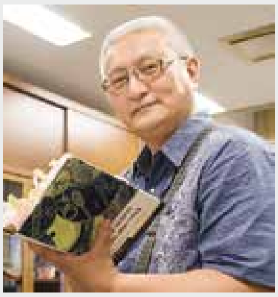
Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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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Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, *etc.*) organic transformation processes. In one active area of investigation, we are developing the heterogeneous aquacatalytic systems. Various types of catalytic organic molecular transformations, *e.g.* carbon–carbon bond forming cross-coupling, carbon–heteroatom bond forming reaction, aerobic alcohol oxidation, *etc.*, were achieved in water under heterogeneous conditions by using amphiphilic polymer-supported transition metal complexes and nanoparticles (**Figure 1**), where self-concentrating behavior of hydrophobic organic substrates inside the amphiphilic polymer matrix played a key role to realize high reaction performance in water.

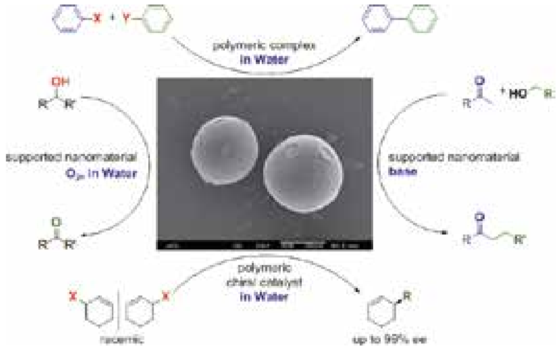

Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

Selected Publications

- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, “Amphiphilic Self-Assembled Polymeric Copper Catalyst to Parts per Million Levels: Click Chemistry,” *J. Am. Chem. Soc.* **134**, 9285–9290 (2012).
- 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. A Vesicular Self-Assembled Amphiphilic Palladium NNC-Pincer Complex-Catalyzed Allylic Arylation of Allyl Acetates with Sodium Tetraarylborates in Water1)

The allylic arylation of various allyl acetates with sodium tetraarylborates proceeded in water in the presence of a vesicular self-assembled amphiphilic palladium NNC-pincer complex to give the corresponding arylated products in high yield, whereas the same complex as an amorphous powder did not promote the reaction efficiently. The formation of a vesicular structure was therefore shown to be essential for efficient promotion of the reaction.

Figure 2. Allylic arylation reaction in water in the presence of a self-assembled vesicular amphiphilic palladium NNC-pincer complex.

2. Organoborane-Catalyzed Hydrogenation of Unactivated Aldehydes with a Hantzsch Ester as a Synthetic NAD(P)H Analogue2)

We have developed a method for the hydrogenation of unactivated aldehydes, using a Hantzsch ester as a NAD(P)H analogue in the presence of an electron-deficient triarylborane as a Lewis acid catalyst. Thus, tris[3,5-bis(trifluoromethyl)phenyl]borane efficiently catalyzes the hydrogenation of aliphatic aldehydes with a Hantzsch ester in 1,4-dioxane at 100 °C to give the corresponding aliphatic primary alcohols in up to 97% yield. Aromatic aldehydes also undergo the hydrogenation, even at 25 °C, to furnish the corresponding aromatic primary alcohols in up to 100% yield.

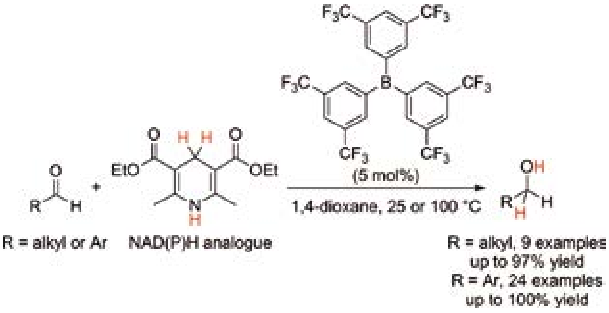

Figure 3. Organoborane-catalyzed hydrogenation of aldehydes with a Hantzsch ester.

3. Recyclable Polystyrene-Supported Copper Catalysts for the Aerobic Oxidative Homocoupling of Terminal Alkynes3)

Polystyrene-supported copper(II) *N*,*N*,*N'*,*N'*-tetraethyldiethylenetriamine [Cu(II)–TEDETA] complexes were prepared by immobilization of TEDETA onto crosslinked polystyrene resin, followed by complexation with copper salts. The polystyrene-immobilized $CuSO_4$–TEDETA complex efficiently catalyzed the oxidative homocoupling of terminal alkynes under air to give the corresponding 1,3-diynes in up to 99% yield. The catalyst was easily recovered by simple filtration and reused eight times without significant loss of catalytic activity.

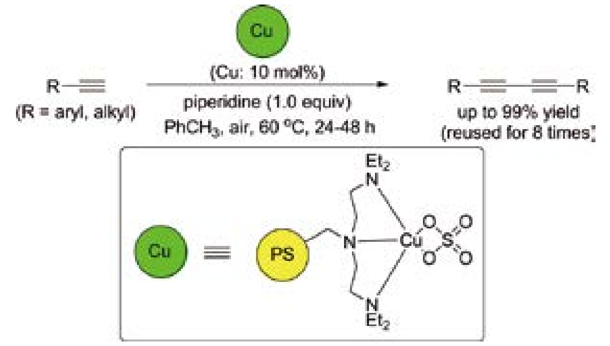

Figure 4. Homocoupling of terminal alkynes in the presence of a polystyrene-supported copper catalyst.

4. Instantaneous Click Chemistry by a Copper-Containing Polymeric-Membrane-Installed Microflow Catalytic Reactor4)

Instantaneous Huisgen cycloaddition has been achieved by developing a novel catalytic dinuclear-copper-complex-containing polymeric-membrane-installed microflow device. The microflow device instantaneously promotes the click reaction with a variety of alkynes and organic azides to afford the corresponding triazoles in quantitative yield.

Figure 5. Homocoupling of terminal alkynes in the presence of a polystyrene-supported copper catalyst.

References

1) G. Hamasaka, F. Sakurai and Y. Uozumi, *Tetrahedron* **71**, 6437–6441 (2015).
2) G. Hamasaka, H. Tsuji and Y. Uozumi, *Synlett* **26**, 2037–2041 (2015).
3) S. Yan, S. Pan, T. Osako and Y. Uozumi, *Synlett* **27**, 1232–1236 (2016).
4) Y. M. A. Yamada, A. Ohno, T. Sato and Y. Uozumi, *Chem. –Eur. J.* **21**, 17269–17273 (2015).