

## The Sixth Green and Sustainable Chemistry Award

Awarded by the Minister of Education, Culture, Sports, Science and Technology

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### *Development of Polymeric Catalysts Realizing Fine Chemical Synthesis in Water*

Chemical transformations producing desired compounds with high efficiency and selectivity under safe and green conditions are what may be considered ideal chemical processes of next generation. Providing that the chemical reaction proceeds in water with a recyclable heterogeneous catalyst, it would be an ultimate green reaction system. Development of aquacatalytic transformations of organic substrates is a major challenge from a fundamental scientific viewpoint. Furthermore, there is good reason to believe that immobilized catalysts exhibiting high catalytic activity in fully aqueous media offer a viable safe and clean alternative to more conventional methods of accomplishing many organic reactions. This awardee has recently developed a variety of amphiphilic polymer resin-supported catalysts, including palladium complexes, rhodium complexes, ammonium salts (PTC), nano metal particles, and so on, bound to a polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG resin) which exhibit excellent catalytic properties in water under mild and heterogeneous conditions. Thus, a wide variety of organic transformations, including carbonylation of aryl halides (Pd), Heck reaction (Pd), allylic substitution (Tsuji reaction) (Pd), Suzuki-Miyaura cross-coupling (Pd), Sonogashira reaction (Pd), Wacker-type cyclization (Pd), cycloisomerization of 1,6-enynes (Pd), cyclotrimerization of alkynes (Rh), hydroformylation of alkenes (Rh), Miyaura-Michael addition of boron reagents (Rh), Michael addition (ammonium base), alkylation of active methylene compounds (ammonium base), were achieved in water with PS-PEG supported palladium, rhodium and ammonium PTC catalysts. Highly enantioselective (up to 99% ee) allylic substitution was also achieved with a palladium complex of (3*R*,9*aS*)-3-[2-(diphenylphosphino)phenyl]-2-phenyl-tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one anchored on PS-PEG resin, which was designed and prepared with a view to use it under aqueous heterogeneous conditions.

Oxidation of alcohols forming carbonyl compounds is one of the most fundamental and important yet immature processes in organic chemistry. The ideal goal of alcohol oxidation should be the aerobic oxidation in water promoted by a heterogeneous catalyst under atmospheric pressure conditions resulting in a much cheaper, safer, and more environmentally benign oxidation protocol. Very recently, catalytic alcohol oxidation was achieved in water under atmospheric pressure of molecular oxygen by use of amphiphilic polymer-supported metal (Pd, Pt) nanoparticles. Thus, this awardee developed PS-PEG resin-dispersions of palladium and platinum nanoparticles via reductive decomposition of a resin-supported Pd- and Pt-complexes, which showed high catalytic activity owing to the large surface area of the nanoparticles and water-based reactivity provided by the amphiphilicity of the PS-PEG matrix. The amphiphilic polymer-supported nanoparticles oxidized not only benzylic and allylic alcohols but also aliphatic alcohols under aerobic conditions in water to form aldehydes, ketones, and carboxylic acids. Nanopalladium-catalyzed reductive hydrodechlorination of haloarenes, reductive aldol reactions, have also been developed.

A PS-PEG resin supported palladium-phosphine complex is now commercially available from several international chemical suppliers to demonstrate its utilities in the industrial research of process chemistry.