

Parameter Screening in Process Development: Ligand-free Heck Reactions



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General

- Search for the best oxidizing agent to reactivate the precipitated Pd⁰ catalysts.
- Test the reactivated Pd catalysts in several successive catalytic cycles.

Reaction Sketch

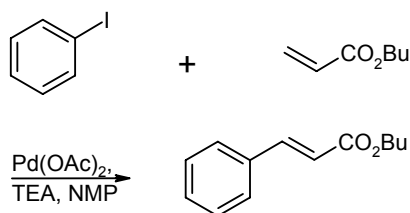


Figure 1

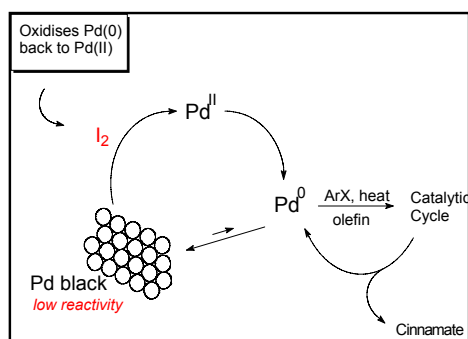


Figure 2: Reactivation cycle of the Pd catalyst

Reaction characteristics

- No ligands were used for the Pd catalyst
- 0.1 – 0.25 mol% catalyst loading
- Fast and with high selectivity to the product
- Precipitation of the palladium catalyst after the reaction and recovery with Celite
- Reactivation of Pd⁰ to restore activity

Experimental Set-Up

- Experiment was performed on a Chemspeed ASW 2000 equipped with one 13 mL filtration reaction block.
- The Heck reaction was performed on the filter side, where the Pd precipitated on the supporting agent Celite.
- After filtering off the reaction mixture, the precipitate was washed with methyl-*tert*-butylether.
- The reactivators (oxidizing agents) were added, followed by the reagents for the next Heck cycle (Fig. 2).

Results

- The scope of the best reactivating agent has been determined in a single run.
- Only bromine and iodine restore the catalytic activity (Fig. 2).
- Oxidizing agents such as hydrogen peroxide, HI, NaIO₄ are detrimental.
- The results for iodine as reactivator obtained on the Chemspeed synthesizer is completely comparable to classical experiments (Fig. 3).
- In parallel and with a single run, the optimal oxidizing agent for reactivating the Pd catalyst used in a ligand-free Heck reaction has been found.
- Easy reactivation of the Pd catalyst makes the ligand-free Heck reaction a valuable and cost decreasing process for the production of fine chemicals.

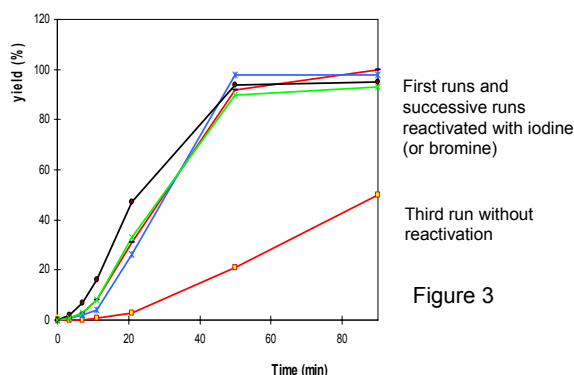


Figure 3

Summary

- By using the Chemspeed synthesizer (Fig. 4), DSM has developed a method to decrease the Palladium costs in Heck type reactions.



Figure 4



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