Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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Education
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Professional Employment
1988 JSPS Research Fellow
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1994 Research Associate, Columbia University
1995 Lecturer, Kyoto University
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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)

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
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2014 The Commendation for Science and Technology by the Minister of MEXT, Prize for Science and Technology

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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 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.

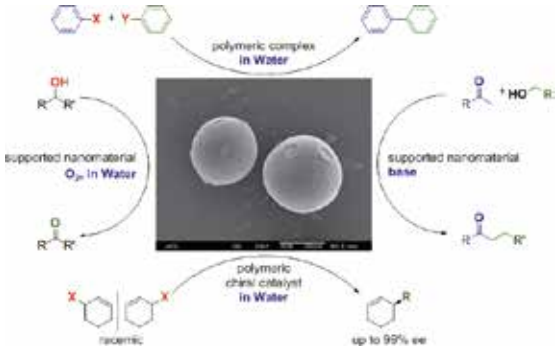

Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

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. Enantioposition-Selective Copper-Catalyzed Azide–Alkyne Cycloaddition for Construction of Chiral Biaryl Derivatives[1,2)]

A highly enantioposition-selective copper-catalyzed azide–alkyne cycloaddition (CuAAC) of dialkynes bearing prochiral biaryls has been developed for the construction of 1,2,3-triazoles bearing axially chiral biaryl groups in up to 76% yield and up to 99% ee.

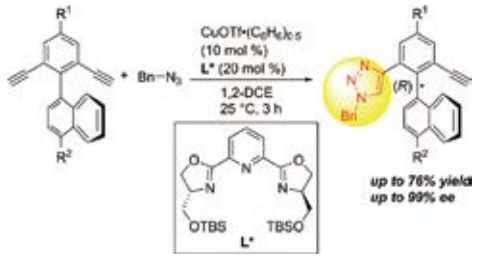

Figure 2. Enatioposition-selective copper-catalyzed azide–alkyne cycloaddition.

2. Continuous-Flow Oxidation of Alcohols and Hydrogenation of Olefines and Nitrobenzenes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Polymer[3,4)]

We have developed a continuous-flow reaction system containing amphiphilic polymer-dispersion of platinum nanoparticles (ARP-Pt) packed in a catalyst cartridge to catalyze the aerobic oxidation of alcohols and the hydrogenation of olefins and nitrobenzenes. In the flow system using O_2, various alcohols were fully oxidized within 73 seconds (100–120 °C, 40–70 bar of the system pressure, 5 vol% of O_2) in water to give the corresponding carbonyl products in up to 99% yield. Olefins and nitrobenzenes underwent hydrogenation with the same flow system under H_2 (25 °C, 5–15 bar of the system pressure, 5 vol% of H_2) within 31 seconds to afford the corresponding hydrogenated products in up to 99% yield.

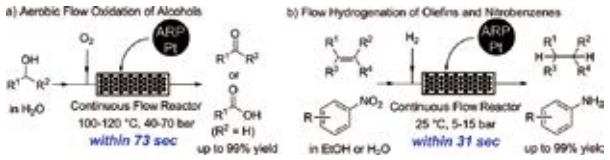

Figure 3. Continuous-flow oxidation of alcohols and hydrogenation of olefins and nitorobenzenes.

3. Palladium NNC-Pincer Complex: An Efficient Catalyst for Allylic Arylation at Perts Per Billion Levels[5)]

Allylic arylation of allylic acetates by sodium tetraarylborates in the presence of ppb to ppm (molar) loadings of a palladium NNC-pincer complex catalyst in methanol at 50 °C gave the corresponding arylated products in excellent yields. Total turnover numbers of up to 500,000,000 and turnover frequencies of up to 11,250,000 h^{-1} were achieved.

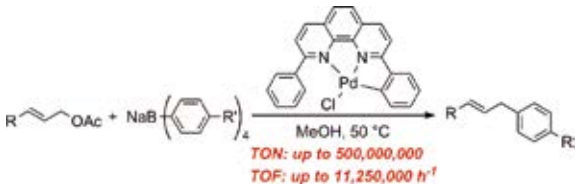

Figure 4. Allylic arylation of allylic acetates with sodium tetraarylborates in the presence of a palladium NNC-pincer complex.

4. Development of an Aquacatalytic System Based on the Formation of Vesicles of an Amphiphilic Palladium NNC-Pincer Complex[6)]

Two amphiphilic palladium NNC-pincer complexes bearing hydrophilic tri(ethylene glycol) chains and hydrophobic dodecyl chains were designed and prepared for the development of a new aquacatalytic system. In water, these amphiphilic complexes self-assembled to form vesicles, the structures which were established by means of a range of physical techniques. When the catalytic activities of the vesicles were investigated in the arylation of terminal alkynes in water, they were found to catalyze the reaction of aryl iodides with terminal alkynes to give good yields of the corresponding internal alkynes. The formation of a vesicular structure was shown to be essential for efficient promotion of this reaction in water.

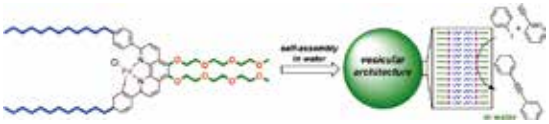

Figure 5. Cu-free Sonogashira reaction in water in the presence of a self-assembled vesicular amphiphilic palladium NNC-pincer complex.

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2) T. Osako and Y. Uozumi, *Synlett* **26**, 1475–1479 (2015).
3) T. Osako, K. Torii and Y. Uozumi, *RSC Adv.* **5**, 2647–2654 (2015).
4) T. Osako, K. Torii, A. Tazawa and Y. Uozumi, *RSC Adv.* **5**, 45760–45766 (2015).
5) G. Hamasaka, F. Sakurai and Y. Uozumi, *Chem. Commun.* **51**, 3886–3888 (2015).
6) F. Sakurai, G. Hamasaka and Y. Uozumi, *Dalton Trans.* **44**, 7828–7834 (2015).

Award

OSAKO, Takao; The 4th NINS Prize for Young Scientists (2015).