

Heterogeneous Catalytic Systems for Organic Chemical Transformations

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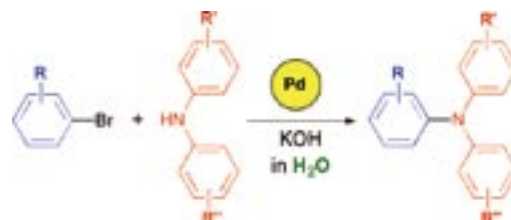
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Various organic molecular transformations catalyzed by transition metals were achieved under heterogeneous conditions by use of amphiphilic resin-supported palladium complexes, palladium membrane-installed microchannel devices, or self-supported bipyridyl-palladium complexes which were designed and prepared by this research group. In particular, Buchwald-Hartwig reaction, Suzuki-Miyaura coupling, and aerobic alcohol oxidation, which were performed in water under heterogeneous conditions with high recyclability of the polymeric catalysts, are highlights among the achievements of the 2009–2010 period to approach what may be considered ideal chemical processes of next generation. Representative results are summarized hereunder.

1. Clean Synthesis of Triarylamines: Buchwald-Hartwig Reaction in Water with Amphiphilic Resin-Supported Palladium Complexes^{1,2)}

Catalytic aromatic amination was achieved in water under heterogeneous conditions by the use of immobilized palladium complexes coordinated with the amphiphilic polystyrene-poly(ethylene glycol) resin-supported di(*tert*-butyl)phosphine ligand. Aromatic amination of aryl halides with diphenylamine and *N,N*-double arylation of anilines with bromobenzene were

found to proceed in water with broad substrate tolerance to give the triarylamines in high yield with high recyclability of the polymeric catalyst beads. Very little palladium leached from the polymeric catalyst under the water-based reaction conditions to provide a green and clean (metal-uncontaminated) protocol for the preparation of triarylamines, including the optoelectronically active *N,N,N',N'*-tetraaryl-1,1'-biphenyl-4,4'-diamines (TPDs).

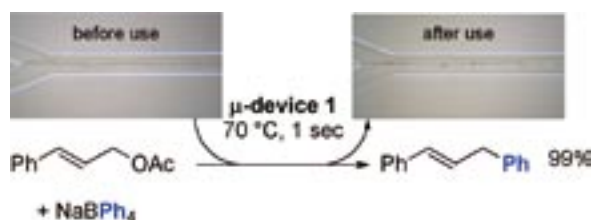


Scheme 1. Buchwald-Hartwig Reaction in Water with Amphiphilic Resin-Supported Palladium Complexes.

2. Palladium Membrane-Installed Microchannel Devices for Instantaneous Suzuki-Miyaura Cross-Coupling and Allylic Arylation^{3,4)}

Instantaneous catalytic carbon-carbon bond-forming reac-

tions were achieved in catalytic membrane-installed microchannel devices that have a polymeric palladium-complex membrane. The catalytic membrane-installed microchannel devices were provided inside the microchannels by means of coordinative and ionic molecular convection at the interface between the organic and aqueous phases flowing laminarly, in which both non-crosslinked linear polymer ligands and palladium species dissolved. The palladium-catalyzed Suzuki–Miyaura reaction of aryl, heteroaryl, and alkenyl halides with arylboronic acids and sodium tetraarylborates was performed with the catalytic membrane-installed microchannel devices to give quantitative yields of biaryls, heterobiaryls, and aryl alkenes within 5 s of residence time in the defined channel region. These microchannel devices were applied to the instantaneous allylic arylation reaction of allylic esters with arylboron reagents under microflow conditions to afford the corresponding coupling products within 1 s of residence time.



Scheme 2. Instantaneous Allylic Arylation with Palladium Membrane-Installed Microchannel Devices.

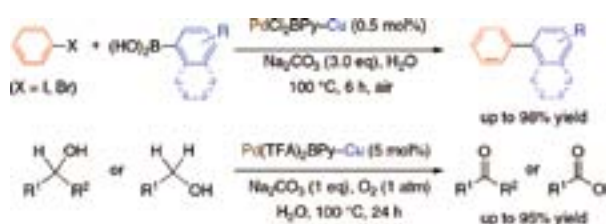
3. Suzuki–Miyaura Coupling and Aerobic Alcohol Oxidation in Water with Self-Supported Bipyridyl–Palladium Complexes^{5,6)}

Self-supported bipyridyl–palladium catalysts ($\text{PdX}_2\text{BPy–Cu}$) were developed *via* construction of metal–organic frame-

works (MOFs) of bipyridyl–palladium complexes bearing carboxylic groups and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Scheme 3). The self-supported catalysts efficiently catalyzed the aerobic oxidation of benzylic alcohols and the Suzuki–Miyaura coupling of phenyl halides with arylboronic acids in water to give the corresponding products in high yield (Scheme 4). The catalysts were reused without a loss of catalytic activity.



Scheme 3. Preparation of Self-Supported Bipyridyl–Palladium Complexes *via* Construction of Metal–Organic Frameworks (MOFs).



Scheme 4. Suzuki–Miyaura Coupling and Aerobic Alcohol Oxidation in Water with Self-Supported Bipyridyl–Palladium Complexes.

References

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Awards

UOZUMI, Yasuhiro; The 26th Inoue Prize for Science.
HAMASAKA, Go; CSJ Presentation Award 2010.