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Feature Article

Isomerization/hydroformylation tandem reaction of a decene isomeric mixture with subsequent catalyst recycling in thermomorphic solvent systems

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ABSTRACT

Herein we report about an efficient isomerization/hydroformylation tandem reaction to convert a technical mixture of decene isomers selectively into the linear undecanal in a thermomorphic solvent system. By applying a rhodium/BIPHEPHOS catalyst a high turnover frequency of 375 h^{-1} and high regioselectivity of 92% for the linear product are achieved. Yields up to 70% of the linear aldehyde are obtained. The catalyst can be successfully separated from the product using a thermomorphic solvent system consisting of dimethyl formamide (catalyst phase) and dodecane (product phase). The leaching of the rhodium (0.6% of the initial amount) and phosphorus (1.2% of the initial amount) is very low. The catalyst was successfully recycled five times.

1. Introduction

The hydroformylation is the most important reaction for the homogeneously catalyzed synthesis of linear aldehydes, which are intermediates of high interest in the chemical industry (e.g. in the synthesis of surfactants, plasticizers or perfumes) (Fig. 1a). Essentially, linear as well as branched aldehydes can be synthesized from a terminal double bond. The hydroformylation of internal double bonds leads to the formation of branched aldehydes. Often the linear aldehydes are of particular interest in technical chemistry. Unfortunately, technical grade olefin feedstocks are often complex mixtures of different olefin isomers, predominately internal olefins. In order to convert these mixtures into linear aldehydes a tandem reaction sequence of double bond isomerization and highly *n*-selective hydroformylation is necessary (Fig. 1b).

For the realization of this reaction sequence the catalyst plays a crucial role. In consequence, much effort was taken into catalyst development. Several metals like Co, Rh, Ru, Pd, Pt, Ir and iron were tested in combination with different ligands [1]. However, the best results are obtained using rhodium as metal in combination with chelating phosphorous ligands like BISBI and IPHOS [2], XANTPHOS-type ligands [3,4], BIPHEPHOS-type ligands (also in solvent mixtures) [5–9], H_8-BINOL-derived diphosphite ligands [10], or electronical nonsymmetric acylphosphite ligands [11]. Very good results are also obtained by application of hemilabile ligands [12], anthracenetriol-based triphosphite ligands [13] or tetraphosphorus ligands (for details see [1]). However, all of the above mentioned catalysts have in common, that they use expensive noble metals and tailored ligands, which makes them very expensive. For that reason, catalyst recycling is an essential step in the development of economical processes from an industrial point of view. Compared to the development of suitable catalysts for the isomerization – hydroformylation tandem reaction, their separation and reuse has attracted less attention in academic research. To the best of our knowledge there is only one example for an isomerizing

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Abbreviations: TMS, thermomorphic solvent systems; TOF, turnover frequency; DMF, *N*,*N*-dimethylformamide; 1, isomeric decene mixture; 3, branched C11 aldehydes; 2, undecanal; 4, decane; BP, highboiling byproducts; v%, volume percentage.

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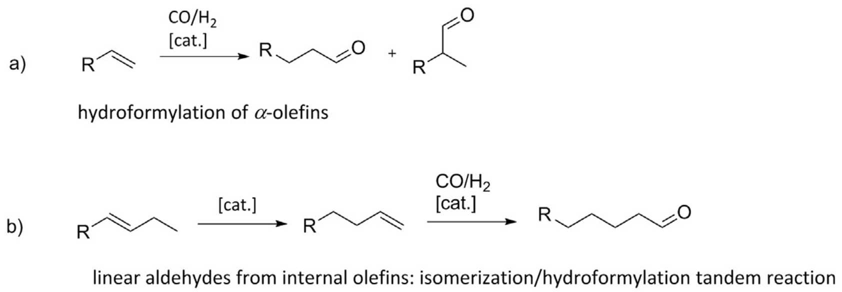

Fig. 1. Hydroformylation and isomerization – hydroformylation tandem reaction.

hydroformylation of higher olefins with a high regioselectivity and a successful catalyst recycling [14].

While techniques like product distillation are well suited for separating homogeneous catalysts from low boiling products, the distillation of higher aldehydes requires high temperatures, which often shortens the lifetime of the temperature sensitive catalysts. One other approach for catalyst recycling is the immobilization of the catalyst on a solid carrier or in liquid phase. There are examples for the cobalt/TPPTS catalyzed isomerization – hydroformylation of 2-pentene [15] and technical decene mixtures [16] in aqueous biphasic solvent systems, where the catalyst is immobilized in the aqueous phase. Also a rhodium/TPPTS catalyzed conversion of olefins present in the light-light cracked naphtha in water [17] and a rhodium/XANTphos-type ligand catalyzed hydroformylation of 2-octene in ionic liquids [18] are described. Unfortunately, these catalysts show relatively low *n*-selectivity (between 50% and 75%) in the hydroformylation step.

In order to achieve a highly *n*-selective hydroformylation, Beller et al. used a rhodium/BINAS catalyst for the hydroformylation of isomeric octene mixtures in an aqueous solvent system, which shows a very high regioselectivity (*n/iso* 98:2). The catalyst is immobilized in water [14]. The turnover frequency (TOF) decreases with increasing chain length of the substrate (TOF 113 h^{-1} for 2-butene, TOF 29 h^{-1} for octene mixtures).

Despite the use of water as solvent in industrial plants is very attractive from an economic and ecologic point of view, the conversion of higher olefins in water usually suffers from mass transfer- and solubility limitations, which is displayed by the relatively low TOF values of 29 h^{-1} for higher olefins reported in literature.

One approach to overcome these limitations is the use of thermomorphic solvent systems (TMS systems). The idea of these systems is to take advantage of the temperature dependent miscibility gap of a mixture of a polar and a non-polar solvent. While the substrate and the product are better soluble in the non-polar solvent, the catalyst has a high solubility in the polar solvent. Heating the solvent system to reaction temperature leads to the formation of one single homogeneous reaction mixture overcoming mass transfer and solubility limitations during the reaction. Cooling after reaction initiates phase separation and the polar, catalyst containing phase can be separated from the non-polar product phase via simple decantation (Fig. 2) [19,20].

The TMS system offers several advantages compared to other catalyst immobilization strategies like a homogeneous reaction mixture (no mass transport and solubility limitations during the reaction), straightforward catalyst separation via decantation after reaction and the use of cheap commercially available solvents. Usually, there is no need to modify the catalyst, which is of great advantage since catalyst modification means higher prices and, not unusual, lower activities [22]. The concept of TMS systems was already successfully applied in the hydroformylation of long chained olefins [23–25]. The hydroformylation of 1-dodecene in a thermomorphic solvent system consisting of *N,N*-dimethylformamide (DMF) and decane using a rhodium/BIPHEPHOS catalyst was already successfully transferred into a continuously operated miniplant [26].

Fig. 3 shows the examples from literature for the isomerization – hydroformylation tandem reaction achieving high selectivity towards the linear aldehydes with subsequent catalyst separation, which are already realized. To the best of our knowledge, there is only one example for the isomerization – hydroformylation tandem reaction (synthesis of *n*-hexanal from 2-pentene) demonstrating a recyclability of the catalyst. This work describes the highly selective tandem isomerization – hydroformylation to convert a mixture of decene isomers into undecanal with relatively high turnover frequencies in a TMS system with subsequent catalyst recycling.

2. Materials and methods

2.1. Chemicals

DMF (>99%), octane (99%), heptane (>99%) and cyclohexane (>99%) were purchased from Acros Organics. Cyclooctane (98%) was purchased from Sigma Aldrich. Dodecane (>99%) and undecanal (97%) were purchased from TCI Chemicals. Nonane (99%) was purchased from Alfa Aesar. BIPHEPHOS (>95%) was purchased from Molisa GmbH. $Rh(CO)_2acac$ was donated by Umicore. The technical decene mixture was donated by Sasol. All chemicals were degassed before use and stored under argon. CO (2.0) and H_2 (5.0) were purchased from Messer Industriegase GmbH.

2.2. Reaction in a 20 mL autoclave

The precursor $Rh(CO)_2acac$ and BIPHEPHOS were weighted and added in a homemade 20 mL autoclave. The autoclave was closed, evacuated and flushed with Argon three times. Afterwards degassed DMF, non-polar solvent and decene mixture were transferred into the reactor via cannula using standard Schlenk technique. The reactor was pressurized with synthesis gas and heated under stirring to reaction temperature. After reaction time the reactor was cooled in an ice bath and the pressure was released carefully. The reaction mixture was analyzed via GC-FID.

2.3. Reaction in a 300 mL autoclave

The precursor $Rh(CO)_2acac$ and BIPHEPHOS were weighted and added into a 300 mL autoclave (Parr Instruments). The autoclave was closed, evacuated and flushed with Argon three times. Afterwards the reactor was evacuated again and degassed DMF, non-polar solvent and decene mixture were transferred into the autoclave via vacuum using standard Schlenk technique. The reactor was pressurized with synthesis gas and heated to reaction temperature under stirring. For time-resolved experiments samples of the reaction solution were taken via a capillary from inside the reactor and analyzed via GC-FID. After reaction time the reactor