

Isomerization / Hydroformylation of Fatty Acid Methyl Esters – Development of a New Bimetallic Tandem Catalytic System

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Abstract

Through the implementation of renewable raw materials, the chemical industry is able to design environmentally friendly and sustainable processes. Because of their long hydrocarbon chains and their relatively low number of functional groups, fatty compounds are particularly suitable for the substitution of conventional polymer precursors from fossil raw materials.^[1] Starting from fatty acid methyl esters (FAMES), different reactions are possible to produce ω -functionalized molecules. On the one hand selfmetathesis of internal or terminal fatty compounds or cross metathesis of those with short chained unsaturated esters and on the other hand the palladium catalysed isomerization / methoxycarboxylation of internal fatty compounds can be used for the formation of diesters.^[2] Beyond these reactions, isomerization / hydroformylation offers the possibility of the synthesis of α,ω -functionalized aldehyde esters, e.g. from methyl oleate **1** (Figure 1).^[2] E.g. by oxidation, hydrogenation or reductive amination many different polymer precursors are accessible from these high-potential intermediates. Former research concentrated on the development of single, auto-tandem catalysts for both reactions, hydroformylation and isomerization, with limited yields of only 26% for the linear aldehyde ester **3**.^[3]

Herein we present a new orthogonal tandem catalytic system for the homogeneously catalyzed isomerization / hydroformylation of FAMES. With the help of model substrates, we developed a highly active and regioselective catalytic system which consists of a palladium based isomerization catalyst and a rhodium based hydroformylation catalyst. Finally, the catalytic system is successfully transferred to the substrate methyl oleate **1**. At conversions of 99% yields of 74% and outstanding regioselectivity of 91/9 are achieved.^[4] These are the highest yields and selectivities yet reported in literature.^[3]

In conclusion, the developed orthogonal catalytic system for the isomerization / hydroformylation of methyl oleate is a promising way to produce polymer precursors from renewable resources.

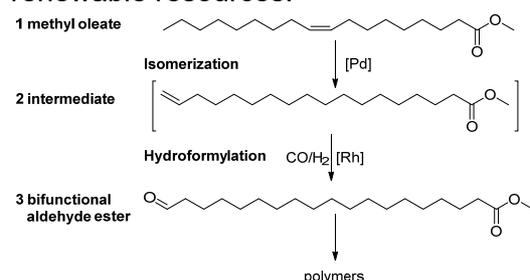


Figure 1: Reaction scheme for methyl oleate.

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