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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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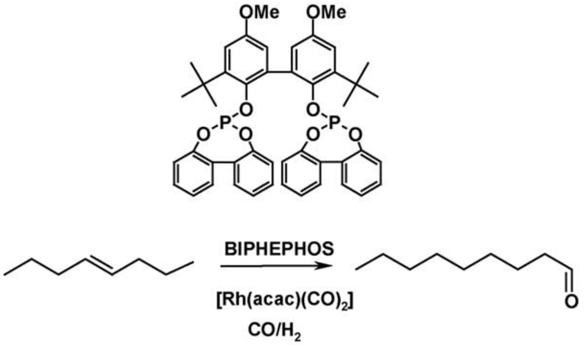

Fig. 1. Isomerizing hydroformylation of *trans*-4-octene to *n*-nonanal.

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