol = 127 °C or water/2-butanol = 110 °C [15].
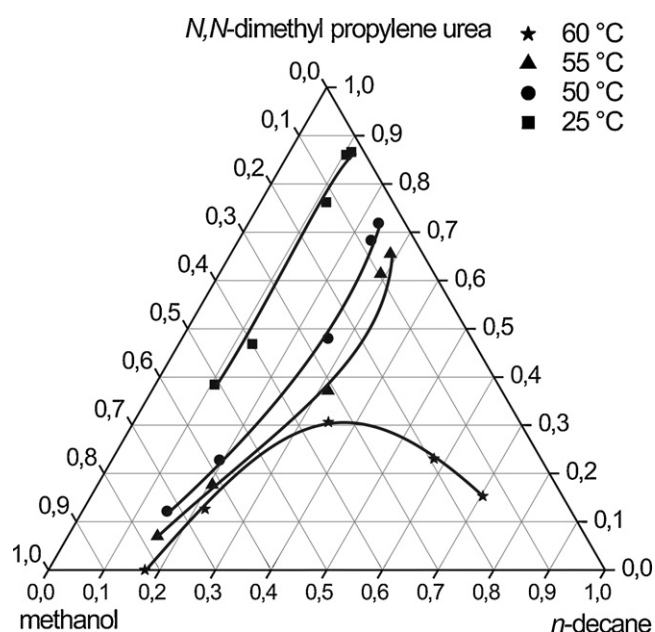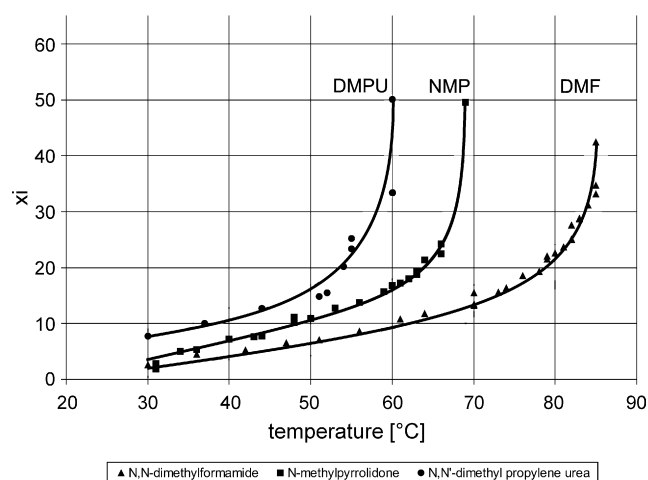

Fig. 7. Liquid/liquid phase diagrams of some nitrogen containing solvents with *n*-decane; x_i = wt.% in *n*-decane.

Considering type II TMS systems described in Section 1.3 (Fig. 1) in respect of the liquid/liquid phase behaviour of type III TMS systems it can be concluded that the miscibility gap closes as soon as the UCST between the mediator and extraction agent is exceeded. Thus it is possible to find new suitable type II TMS systems, predict their temperature behaviour as well as their transition from a closed to an open miscibility gap both by usage of HANSEN solubility parameters and by search or determination of the appropriate UCST.

3.4. Catalyst leaching

Recent publications show good results for homogeneous catalysis in type I TMS systems but with unsatisfactory catalyst leaching [3–5]. Significant improvement could be reached

Fig. 6. Temperature behaviour of methanol/*N,N′*-dimethyl propylene urea/*n*-decane between 25 and 60 °C.

Table 4
Type IIIb TMS systems with *n*-decane as extraction agent and their upper critical solution temperature (UCST)

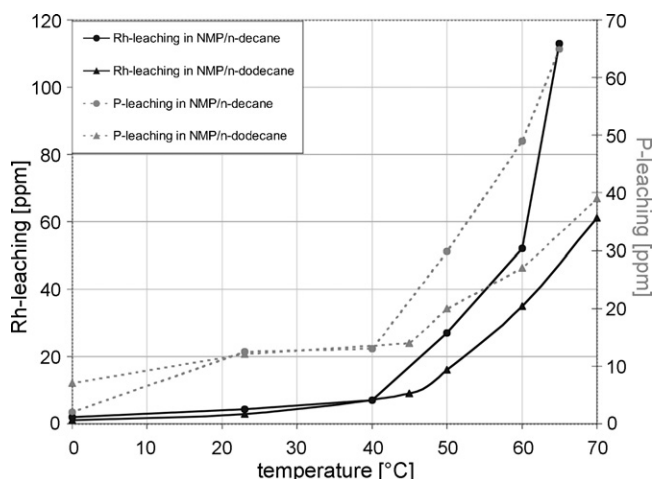| Catalyst solvent	wt.% in *n*-decane at 25 °C	UCST (°C)
N,N-Dimethylformamide (DMF)	3.0	85
N-Methylpyrrolidone (NMP)	1.7	69
N,N′-Dimethyl propylene urea (DMPU)	1.4	60

Fig. 8. Temperature dependent catalyst leaching of the type IIIb TMS systems NMP/n-decane and NMP/n-dodecane (50:50 wt.%, 100.0 g mixture, 262.0 mg (1 mmol) PPh$_3$ and 64.7 mg (0.25 mmol) Rh(acac)(CO)$_2$).

by utilising type II TMS systems based on cyclic carbonates for isomerising hydroformylation where the catalyst leaching was suppressed below 0.1% relating to rhodium and 0.5% relating to the phosphorous ligand [8].

To prove the expected efficiency of the new type II as well as type III TMS systems experiments concerning catalyst leaching were performed. Mixtures of three and two solvents, respectively were charged with different concentrations of rhodium acetylacetonatobiscarbonyl (Rh(acac)(CO)$_2$) and triphenylphosphine (PPh$_3$), homogenised by heating, cooled down to room temperature, separated by phase split and analysed. The results are given in Table 5.

It can be seen that even at elevated catalyst concentrations in the catalyst layer rhodium leaching can be suppressed below 5 ppm. Relatively the phosphorous leaching is similar low. At low catalyst concentrations in the catalyst layer the systems consisting of N,N-dimethylformamide/N,N′-dimethyl propylene urea/n-decane, N,N-dimethylformamide/N-methylpyrrolidone/n-decane and N-methylpyrrolidone/n-decane seem to be the most promising. At high catalyst concentrations the systems consisting of N,N-dimethylformamide/N,N′-dimethyl propylene urea/n-decane and N-methylpyrrolidone/n-decane show a good performance.

In further experiments it was investigated whether the catalyst leaching is proportional to the temperature of phase separation of type IIIb TMS systems. Fig. 8 shows as an example the temperature dependent catalyst leaching of the systems

NMP/n-decane and NMP/n-dodecane. It can be seen, that with rising temperature both rhodium and phosphorous leaching is increasing as it was expected. The leaching curves in Fig. 8 for NMP/n-decane resemble the course of their appropriate liquid/liquid phase equilibrium shown in Fig. 7. So it can be reasoned that phase separation should be performed at low temperatures.

3.5. Examples of use

Several homogeneous catalysed reactions like cooligomerisations [3,16], codimerisations [4] or telomerisations [6] were conducted effectively in type I TMS systems. So far the successful concept of type II TMS systems was used in hydroaminomethylation (HAM, Fig. 9) of 1-octene with morpholine [7] and in isomerising hydroformylation of 4-octene (Fig. 10) [5,8]. For both reactions a TMS system consisting of propylene carbonate, N-methylpyrrolidone and n-dodecane is suitable to suppress catalyst leaching 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 turn over numbers (TON) of about 200–1000.

The new concept of type IIIb TMS systems was successfully implemented for the hydrogenation of 1-octene and 1-dodecene in DMF/n-decane, NMP/n-decane as well as water/1-butanol. The results are given in Table 6.

It was observed that the hydrogenation of long chain alkenes could successfully be carried out both in organic/organic and in aqueous/organic solvent systems. High conversions of over 95% were achieved. The catalyst leaching into the product layer regarding rhodium was always lower than 1 ppm, while phosphorous leaching was 3 ppm at most. With organic/organic solvent systems it was even possible to substitute the non-polar solvent by equally amounts of non-polar substrate, which has a similar UCST, yielding the pure alkane as product phase with negligible low catalyst leaching.

Based on these results recycling experiments of entries 3, 5 and 6 (Table 6) were carried out by reusing the catalyst layer and adding fresh extraction agent and substrate. The results are given in Table 7.

Reusing the catalyst layer leads to similar results which were obtained with fresh catalyst. In both aqueous/organic and organic/organic solvent systems alkene conversions of 97% and above were achieved accompanied by a catalyst leaching below 1 ppm regarding rhodium and below 2 ppm regarding phosphorous.
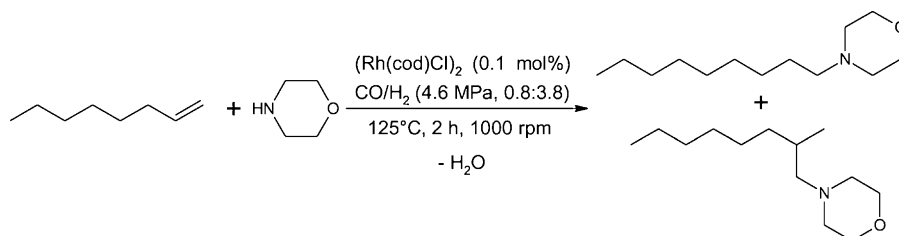

Fig. 9. Hydroaminomethylation (HAM) of 1-octene in TMS systems.

Table 5
Catalyst leaching in type II and type III TMS systems

Type	TMS	Rh in extract layer (ppm)		P in extract layer (ppm)	
		High	Low	High	Low
II	N,N-Dimethylformamide, N,N′-dimethyl propylene urea, n-decane	4.4	2.2	15.6	2.1
II	N,N-Dimethylformamide, N-methylpyrrolidone, n-decane	1.5	<1.0	130.3	9.3
II	Methanol, N,N′-dimethyl propylene urea, n-decane	2.6	<1.0	245.1	45.3
IIIb	N,N′-Dimethyl propylene urea, n-decane	<1.0	<1.0	67.3	11.4
IIIb	N-Methylpyrrolidone, n-decane	<1.0	<1.0	50.3	<1.0
IIIb	N,N-Dimethylformamide, n-decane	4.2	2.8	228.9	54.9

Catalyst solvent + mediator = 40 wt.%, extraction agent = 60 wt.%; high = 520 ppm Rh and 2080 ppm PPh_3 in catalyst layer; low = 175 ppm Rh and 525 ppm PPh_3 in catalyst layer.
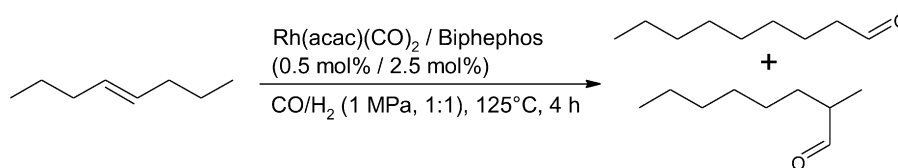

Fig. 10. Hydroformylation of 4-octene in TMS systems.

Table 6
Hydrogenation in type IIIb TMS-systems

Entry	Solvents (S1/S2)	Substrate	n (mmol)	V_{S1} (mL)	V_{S2} (mL)	p (bar)	Conversion (%)	Leaching (ppm)	
								Rh	P
1	DMF/n-decane	1-Octene	10	30	30	20	99	<1	1
2	DMF/n-decane	1-Dodecene	10	30	30	20	95	<1	3
3	NMP/n-decane	1-Octene	10	30	30	20	100	<1	<1
4	DMF	1-Octene	130	30	–	20	100	<1	1
5	DMF	1-Dodecene	130	30	–	20	99	<1	2
6	Water/1-butanol[a]	1-Octene	20	45	15	40	95	<1	3

130 °C, t = 4 h, c(catalyst) = 1.7×10^{-3} mol L^{-1}.

[a] $Rh(acac)(CO)_2$ and Na-TPPTS instead of Wilkinson's catalyst.

Table 7
Recycling experiments of hydrogenation in type IIIb TMS-systems

Recycle of entry	Solvents (S1/S2)	Substrate	n (mmol)	V_{S2} (mL)	p (bar)	Conversion (%)	Leaching (ppm)	
							Rh	P
3	NMP/n-decane	1-Octene	10	30	20	99	<1	<1
5	DMF	1-Dodecene	130	–	20	98	<1	1
6	Water/1-butanol[a]	1-Octene	20	15	40	97	<1	2

130 °C, t = 4 h, first recycle of catalyst layer.

[a] $Rh(acac)(CO)_2$ and Na-TPPTS instead of Wilkinson's catalyst.

4. Conclusions

The catalyst recycling concept of temperature dependent multi-component solvent systems has been widened and simplified:

- Several new type I TMS systems consisting of common solvents like acetonitrile, methanol, MTBE and aliphatic alkanes were found.
- Using especially amides like N-methylpyrrolidone, N,N-dimethylformamide and others as mediator new type II TMS systems could be composed which exhibit only low catalyst leaching. Based on the upper critical solution temperature (UCST) of the catalyst solvent/mediator and extraction agent a well calculated solvent selection for type II TMS systems is possible.
- Moreover a new and much simpler type of TMS systems (type III) has been investigated consisting of only two solvents leading to high conversions in hydrogenations with very low catalyst losses. Recycling the catalyst layer leads to equally high conversions and almost no catalyst losses. In this way a powerful method for catalyst recycling was developed which could find application in the field of asymmetric hydrogenation for example.

Often the solvent affects an accurate catalyst activity and selectivity and thus cannot be substituted. In these cases type II TMS systems can be applied combining optimum catalytic conditions with an integrated downstream processing. In cases where the catalyst solvent is exchangeable without loss of catalytic activity the use of type III TMS systems is advised.

Acknowledgements

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