

Heterogeneous Catalytic Systems for Organic Chemical Transformations in Water

Department of Life and Coordination-Complex Molecular Science
Division of Complex Catalysis



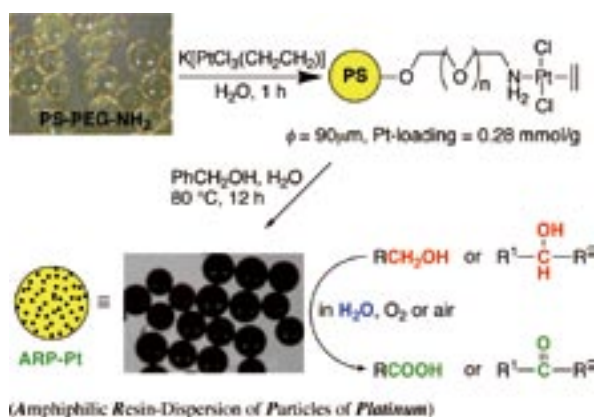
UOZUMI, Yasuhiro
YAMADA, Yoichi M. A.
OE, Yohei
SUZUKA, Toshimasa
KIMURA, Tsutomu
MINAKAWA, Maki
MATSUURA, Yutaka
TAKENAKA, Hiroe
TORII, Kaoru
ARAKAWA, Takayasu
BEPPU, Tomohiko
SASAKI, Tokiyo
HIGASHIBAYASHI, Azumi
TANIWAKE, Mayuko

Professor
Assistant Professor
IMS Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Research Fellow
Research Fellow
Graduate Student
Graduate Student
Secretary
Secretary
Secretary

Various organic molecular transformations catalyzed by transition metals were achieved under heterogeneous aqueous conditions by use of amphiphilic resin-supported metal complexes or metal nanoparticles which were designed and prepared by this research group. In particular, highly stereoselective asymmetric allylic substitutions and aerobic alcohol oxidation, both of which were performed in water under heterogeneous conditions with high recyclability of the polymeric catalysts, are highlights among the achievements of the 2006–2007 period to approach what may be considered ideal chemical processes of next generation. Representative results are summarized hereunder.

1. Nanometal Particle Catalysts Dispersed in Amphiphilic Resin Supports^{1,2)}

An amphiphilic polystyrene-polyethylene glycol (PS-PEG) resin-dispersion of nanoparticles of platinum (ARP-Pt) was developed which had a mean diameter of 5.9 nm with a narrow size distribution throughout the resin (Scheme 1). ARP-Pt was found to be a useful and readily recyclable catalyst for aerobic oxidation of a wide variety of alcohols, including non-activated aliphatic and alicyclic alcohols, in water with an oxygen or air

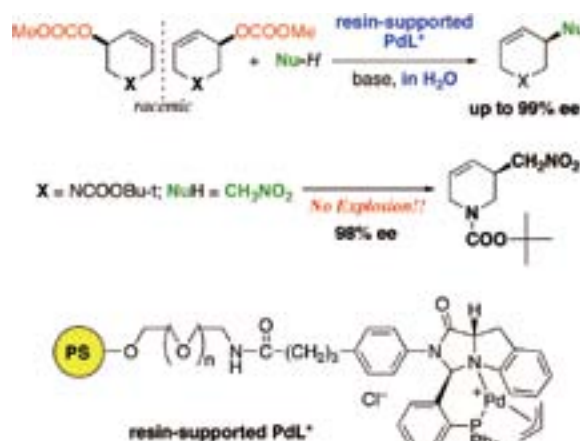


Scheme 1. Catalytic Aerobic Oxidation of Alcohols in Water with Amphiphilic Resin-Dispersion of Nanoparticles of Platinum.

atmosphere under heterogeneous conditions to meet green chemical requirements. A PS-PEG resin-dispersion of nanopalladium catalyst was also prepared which catalyzed aerobic oxidation of alcohols and hydrodechlorination of aryl halides under heterogeneous aqueous conditions.

2. Chiral Palladium Complexes Immobilized with Amphiphilic Resin Supports^{3,4)}

Stereoselective polymeric palladium catalysts supported on an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin were developed to realize asymmetric allylic substitutions in water under heterogeneous conditions. A polymeric (*R*)-2-(diphenylphosphino)binaphthyl (MOP) ligand anchored onto the PS-PEG resin by an (*S*)-alanine tether unit was identified through the library-based screening to be an effective chiral ligand for the asymmetric palladium-catalyzed π -allylic substitution of 1,3-diphenylpropenyl acetate with malonate nucleophiles under heterogeneous aqueous conditions. Nitromethane was safely applied as a C1 nucleophile for palladium-catalyzed

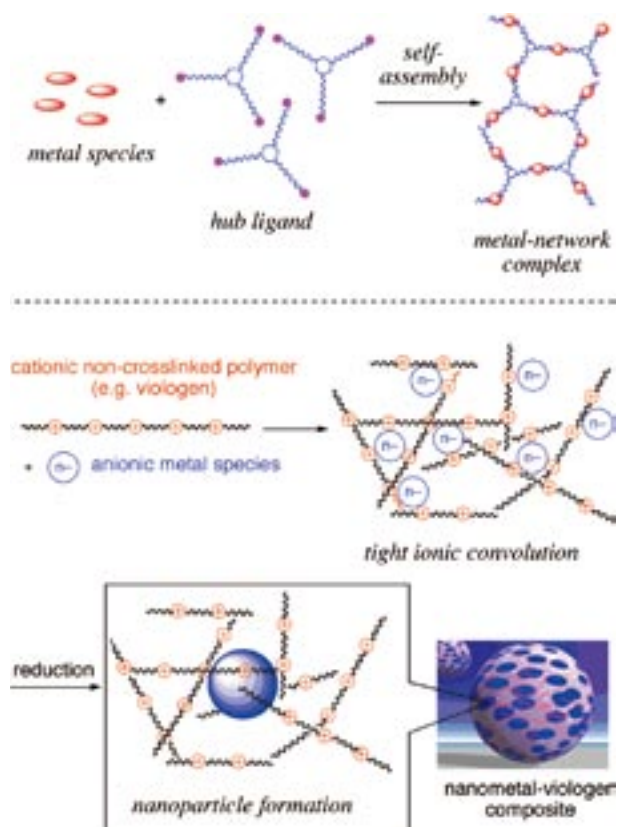


Scheme 2. Catalytic Asymmetric Allylic Substitution of Cycloalkenyl Esters in Water with an Amphiphilic Polymeric Chiral Palladium Complex.

π -allylic substitution of cyclic allylic substrates in water with amphiphilic PS-PEG resin-supported chiral imidazoindolephosphine-palladium complexes (Scheme 2). Catalytic asymmetric nitromethylation of cycloalkenyl esters was achieved in water as a single reaction medium under heterogeneous conditions using 5 mol% palladium of a PS-PEG resin-supported palladium-imidazoindolephosphine complex to give optically active (cycloalkenyl)nitromethanes with up to 98% ee.

3. Self-Organized Polymeric Metal Complexes^{5,6,7}

A novel solid-phase 3D metal-organic coordination network catalyst was prepared *via* self-assembly from PdCl₂(CH₃CN)₂ and a trisphosphine hub with three flexible alkyl-chain linkers. This insoluble network complex efficiently catalyzed the Suzuki-Miyaura reaction under atmospheric conditions in water. This catalyst was reused without loss of catalytic activity. A novel solid-phase self-organized catalyst of palladium nanoparticles was also prepared from PdCl₂ with main-chain viologen polymers *via* ionic convolution and



Scheme 3. Concepts of Self-Organized Network Complexation and Ionic Convolution.

Awards

UOZUMI, Yasuhiro; Chemical Society of Japan Award for Creative Research.

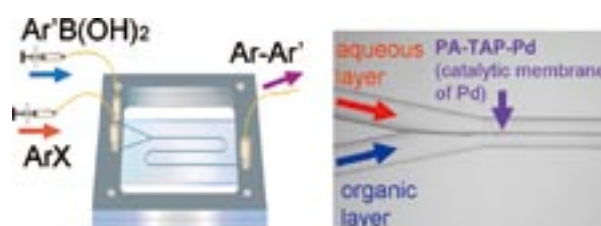
UOZUMI, Yasuhiro; Green-Sustainable Chemistry Award and MEXT Minister Award for Green-Sustainable Chemistry.

YAMADA, Yoichi M. A.; Thieme Journal Award.

reduction. This insoluble nanocatalyst nano-Pd-Viologen efficiently promoted α -alkylation of ketones with primary alcohols in the presence of Ba(OH)₂·H₂O under atmospheric conditions without organic solvents. The nano-Pd-Viologen catalyst was reused without loss of catalytic activity. The both concepts of network complexation and ionic convolution are depicted in Scheme 3.

4. Microchannel Reactor with a Catalytic Membrane⁸⁾

Instantaneous catalytic carbon-carbon bond forming reactions were achieved in a microchannel reactor having a polymeric palladium complex membrane (Scheme 4). The catalytic membrane was constructed inside the microchannel *via* self-assembling complexation at the interface between the organic and aqueous phases flowing laminarly, where non-crosslinked polymer-bound phosphine and ammonium tetrachloropalladate dissolved, respectively. Palladium-catalyzed coupling reaction of aryl halides and arylboronic acids was performed using the microchannel reactor to give quantitative yields of biaryls within 4 seconds of retention time in the defined channel region.



Scheme 4.

References

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