

Catalyst and Process Development for Production of Oleochemicals from Palm Oil Using High Throughput Experimentation

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Introduction

Palm oil and palm kern oil are commonly used as starting materials for the production of C₁₂ – C₁₈ fatty alcohols, via hydrogenation / hydrogenolysis of fatty acids and fatty esters [1]. These fatty alcohols are well-known intermediates for the production of surfactants, soaps and additives for lubricants. The production of upgraded oleochemicals such as higher aliphatic alcohols from palm oil is, however, a major challenge due to the severe reaction conditions required.

Toxic copper-chromium catalysts are the standard materials used to carry out the hydrogenation reaction in commercial processes, that usually take place at temperatures as high as 200 – 300°C and H₂ pressures up to 200 – 300 bar [2-5]. The goal of the described project was to develop novel Cr-free catalysts for the production of fatty alcohols from palm oil derived raw materials that would allow operation under milder conditions, i.e. under reduced pressure and possibly at lower temperature. Using High-Throughput tools such as parallel catalyst preparation platforms and parallel catalyst testing units, together with rational experimental designs, novel Cr-free catalysts with high potential, i.e. operating at low pressure and relatively low temperature, were successfully developed [6].

Materials and Methods

The catalysts investigated were prepared by incipient wetness impregnation, amorphous drying or co-precipitation using Avantium's parallel catalyst preparation platforms. The catalysts were pre-treated with hydrogen in the pre-treatment unit consisting of 12 parallel reactors with glass bulbs, controlled gas feed and temperature control (up to 650°C). Catalyst screening and optimization (Phases 1 and 2, respectively) were performed in Avantium's high-pressure reactor platform, consisting of 12 parallel batch reactors that can operate up to 200 bar and 350°C. Methyl laurate (Fluka, > 97%) was used as a model feed and the reaction products were analyzed by GC. The best catalysts identified in Phases 1 and 2 were tested under industrially relevant continuous trickle flow conditions, in parallel fixed-bed reactors that can operate up to 100 bar and 550°C.

Results and Discussion

In the Phase 1 of the project, the screening of over 700 catalysts was carried out at 100 bar and 250°C in high pressure slurry reactors for the hydrogenation of methyl laurate. Various catalyst preparation methods and parameters such as (i) the type of support, (ii) the metal loading, (iii) the metal ratio for bimetallic materials, (iv) the salt precursor, (v) the effect of noble metal promoters, and (vi) the pH of the salt solution were investigated. This screening phase enabled the identification of parameters favorable in obtaining catalysts displaying a

high activity: (i) the use of particular supports (see Fig. 1) resulted in catalysts with the best performance, (ii) for some catalysts, impregnation with noble metals improved the activity and resulted in a higher productivity of lauryl alcohol per gram of catalyst, (iii) the catalyst synthesis based on metal nitrate solutions with citric acid at pH 7 was the best preparation method for the CuFe and CuZn catalysts, (iv) the catalyst synthesis based on metal citrates in ammonia resulted in highly active and selective CuZn catalysts.

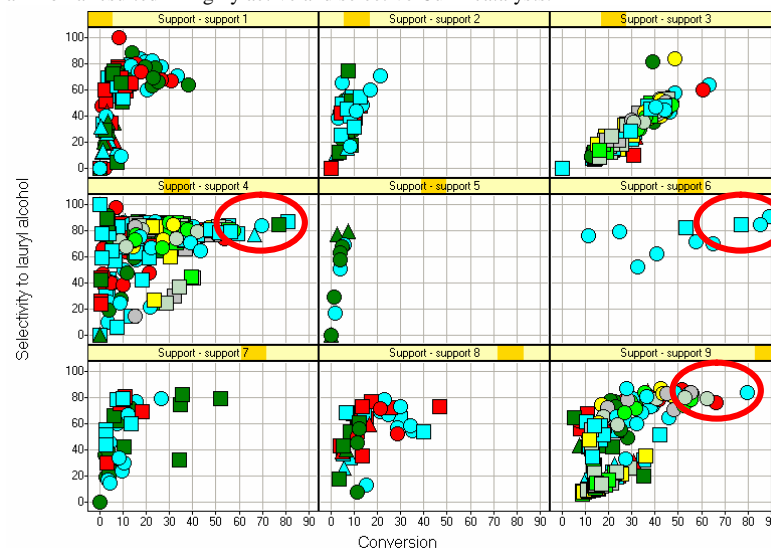


Figure 1. Influence of the support on the hydrogenolysis of methyl laurate to lauryl alcohol carried out at 100 bar and 250°C. Mono-, bimetallic and trimetallic catalysts: color by metal 3; shape by metal 2.

In the next Phase 2, eight catalysts identified in the screening phase were optimized for the liquid phase hydrogenolysis of methyl laurate to lauryl alcohol using a rational design of experiments (DoE). All variables of interest were grouped into three different designs: a preparation DoE (including the metal ratio, metal loading and promoter concentration; Fig. 2), an activation DoE (including the calcination and reduction temperature) and a process DoE (including the pressure, temperature and run time).

The experimental designs were used to gain an understanding of how variations in synthesis, pre-treatment and process parameters affect the catalyst performance. The correlation between these variables and responses as described by a response surface model (RSM), allowed identification of the optimum synthesis, pre-treatment and process conditions for the conversion of methyl laurate to lauryl alcohol. To limit the number of experiments several RSMs were generated for each component of the process (catalyst synthesis, pre-treatment, process conditions). The groups were studied separately, which means that interactions

between the different parameter groups were not visible. This approach can be considered adequate if the interactions between the different groups of variables are expected to be negligible.

Thanks to the optimization of the composition of the starting catalysts carried out in the Phase 2, an improvement by up to 80% in the alcohol productivity was achieved compared to the productivity obtained in Phase 1. Optimization of the catalyst pretreatment procedure further improved the catalyst performance by up to 53%. Additional improvement in alcohol productivity was observed after optimization of the test conditions. All catalysts had the highest productivity at 275°C and 125 bar.

In the last phase, high throughput experiments were carried out under trickle phase conditions in order to directly compare the novel catalyst performance to industrially applied commercial catalysts. A catalyst ranking performed for several reaction conditions (Table 1) highlighted the promising behavior of Avantium's newly developed catalysts.

Table 1. Catalyst ranking at 250°C and 50 bar in the hydrogenolysis of methyl laurate to lauryl alcohol and of methyl myristate to myristic alcohol

Ranking	Catalyst code	H ₂ /Ester ratio	LHSV (h ⁻¹)	Yield, both alcohols %	Selectivity, both alcohols %
1	CuZn-Pt Catalyst 1	95	5	100.00	100.00
2	CuZn-Ni Catalyst	50	5	100.00	100.00
3	CuZn-Rh Catalyst	95	2	99.24	99.24
4	CuZn-Ru Catalyst 1	95	2	99.10	99.17
5	CuZn-Pt Catalyst 2	50	5	98.31	98.71
6	CuZn-Ru Catalyst 2	95	2	98.20	98.42
7	Commercial Catalyst 8 (CuAlZn)	50	2	98.15	98.15
8	CuZn-Pd Catalyst	95	2	97.99	97.99
9	Commercial Catalyst 4 (CuAlMn)	95	2	97.74	97.92
10	Commercial Catalyst 9 (CuMnZn)	95	5	97.71	97.71

In all, this program resulted in the identification of a novel catalyst family with high potential in the hydrogenation / hydrogenolysis of fatty esters to fatty alcohols [6]. The performance of these materials was found to strongly depend on their composition as well as on their method of preparation. The best novel catalysts resulted in similar or higher yields, and higher selectivity to alcohols, than the best commercial catalysts.

Significance

Potential benefits such as a reduction in utility cost and a reduction in capex investment (possibility to operate at lower pressure) could be expected from the use of Avantium's catalyst in industrial processes.

References

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