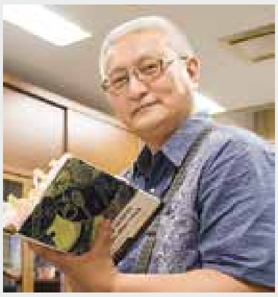
Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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



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Education

1984	B.S. Hokkaido University
1990	Ph.D. Hokkaido University

Professional Employment

1988	JSPS Research Fellow
1988	Research Associate, Hokkaido University
1990	Assistant Professor, Hokkaido University
1994	Research Associate, Columbia University
1995	Lecturer, Kyoto University
1997	Professor, Nagoya City University
2000	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2007	Research team leader, RIKEN
2014	Distinguished Professor, Three George University
2003	Research Project Leader, JST CREST Project (–2008)
2008	Research Project Leader, NEDO Project (–2012)
2011	Deputy Research Project Leader, JST CREST (–2016)
2014	Research Project Leader, JST ACCEL Project (–2019)

Awards

1991	Eisai Award, Synthetic Organic Chemistry
1998	The Pharmaceutical Society of Japan Award for Young Scientist
2007	The Chemical Society of Japan (CSJ) Award for Creative Work
2007	MEXT Ministerial Award for Green Sustainable Chemistry
2010	Inoue Prize for Science
2014	The Commendation for Science and Technology by the Minister of MEXT (Research Category)

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Keywords Transition Metal Catalysis, Green Chemistry, Organic Synthesis

Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, we have recently been developing the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels. Thus, for example, a variety of palladium catalysts were designed and prepared promoting carbon–carbon bond forming reactions at ppm-ppb loading levels (Figure 1).

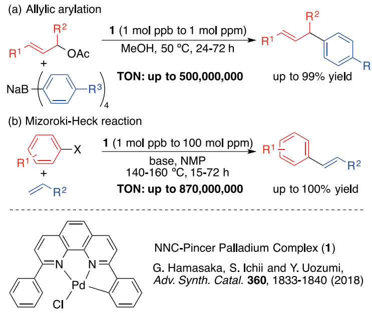

Figure 1. Typical Examples of Pd-Catalyzed Carbon–Carbon Bond Forming Reactions with ppm-ppb Loading Levels of an NNC-Pincer Pd Comples.

Selected Publications

- R. David and Y. Uozumi, "Recent Advances in Palladium-Catalyzed Cross-Coupling Reactions at ppm-ppb Molecular Catalyst Loadings (review)," *Adv. Synth. Catal.* **360**, 602–625 (2018).
- T. Osako, K. Torii, S. Hirata and Y. Uozumi, "Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin," *ACS Catal.* **7**, 7371–7377 (2017).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels," *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
- G. Hamasaka, T. Muto and Y. Uozumi, "Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex," *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, "Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Pallasium Catalyst Supported on Amphiphilic Resin," *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, "A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water," *Angew. Chem., Int. Ed.* **46**, 704–706 (2007).
- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, "Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane," *J. Am. Chem. Soc.* **128**, 15994–15995 (2006).

1. Self-Assembled Polymeric Pyridine Copper Catalysts for the Huisgen Cycloaddition with Alkynes and Acetylene Gas: Application in Synthesis of Tazobactam(1)

Novel convoluted polymeric pyridine copper(I) catalysts PVPy-Cu were developed for Huisgen cyclization of organic azides with alkynes and acetylene gas. They were readily prepared by our molecular convolution of $CuSO_4 \cdot 5H_2O$ and poly(4-vinylpyridine) (PVPy) in the presence of sodium ascorbate with/without various sodium salts in water. Their structural investigation was conducted with XANES and EXAFS as well as DFT calculation. The Huisgen cycloaddition of a variety of alkynes and acetylene gas was carried out with 100 to 800 mol ppm Cu of PVPy-Cu in water whose turnover numbers reached up to 10,000. This catalytic system was applied to synthesis of tazobactam, an inhibitor of bacterial β-lactamases.

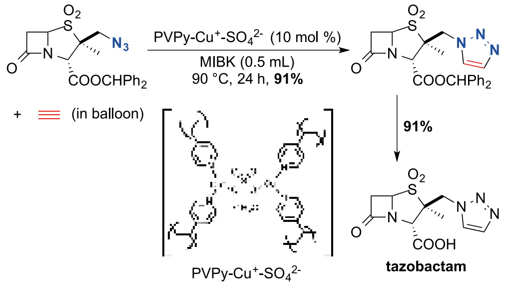

Figure 2. Synthesis of Tazobactam through the Huisgen Cyclization with Acetylene Gas Using a Polymeric Cu Catalyst.

2. Iterative Preparation of Platinum Nanoparticles in an Amphiphilic Polymer Matrix: Regulation of Catalytic Activity in Hydrogenation(2,3)

We have demonstrated that iteration of the seeded preparation of platinum nanoparticles dispersed in an amphiphilic polystyrene–poly(ethylene glycol) resin (ARP–Pt) regulates the activity of the catalyst in the hydrogenation of aromatic compounds in water and is accompanied by a slight modification of its structural properties. Platinum nanoparticles dispersed in the amphiphilic polymer prepared through four iterations (ARP–Pt G5) showed a much higher catalytic activity than that of the initial ARP–Pt (G1) in the hydrogenation of aromatic compounds in water. These results suggest that iteration of the seeded preparation of nanoparticles can be an effective method for the precise regulation of the catalytic activity and the structural properties of the resulting catalyst.

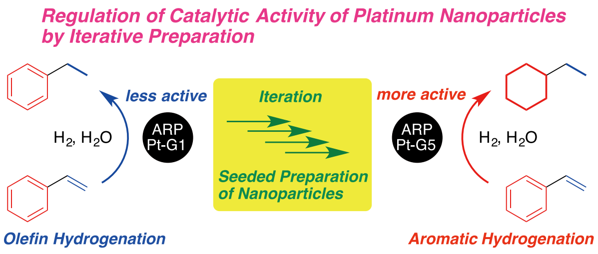

Figure 3. Regulated Hydrogenation with Iteratively Generated Polymeric nanoPt Catalysts.

3. Solvent-Free A^3 and KA^2 Coupling Reactions with Mol ppm Level Loadings of a Polymer-Supported Copper(II)-Bipyridine Complex for Green Synthesis of Propargylamines(4)

A copper(II)–bipyridine complex immobilized on amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin (PS–PEG-BPy–$CuBr_2$) has been developed. The immobilized copper(II)–bipyridine complex at a mol ppm level of loading efficiently catalyzed the three-component coupling of aldehydes or ketones, amines, and alkynes (A^3 or KA^2 coupling) under solvent-free conditions to give the corresponding propargylamines in good-to-excellent yields. Moreover, a ten-gram-scale green syntheses of propargylamines proceeded with excellent atom economy (*E* factor ≥ 0.38) through a solvent-free A^3 coupling using 5 mol ppm of PS–PEG-BPy–$CuBr_2$. The total turnover number and turnover frequency of the catalyst reached as high as 178 800 and 7450 h^{-1}, respectively.

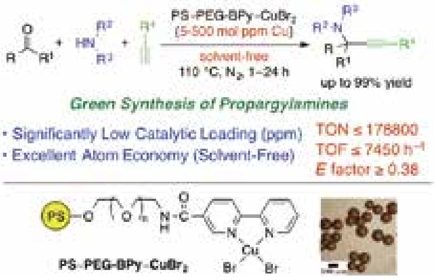

Figure 4. Preparation of Propargylamines by A^3 Coupling Reaction with ppm Loading Level of a Polymeric Cu(II) Catalyst.

References

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2) T. Osako, J. Srisa, K. Torii, G. Hamasaka and Y. Uozumi, *Synlett*, in press (2019). DOI: 10.1055/s-0037-1611813

3) T. Osako, K. Torii, S. Hirata and Y. Uozumi, *ACS Catal.* **7**, 7371–7377 (2017).

4) S. Yan, S. Pan, T. Osako and Y. Uozumi, *ACS Sus. Chem. Eng.* **7**, 9097 (2019).