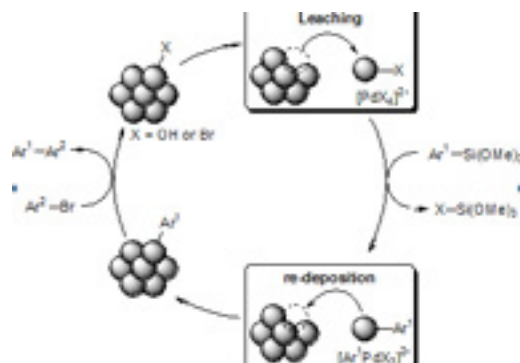


Catalytic specificity of polystyrene-stabilized PdO nanoparticles for Hiyama coupling reaction in water and the associated mechanism

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Metal nanoparticles have attracted considerable interest in the context of green chemistry because they are efficient catalysts for organic reactions in water. Recently, we developed linear polystyrene-stabilized PdO nanoparticles (PS-PdONPs) which showed high catalytic activity for several carbon-carbon coupling reactions in water.¹⁻⁴ In the research of Hiyama coupling reaction catalyzed by PS-PdONPs,⁵ we got finding that the reaction would occur through the different mechanism from that in the case of metal complex catalyst. In general, the mechanism of the Hiyama coupling reaction involves the oxidative addition of aryl halides to Pd⁽⁰⁾ to form the organopalladium halide (Ar-Pd-X). This is followed by transmetalation with organosilanes to provide the diorganopalladium species (Ar-Pd-R), which undergoes reductive elimination, leading to carbon-carbon bond formation and regeneration of Pd⁽⁰⁾. When a Pd^(II) species was used as the catalyst, it is supposed that reduction from Pd^(II) to Pd⁽⁰⁾ must first take place to generate the catalytically active species. However, we found that PS-PdONPs (Pd^(II) species) exhibit high catalytic activity for the Hiyama coupling reaction of aryltrimethoxysilanes with a variety of bromoarenes under air in water. In contrast, no desired coupling product was obtained from the Hiyama coupling reaction using linear polystyrene-stabilized Pd nanoparticles (PS-PdNPs, Pd⁽⁰⁾ species) as a catalyst. No formation of Pd⁽⁰⁾ species was confirmed by XPS analysis of the recovered catalyst after the reaction. These data prompted us to examine the detailed mechanism of Hiyama coupling reaction in water using PS-PdONPs as a catalyst. The different reactivities of PdONPs and PdNPs will be also discussed.

**Biography**

Atsushi Ohtaka received his PhD from Osaka University in 2003 under the direction of Professor Hideo Kurosawa. He then worked for two years as a Post-Doctorate Research Fellow in National Cardiovascular Center, for a year at Institute for Molecular Science under the direction of Professor Yasuhiro Uozumi, and for six months as a Visiting Researcher in Alicante University under the direction of Professor Carmen Najera. He became an Assistant Professor (2006) and Associate Professor (2013) at Osaka Institute of Technology where he won an award for encouragement of Research in Materials Science in 2008. His current research interests include: (1) transition-metal nanoparticles catalyst; (2) catalytic reaction in water.

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