

# Heterogeneous Catalytic Systems for Organic Chemical Transformations in Water

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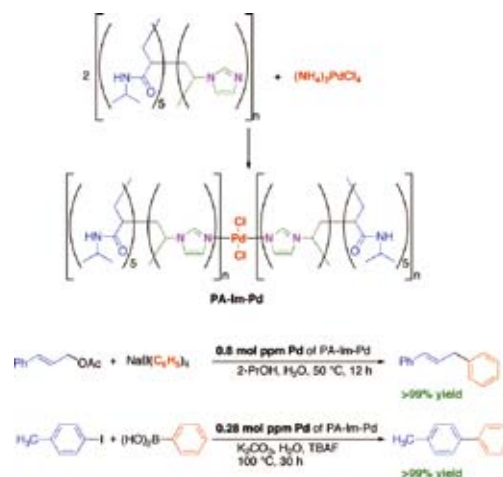
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Various transition metal-catalyzed organic molecular transformations in water were achieved under heterogeneous conditions by use of poly(imidazole-palladium), amphiphilic resin-supported palladium complexes, or a microflow device containing a polymeric palladium nanoparticle membrane which were designed and prepared by this research group. The enantioselective carbenoid insertion into phenolic O–H bonds with a new chiral copper(I) imidazoindolephosphine complex has been also developed. In particular, development of a highly active reusable poly(imidazole-palladium) and a micro-flow device containing a polymeric Pd nanoparticle membrane for organic transformations in water and the highly enantioselective O–H insertion using a new chiral copper(I) complex are highlights among the achievements of the 2011–2012 period to approach what may be considered ideal chemical processes of next generation. Representative results are summarized hereunder.

## 1. Self-Assembled Poly(Imidazole-Palladium): A Highly Active, Reusable Catalyst<sup>1,2)</sup>

A polymeric imidazole Pd catalyst (MEPI-Pd) was readily prepared by the coordinative convolution of  $(\text{NH}_4)_2\text{PdCl}_4$  and poly[*N*-vinylimidazole-*co*-(*N*-isopropylacrylamide)<sub>5</sub>] in a methanol/water solution at 80 °C for 30 min. The polymeric Pd catalyst was utilized for the allylic arylation/alkenylation/vinylation of allylic esters and carbonates with aryl/alkenylboronic acids, vinylboronic acid esters, and tetraaryl borates. Even 0.8–40 mol ppm Pd of the catalyst efficiently promoted allylic arylation/alkenylation/vinylation in alcohol and/or water with a catalytic turnover number (TON) of 20,000–1,250,000. Furthermore, the polymeric Pd catalyst efficiently

promoted the Suzuki-Miyaura reaction of a variety of inactivated aryl chlorides, as well as aryl bromides, and iodides in water with a TON of up to 3,570,000.

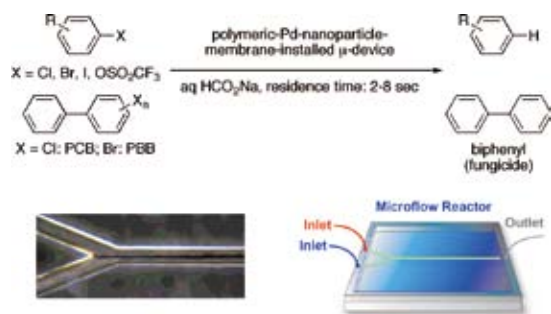


Scheme 1. Preparation of Self-Assembled Poly(Imidazole-Palladium) (top) and Application to Allylic Arylation and Suzuki-Miyaura Reaction.

## 2. Instantaneous Hydrodehalogenation of Haloarenes by a Microflow Device Containing a Polymeric Pd Nanoparticle Membrane<sup>3)</sup>

An architecture-based system of transition metal catalysis using We developed a variety of polymeric Pd nanoparticle membrane-installed microflow devices for the first time. Three types of polymers were convoluted with palladium salts under laminar flow conditions in a microflow reactor to form polymeric Pd membranes at the laminar flow interface. These

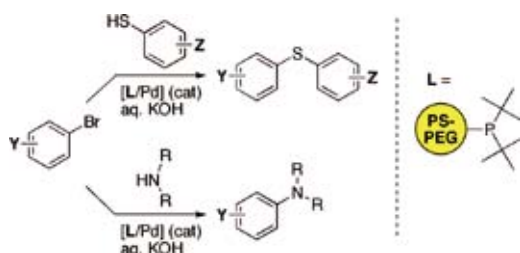
membranes were reduced with aqueous sodium formate or with heat to create microflow devices containing polymeric palladium nanoparticle membranes. These microflow devices achieved instantaneous hydrodehalogenation of 10–1,000 ppm of aryl chlorides, bromides, iodides, and triflates, within a residence time of 2–8 s at 50–90 °C using a safe, nonexplosive aqueous sodium formate to quantitatively afford the corresponding hydrodehalogenated products. PCB (10–1,000 ppm) and PBB (1,000 ppm) were completely decomposed under similar conditions, yielding biphenyl as a fungicidal compound.



**Scheme 2.** Instantaneous Hydrodehalogenation of Haloarenes by a Microflow Device Containing a Polymeric Pd Nanoparticles Membrane.

### 3. C–N and C–S Bond Forming Cross Coupling in Water with Amphiphilic Resin-Supported Palladium Complexes<sup>4</sup>

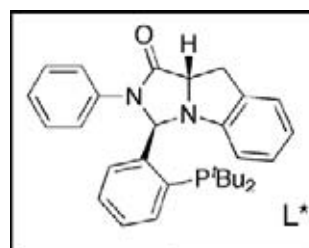
Catalytic C–N and C–S bond forming reactions of haloarenes with secondary amines and thiophenols were achieved in water under heterogeneous conditions by the use of immobilized palladium complexes coordinated with the amphiphilic polystyrene-poly(ethylene glycol) resin-supported di(*tert*-butyl)phosphine ligand to afford aryl(dialkyl)amines and diarylsulfides in high yield.



**Scheme 3.** C–N and C–S Bond Forming Cross Coupling in Water with Amphiphilic Resin-Supported Pd Complexes.

### 4. Enantioselective Carbenoid Insertion into Phenolic O–H Bonds with a Chiral Copper(I) Imidazoindolephosphine Complex<sup>5</sup>

The enantioselective O–H carbenoid insertion reaction with a new chiral copper(I) imidazoindolephosphine complex has been developed. The chiral copper(I) complex catalyzed the insertion of carbenoids derived from  $\alpha$ -diazopropionates into the O–H bonds of various phenol derivatives to give the corresponding  $\alpha$ -aryloxypropionates with up to 91% ee.



**Scheme 4.** Enantioselective Carbenoid Insertion into Phenolic O–H Bonds with a Chiral Copper(I) Imidazoindolephosphine Complex.

#### References

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