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Isomerizing hydroformylation of *trans*-4-octene to *n*-nonanal in multiphase systems: acceleration effect of propylene carbonate

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Abstract

In this contribution we present the isomerizing hydroformylation of *trans*-4-octene to *n*-nonanal in a two-phase catalytic reaction system. Based on this two-phase system, the application of a thermomorphic multi-solvent catalytic reaction system will be presented which changes from a two-phase to a single-phase system by simply raising the temperature. This concept provides the possibility to overcome mass transport limitations which are typical problems in conventional two-phase reactions.

Keywords: Isomerization-hydroformylation; Multiphase catalysis; Internal olefin; Rhodium; BIPHEPHOS

1. Introduction

The transition metal catalyzed hydroformylation of olefins is a very important reaction in chemical industry [1]. Almost exclusively this reaction is carried out by the use of homogeneous rhodium or cobalt catalysts. The advantages of the rhodium catalysts are both the milder reaction conditions and the higher activity and selectivity towards the corresponding oxo-products [2]. In the last few years feedstocks with mostly internal (C,C)-double bonds have also been used for the production of linear aldehydes and the corresponding alcohols [3–16]. These alcohols are converted to plasticizers for the polymer industry.

The isomerizing hydroformylation of *trans*-4-octene in toluene as solvent using a rhodium–BIPHEPHOS catalyst can be carried out with a conversion of the olefin of 75% and a selectivity to the linear aldehyde of 94% (see Fig. 1). The reaction time amounts to 4 h at a temperature of 125 °C and at a synthesis gas ($CO/H_2 = 1/1$) pressure of 10 bar [17].

For a technical application the catalyst recycling is one of the most important topics because of the very high prices of the rhodium metal and the ligand. To recycle the catalyst toluene as solvent is not the best choice for it has nearly the same polarity as the product *n*-nonanal. We chose propylene carbonate as solvent which increased the activity of the catalyst to conversions of 95% as well as the selectivity to the linear aldehyde up to 95% [17]. Propylene carbonate is a good solvent of the rhodium precursor [$Rh(acac)(CO)_2$] and the phosphite ligand BIPHEPHOS. The catalyst recycling can be carried out by an extraction with a long-chain hydrocarbon like dodecane, which poorly solves the catalyst but perfectly the reaction products. After several recycle runs the catalytic conversion of the octene and the selectivity to the linear aldehyde stayed on nearly the same high level as mentioned above. Although ICP investigations showed that there is a strong rhodium leaching of 14% after the first reaction run.

In this contribution we will present new results concerning the isomerizing hydroformylation of *trans*-4-octene to *n*-nonanal in a two-phase catalytic reaction system. Furthermore we present the application of a thermomorphic multi-solvent catalytic reaction system which changes from a two-phase to a single-phase system by simply raising the temperature [18,19]. This concept provides the possibility to overcome mass transport limitations which are typical problems in conventional two-phase reactions.

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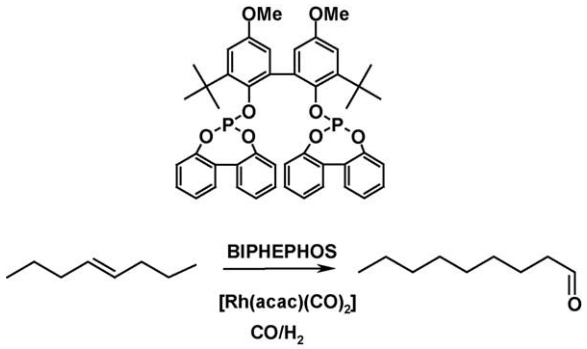


Fig. 1. Isomerizing hydroformylation of *trans*-4-octene to *n*-nonanal.

2. Results and discussion

2.1. Two-phase catalysis

2.1.1. In situ extraction

As already mentioned, the reaction products can be extracted with the hydrocarbon dodecane. Instead of an additional extraction after the catalytic reaction, we carried out in situ extraction experiments, where the products are separated from the catalytic propylene carbonate phase while the reaction is still in progress. To enhance the mass transfer the extraction was carried out under a strong stirring. Table 1 shows the influence of the stirring velocity which was varied in the range of 500–1500 rpm.

The investigation shows, that with increasing stirring velocity the conversion of the olefin stays on the same high level of around 96% and that the selectivity to the linear aldehyde also remains at a constant level of about 70%. Obviously there is no mass transfer limitation in this two-phase reaction system. In comparison to the single-phase reaction in propylene carbonate as the only solvent [17], the selectivity decreases from 95 to 70%, which can be explained by the high concentration of the non-electron donating solvent dodecane in the propylene carbonate phase. The presence of the dodecane leads to a deceleration of the isomerization velocity, which results in a lower linearity of the formed aldehydes.

Table 1
Influence of the stirring velocity in the two-phase system propylene carbonate/dodecane

Stirring velocity (rpm)	Conversion (*trans*-4-octene) (%)	Selectivity (*n*-nonanal) (%)
500	97	72
750	96	73
1000	96	73
1250	96	68
1500	96	72

Reaction conditions: 0.1 mmol [Rh(acac)(CO)$_2$], 0.5 mmol BIPHEPHOS, 19.4 mmol *trans*-4-octene, 20 ml propylene carbonate, 20 ml dodecane, p(CO/H$_2$ = 1/1) = 10 bar, T = 125 °C, t = 4 h.

Table 2
Influence of the addition of methylated β-cyclodextrin in the two-phase system propylene carbonate/dodecane

Concentration of β-cyclodextrin (mol%)	Conversion (*trans*-4-octene) (%)	Selectivity (*n*-nonanal) (%)
0.2	97	64
1.0	97	68
2.0	96	72

Reaction conditions: 0.1 mmol [Rh(acac)(CO)$_2$], 0.5 mmol BIPHEPHOS, 19.4 mmol *trans*-4-octene, 20 ml propylene carbonate, 20 ml dodecane, p(CO/H$_2$ = 1/1) = 10 bar, T = 125 °C, t = 4 h, stirring velocity 500 rpm.

2.1.2. Influence of methylated β-cyclodextrin

Cyclodextrins are often used in phase transfer catalysis reactions [20–23]. They are able to intercalate hydrophobic substances and to transport them into a polar phase like water. To study the influence of cyclodextrins on the isomerizing hydroformylation of *trans*-4-octene in the biphasic solvent system propylene carbonate/dodecane we varied the concentration of methylated β-cyclodextrin from 0.2 up to 2.0 mol% related to the substrate *trans*-4-octene. The results are given in Table 2.

With increasing concentration of methylated β-cyclodextrin the selectivity to *n*-nonanal increases from 64 to 72%, while the conversion of the olefin is constantly as high as 97%. Obviously the addition of the methylated β-cyclodextrin has no great influence on the isomerizing hydroformylation of *trans*-4-octene to *n*-nonanal. The addition of only 0.2 mol% of methylated β-cyclodextrin lowers the isomerization velocity which results in the formation of more branched aldehydes. In pharmacy β-cyclodextrins are established as solvation mediators between polar and less polar solvents. This is one possible explanation for the raise of the selectivity to *n*-nonanal with an increasing β-cyclodextrin concentration. Here the former two-phase reaction system changes into a single-phase reaction system which leads to a higher linearity of the aldehydes.

2.2. Temperature-depending multi-component solvent (TMS)-systems

The TMS-systems consist of a polar (S1) and a non-polar (S2) solvent, which show no or at least only very poor solubility for each other. The third solvent which needs middle polarity acts as a mediator for the two other solvents. In these TMS-systems the reaction takes place in a single phase at a high reaction temperature, while lower temperatures (room temperature for example) cause the single phase to split up in two separate phases again. The general principle of the TMS's is illustrated in Fig. 2.

The operating point describes a designated composition of the solvent system. This point is located in the single-phase regime when the reaction temperature is above the phase separation temperature T2. Cooling down the reaction mixture (T1 < T2) to room temperature leads to the separation of the single phase into two phases. The catalyst will be found in

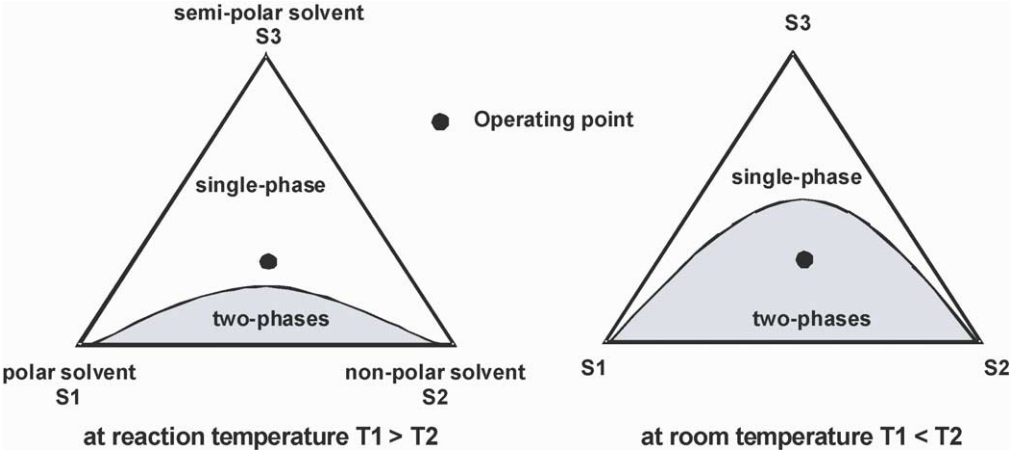


Fig. 2. Principle of temperature dependent multi-component solvent systems.

one of the two phases and can be reused by a simple phase separation. This concept combines the advantages of a reaction in a single-phase system with the advantages of the catalyst recycling of a two-phase system.

Actually the isomerizing hydroformylation in the single-phase system with propylene carbonate as the only solvent leads to the best selectivity to *n*-nonanal of 95% with a conversion on *trans*-4-octene of also 95%. For the combination of the isomerizing hydroformylation and the use of TMS's, we investigated a solvent system consisting of propylene carbonate (PC), dodecane and *p*-xylene. *p*-Xylene acts as solvation mediator between the polar phase propylene carbonate, in which the catalyst is dissolved, and the substrate/product-phase dodecane.

To determine the exact operating zone within this solvent system we carried out several cloud titrations. PC/dodecane/*p*-xylene shows the following phase behavior (see Fig. 3).

PC/dodecane/*p*-xylene is a solvent system with a closed mixture gap, which shows a strong temperature dependence. The possible operating points are defined by the area between the two binodal curves at the temperatures of 25 and 80 °C.

Another important point is the behavior of the starting olefin and the generated aldehydes in this temperature-controlled system. To investigate this effect we added a constant amount of *trans*-4-octene to the solvent system (0.15 g *trans*-4-octene/g of the two-phase system PC/dodecane) and measured it again at 80 °C, the starting point of the reaction. To insure phase separation after the reaction, we added *n*-nonanal to the solvents (0.17 g *n*-nonanal/g of the two-phase system PC/dodecane) and measured again at 25 °C. This more realistic TMS-system is presented on the right side of Fig. 3.

As it can be seen, the addition of *trans*-4-octene does not affect the position of the binodal curve at all. On the other side, the addition of *n*-nonanal has a significant influence on the solvent system. The two binodal curves move closer to each other which results in a diminished working area.

The isomerizing hydroformylation of *trans*-4-octene has been executed in PC/dodecane/*p*-xylene with varying compositions of the three solvents. The phase diagram with the corresponding working points is presented in Fig. 4.

The conversion of *trans*-4-octene is very high in this TMS-system and reaches a level of 99%. The selectivity to the desired linear aldehyde amounts to about 90% and is higher compared to the two-phase catalysis with in situ extraction (Section 2.1.1) or with addition of methylated β-cyclodextrin (Section 2.1.2). Further the *n*-selectivity

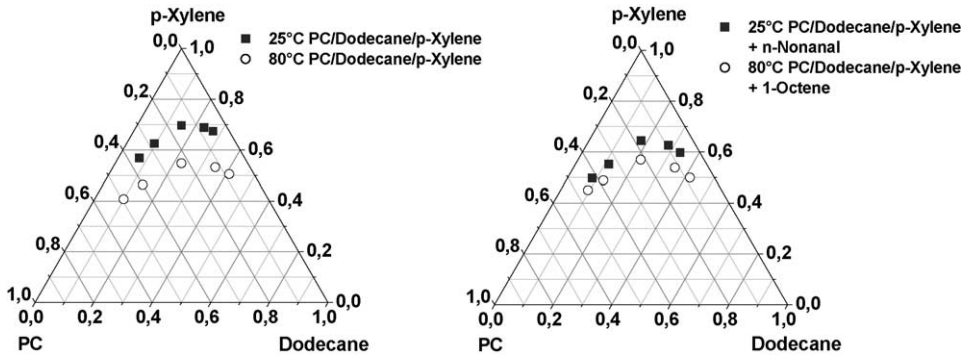
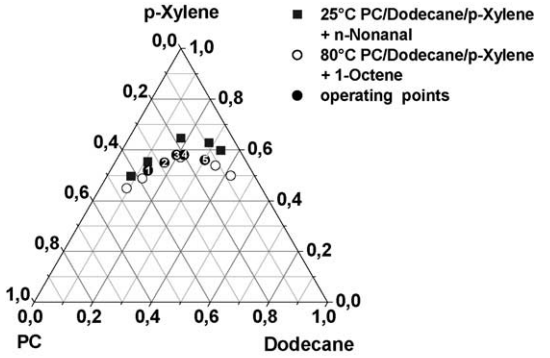


Fig. 3. Solvent system propylene carbonate (PC)/dodecane/*p*-xylene.



PC/Dodecane/p-Xylene [wt.-%]	Selecitivity (n-Nonanal) [%]
Point 1: 35/13/52	90
Point 2: 28/17/55	86
Point 3: 22,5/19,5/58	90
Point 4: 20/22/58	79
Point 5: 14/30/56	82

Fig. 4. Isomerizing hydroformylation of *trans*-4-octene in the TMS-system PC/dodecane/*p*-xylene.

increases with a higher PC-concentration in the solvent system. This is once more a very illustrating example for the high influence of propylene carbonate on the *n*-selectivity in the isomerizing hydroformylation of *trans*-4-octene.

2.3. Mechanistic considerations

The isomerization of the starting olefin *trans*-4-octene can potentially be explained by a rhodium mechanism, which is shown in Fig. 5. We suppose that propylene carbonate with its three strongly electron withdrawing oxygen atoms has the possibility to interact with the β-hydride atoms of the σ-rhodium-complex. This interaction leads to a weakening of the H–C bond which results in a faster β-hydride elimination. Faster β-hydride elimination means faster isomerization and a faster isomerization means higher linearity of the oxo-products.

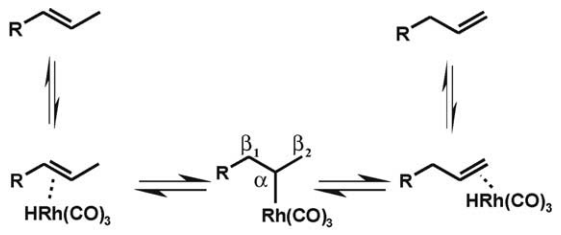


Fig. 5. Proposal on the isomerization of the internal to the α-olefin.

3. Conclusions and outlook

It could be shown that the isomerizing hydroformylation of *trans*-4-octene in a two-phase solvent system of propylene carbonate (PC) and dodecane leads to very high conversions of 95% of the olefin. In this biphasic reaction system the selectivity of *n*-nonanal decreases to a level of around 70%. The addition of catalytic amounts of methylated β-cyclodextrin does not have a great influence on the selectivity of the *n*-nonanal.

The thermomorphic TMS-system PC/dodecane/*p*-xylene leads to very high conversions (99%) of the *trans*-4-octene and also to very attractive selectivities of *n*-nonanal ranging from 79 to 90%. This selectivity is dependant on the concentration of the used PC: the higher this concentration, the higher the selectivity of *n*-nonanal. This significant influence of the PC on the selectivity can be explained by electronic effects of the carbonate group.

Although this contribution describes an excellent TMS-system, it has to be stated that these systems are far from being ready for industrial use. Via ICP-investigations we observed a strong rhodium leaching of 47% of the rhodium catalyst. Furthermore we observed a correlation between the amount of the solvation mediator *p*-xylene and the amount of leaching. The more *p*-xylene is used, the more rhodium is transferred into the unpolar dodecane phase. Therefore, catalyst recycling in these systems is impossible at the moment.

In the next steps of our investigations we will have to find other mediators, which show no solvation inside the product phase at all. This should lead to a much lower leaching of the rhodium catalyst.

4. Experimental

The phosphite ligand BIPHEPHOS was synthesized according to [24–26].

In a standard reaction we used the following amounts of chemicals:

- *Single-phase systems*: 26 mg (0.1 mmol) [Rh(acac)(CO)$_2$], 393 mg (0.5 mmol) BIPHEPHOS, 2420 mg (19.4 mmol) *trans*-4-octene, 20 ml toluene.
- *Biphasic systems*: 26 mg (0.1 mmol) [Rh(acac)(CO)$_2$], 393 mg (0.5 mmol) BIPHEPHOS, 2420 mg (19.4 mmol) *trans*-4-octene, 0.2–2.0 mol% randomly methylated beta-cyclodextrin (Cavasol® W7M, positions 2, 3 and 6 are randomly methylated) from Wacker Chemie GmbH (Wacker Specialties), 20 ml propylene carbonate, 20 ml dodecane.
- *TMS-systems*: 26 mg (0.1 mmol) [Rh(acac)(CO)$_2$], 393 mg (0.5 mmol) BIPHEPHOS, 2420 mg (19.4 mmol) *trans*-4-octene, 30 g (propylene carbonate + dodecane + toluene).

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References

[1] K. Weissermel, H.J. Arpe, Industrial Organic Chemistry, 4th ed., Wiley–VCH, 2003.
[2] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Catal. A: Chem. 104 (1995) 17.
[3] A. Goethlich, P. Hofmann, W. Ahlers, R. Paciello, M. Röper, M. Tensfeldt, BASF, German Patent DE 10101939A1 (2002).
[4] D. Hess, R. Kadyrov, D. Selent, A. Börner, D. Röttger, Oxeno, German Patent DE 10031493A1 (2002).
[5] H. Bohnen, J. Herwig, Celanese, German Patent DE 10108475A1 (2002).
[6] H. Bohnen, J. Herwig, Celanese, German Patent DE 10108474A1 (2002).
[7] H. Bohnen, J. Herwig, Celanese, German Patent DE 10108476A1 (2002).
[8] W. Ahlers, M. Bartsch, R. Baumann, R. Paciello, D. Wiebelhaus, D. Vogt, A. Hewat, BASF, German Patent DE 10046026A1 (2002).
[9] L. van der Veen, P. Kamer, P. van Leeuwen, CATTECH 6 (2002) 116–120.
[10] L. van der Veen, P. Kamer, P. van Leeuwen, Angew. Chem. 111 (1999) 349.
[11] L. van der Veen, P. Kamer, P. van Leeuwen, Organometallics 18 (1999) 4765–4777.
[12] D. Selent, W. Baumann, K. Wiese, A. Börner, Organometallics 22 (2003) 4265–4271.
[13] D. Selent, W. Baumann, K. Wiese, A. Börner, Angew. Chem. 113 (2001) 1739–1741.
[14] D. Selent, W. Baumann, K. Wiese, A. Börner, Angew. Chem. 112 (2000) 1694–1696.
[15] R. Jackstell, H. Klein, M. Beller, K. Wiese, D. Röttger, Eur. J. Org. Chem. (2001) 3871–3877.
[16] H. Klein, R. Jackstell, K. Wiese, C. Borgmann, M. Beller, Angew. Chem. 113 (2001) 3505–3508.
[17] A. Behr, D. Obst, C. Schulte, T. Schosser, J. Mol. Catal. A: Chem. 197 (2003) 115.
[18] C. Fängewisch, A. Behr, Chem. Eng. Technol. 25 (2002) 143–147.
[19] A. Behr, C. Fängewisch, J. Mol. Catal. A: Chem. 197 (2003) 115–126.
[20] S. Tilloy, F. Bertoux, A. Mortreux, E. Monflier, Catal. Today 48 (1999) 245–253.
[21] E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, Angew. Chem. Int. Ed. Eng. 34 (1995) 2269–2271.
[22] T. Mathivet, C. Méliet, Y. Castanet, A. Mortreux, L. Caron, S. Tilloy, E. Monflier, J. Mol. Catal. A: Chem. 176 (2001) 105–116.
[23] E. Monflier, H. Bricout, F. Hapiot, S. Tilloy, A. Aghmiz, A.M. Masdeu-Bultó, Adv. Synth. Catal. 346 (2004) 425–431.
[24] F. Hewgill, D. Hewitt, J. Chem. Soc. C: Org. (1967) 726.
[25] G. Cuny, S.L. Buchwald, J. Am. Chem. Soc. 115 (1993) 2066.
[26] Y. Butsugan, M. Mute, M. Kawai, S. Araki, Y. Murase, K. Saito, J. Org. Chem. 54 (1989) 4215.