Heck Reaction Under Heterogeneous Pd Catalyst Systems and Application into Continuous-flow Reactions

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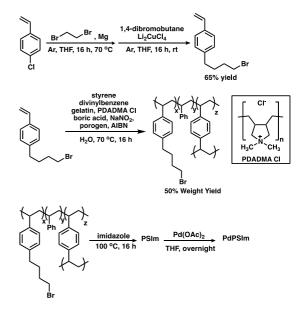
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Mizoroki-Heck reaction, as a facile method to form multiply substituted alkenes, is widely utilized in chemical industry including pharmaceutical manufacturing. Current interests in this chemistry are focusing on catalysis with designing precise ligands to attain high catalyst turnover. Despite strong demands on carrying out this process under heterogeneous catalytic conditions, effective methods beyond homogeneous counterparts accompanying advantages on solid-phase catalysts are still very limited, and only a few examples of reactions under heterogeneous catalytic continuous-flow conditions using catalyst-packed column reactors were reported.

In this study, heterogeneous palladium catalysts for Mizoroki-Heck reaction toward continuous-flow vinyl arene production were investigated by utilizing a porous polymer approach. A porous polymer-bound imidazolinium was designed as a scaffold of heterogenization of palladium through non-bonding interaction. To install a sufficient hydrophobic environment around functional groups in the target polymer, 4-(4-

bromobutyl)styrene was prepared and utilized as a comonomer^[1], and various polymerization conditions were tested to obtain an optimal porous polymer. Immobilization of palladium was successfully conducted by simply mixing Pd(OAc)₂ and a imidazolinium polymer^[2] with or without ligands. The resulting Pdimmobilized polymer was tested in the titled reaction between aryl iodides and olefins. In this presentation, we will also mention about application of these catalysts synthesized into continuous-flow reactions.



1) Kubota, H., Kudo, K., Watanabe, J. JP 11060519A.

2) Mahmoudi, H. et al., Green Chem., 2019, 21, 355.