# Coupling Of Heck And Hydrogenation Reactions In A Continuous Compact Reactor

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Introduction

Performing selective catalytic reactions of fine synthesis under flow conditions is an actively developing area of strong industrial relevance, often designated as 'flow chemistry'. In our earlier studies we have demonstrated the effectiveness of a compact (mm-scale channel hydraulic diameter) multifunctional reactor system in reactions of selective oxidation [1] and reduction [2]. The main benefits of the compact flow reactor were in establishing effective mass and heat transfer regimes, thus ensuring safe operation using pure oxygen or hydrogen at high conversions. In this work we are extending the functionality of this reaction system to C-C coupling reaction and performing sequential reactions of C-C coupling and hydrogenation, Scheme 1.
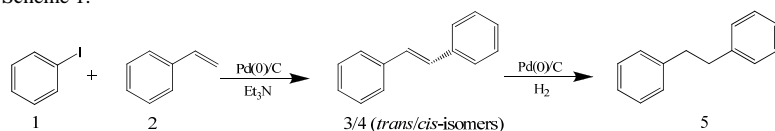
Scheme 1. Consecutive synthesis of dibenzyl 5 involving Heck C-C coupling followed by hydrogenation.

Materials and Methods

In this study the compact multifunctional reactor described elsewhere [1] has been used. Reactor was configured to have C-C coupling section packed with Pd/C catalyst and purged with nitrogen, followed by hydrogenation section, packed with Pd/C catalyst. Nitrogen was used in the first section to avoid the side hydrogenation reactions competing with C-C coupling reactions. Pd/C catalyst was synthesized using synthetic mesoporous carbon support obtained from MAST Carbon Ltd.

Results and Discussion

C-C coupling and hydrogenation reactions were first investigated separately in batch and in flow conditions. For both reactions flow conditions gave higher overall productivity (in terms of volumetric yield) at the same selectivity. A higher selectivity to C-C coupling products was obtained under flow conditions.

C-C coupling reaction necessarily leads to leaching of Pd, due to the mechanism of reaction. This requires the presence of a scavenger support in the second reaction module. The sequential C-C coupling – hydrogenation reactions were performed under flow conditions reversing the flow through the reactor, thus recovering the leached catalyst. Successful two sequential reactions are shown in Fig. 1.
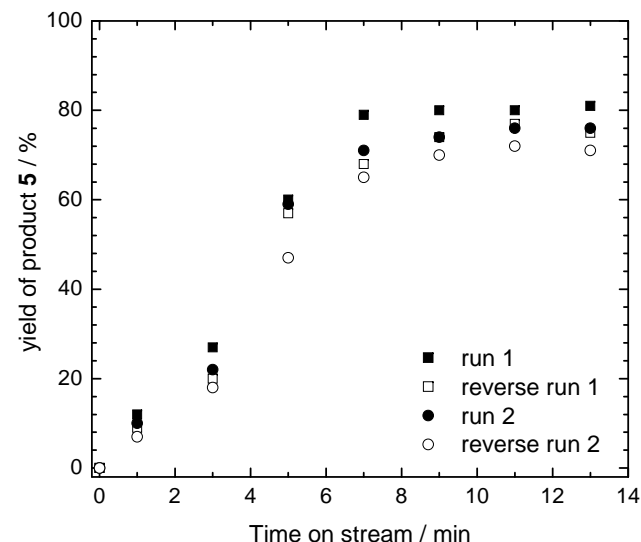

Figure 1. Time yield of dibenzyl **5** for forward and reverse flow runs. Reaction conditions: initial concentration of **1** (in EtOH) = 0.4 mol l^{-1}, reaction temperature 120 °C, F_{liquid} = 0.20 ml min^{-1}, $F_{hydrogen}$ = 8 ml min^{-1}, four channels in series, approximately 0.9 g catalyst for Heck reaction, approximately 0.75 g catalyst for the alkene hydrogenation.

Significance

The significance of this work is in the demonstration of the feasibility of performing C-C coupling reactions in flow, despite the leaching of Pd from catalyst, and demonstrating the sequential C-C coupling – hydrogenation reaction in flow using periodic flow reversal operation, which allows to avoid the loss of Pd from the system.

References

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2. Fan, X., H. Chen, Y. Ding, P.K. Plucinski, A.A. Lapkin, Potential of "nanofluids" to further intensify microreactors. *Green Chem.* 10, (6), 670-677 (2008).