Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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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
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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 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).

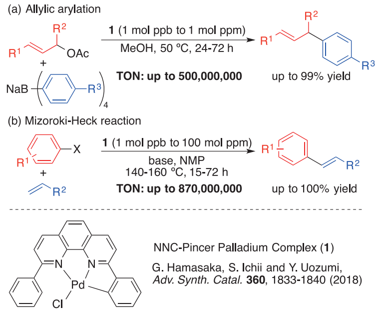

Figure 1. Typical Examples of Pd-Catalyzed Carbon–Carbon Bond Forming Reactions with ppm-ppb Loading Levels of an NNC-Pincer Pd Comples.

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).
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- 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. Arylation of Terminal Alkynes by Aryl Iodides Catalyzed by a Parts-per-Million Loading of Palladium Acetate[1)]

Arylation of terminal alkynes (16 varieties) by aryl iodides (28 varieties) was achieved with a mol ppm loading level of palladium catalyst, where a variety of functional groups including heteroarenes were tolerated. Thus, the arylations were carried out in the presence of palladium acetate at ppm loadings and potassium carbonate in ethanol at 80 °C to give the corresponding internal alkynes in good to excellent yields. Synthesis of 2-phenyl-3-(phenylalkynyl)benzofuran was achieved by iterative use of the alkyne arylation under mol ppm catalytic conditions. Reaction-rate analysis, transmission electron microscopic (TEM) examination of the reaction mixture, and mercury-amalgamation test were performed to gain insight into the active species of the highly active ppm catalytic species. TEM examination of the reaction mixture revealed that palladium nanoparticles were generated in situ under the reaction conditions, and their cluster size was variable during the catalytic reaction. A variation in size of palladium particles suggested that the composition-decomposition process of Pd aggregates should take place in situ via monomeric palladium(0) species and/or fine palladium(0) clusters, which might be real catalytic species in this reaction.

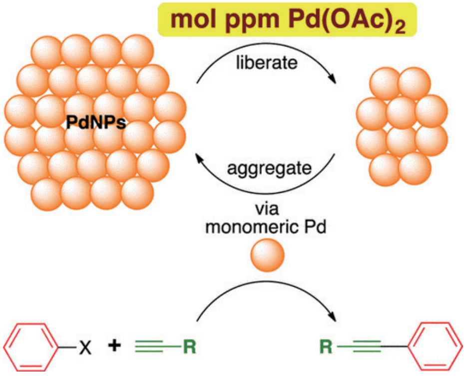

Figure 2. Arylation of Terminal Alkynes with a mol ppm Loading Level of a Palladium Catalyst.

2. Second-Generation *meta*-Phenolsulfonic Acid–Formaldehyde Resin as a Catalyst for Continuous-Flow Esterification[2)]

A second-generation *m*-phenolsulfonic acid–formaldehyde resin (PAFR II) catalyst was prepared by condensation polymerization of sodium *m*-phenolsulfonate and paraformaldehyde in an aqueous H_2SO_4 solution. This reusable, robust acid resin catalyst was improved in both catalytic activity and stability, maintaining the characteristics of the previous generation catalyst (*p*-phenolsulfonic acid–formaldehyde resin). PAFR II was applied in the batchwise and continuous-flow direct esterification without water removal and provided higher product yields in continuous-flow esterification than any other commercial ion-exchanged acid catalyst tested.

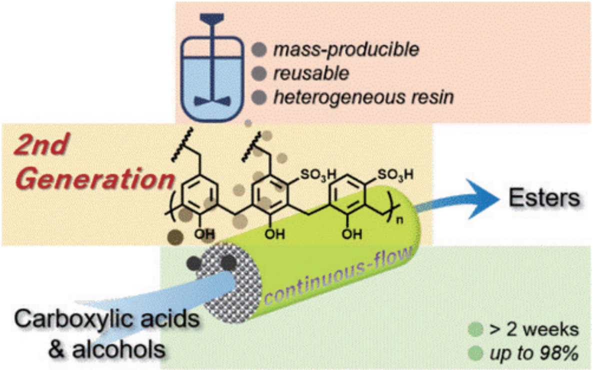

Figure 3. Continuous-Flow Esterification of Carboxylic Acid with Alcohols Using PAFR II Catalyst.

3. The Hiyama Cross-Coupling Reaction at Parts Per Million Levels of Pd: In Situ Formation of Highly Active Spirosilicates in Glycol Solvents[3)]

A palladium NNC-pincer complex at a 5 molppm loading efficiently catalyzed the Hiyama coupling reaction of aryl bromides with aryl(trialkoxy)silanes in propylene glycol to give the corresponding biaryls in excellent yields. This method was applied to the syntheses of adapalene and a biaryl-type liquid-crystalline compound, as well as to the derivatization of dextromethorphan and norfloxacin. ESI-MS and NMR analyses of the reaction mixture suggested the formation of pentacoordinate spirosilicate intermediates in situ. Preliminary theoretical studies revealed that the glycol-derived silicate intermediates formed in situ are quite reactive silicon reagents in the transmetalation step.

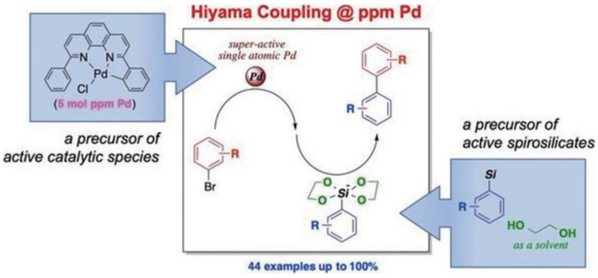

Figure 4. Hiyama Cross-Coupling Catalyzed by ppm Palladium NNC-Pincer Complex in Glycol Solvents.

References

1) G. Hamasaka, D. Roy, A. Tazawa and Y. Uozum, *ACS Catal.* **9**, 11640–11646 (2019).
2) H. Hu, H. Ota, H. Baek, K. Shinohara, T. Mase, Y. Uozumi and Y. M. A. Yamada, *Org. Lett.* **22**, 160–163 (2020).
3) S. Ichii, G. Hamasaka and Y. Uozumi, *Chem. –Asian J.* **14**, 3850–3854 (2019).