

# Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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



**UOZUMI, Yasuhiro**  
Professor  
[uo@ims.ac.jp]

#### 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

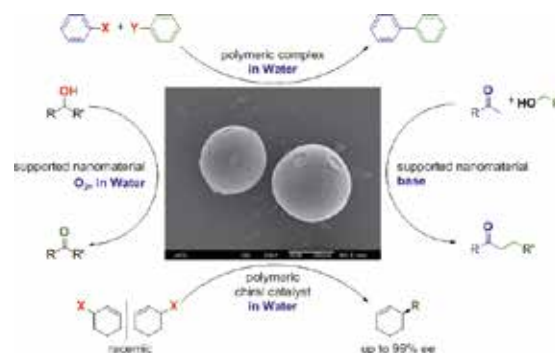
1991 Eisai Award, Synthetic Organic Chemistry  
1998 The Pharmaceutical Society of Japan Award for Young Scientist  
2007 The Chemical Society of Japan (CSJ) Award for Creative Work  
2007 MEXT Ministerial Award for Green Sustainable Chemistry  
2010 Inoue Prize for Science  
2014 The Commendation for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

#### Member

Visiting Professor  
MASE, Toshiaki  
KOTORA, Martin  
Assistant Professor  
OSAKO, Takao  
HAMASAKA, Go  
Post-Doctoral Fellow  
PAN, Shiguang  
HIRATA, Shuichi  
PUTRA, Anggi Eka  
KIM, Kiseong  
SUGIYAMA, Yuya  
Graduate Student  
ICHII, Shun  
SHEN, Guanshuo  
NIIMI, Ryoko  
TANI, Kazuki  
Technical Fellow  
TORII, Kaoru  
TAZAWA, Aya  
Secretary  
SASAKI, Tokiyo  
TANIWAKE, Mayuko

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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.



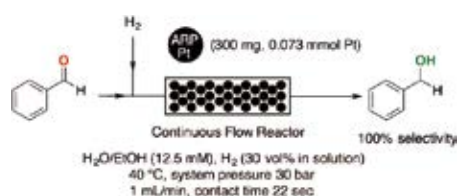
**Figure 1.** Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

#### Selected Publications

- 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 Palladium 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. Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin<sup>1)</sup>

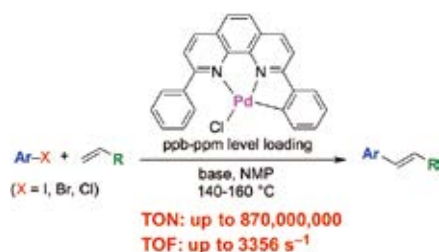
A chemoselective continuous-flow hydrogenation of aldehydes catalyzed by a dispersion of platinum nanoparticles in an amphiphilic polymer (ARP-Pt) has been developed. Aromatic and aliphatic aldehydes bearing various reducible functional groups, such as keto, ester, or amide groups, readily underwent flow hydrogenation in aqueous solutions within 22 seconds in a continuous-flow system containing ARP-Pt to give the corresponding primary benzylic or aliphatic alcohols in up to 99% yield with excellent chemoselectivity. Moreover, the long-term continuous-flow hydrogenation of benzaldehyde for eight days was realized, and the total turnover number of the catalyst reached 997. The flow hydrogenation system provides an efficient and practical method for the chemoselective hydrogenation of aldehydes bearing reducible functional groups.



**Figure 2.** Aqueous continuous flow hydrogenation of benzaldehyde in water in the presence of amphiphilic resin-supported nano particles of platinum (ARP-Pt).

## 2. A Palladium NNC-Pincer Complex as an Extremely Efficient Catalyst Precursor for the Mizoroki–Heck Reaction<sup>2,3)</sup>

The Mizoroki–Heck reaction of aryl halides (iodides, bromides, or chlorides) with activated alkenes in the presence of a palladium NNC-pincer complex at ppb to ppm loadings gave the corresponding internal alkenes in excellent yields. The total turnover number and turnover frequency reached up to  $8.70 \times 10^8$  and  $1.21 \times 10^7 \text{ h}^{-1}$  ( $3.36 \times 10^3 \text{ s}^{-1}$ ), respectively.



**Figure 3.** Heck reaction with a mol ppb loading level of an NNC-pincer palladium complex.

### Awards

OSAKO, Takao; Thieme Chemistry Journals Award 2018 (2018).

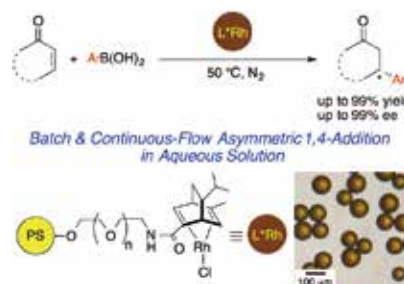
HAMASAKA, Go; Mitsubishi Gas Chemical Award in Synthetic Organic Chemistry, Japan (2018).

HAMASAKA, Go; The Chemical Society of Japan Lecture Award for Young Chemists (2018).

The catalyst was applied in a ten-gram-scale synthesis of the UV-B sunscreen agent octinoxate (2-ethylhexyl 4-methoxycinnamate). Reaction-rate analyses, transmission electron microscopic examination of the reaction mixture, and poisoning tests suggested that a monomeric palladium species is the catalytically active species in the catalytic cycle.

## 3. Aqueous Asymmetric 1,4-Addition of Arylboronic Acids to Enones Catalyzed by an Amphiphilic Resin-Supported Chiral Diene Rhodium Complex Under Batch and Continuous-Flow Conditions<sup>4)</sup>

A rhodium–chiral diene complex immobilized on amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin (PS–PEG–diene\*–Rh) has been developed. The immobilized rhodium–chiral diene complex (PS–PEG–diene\*–Rh) efficiently catalyzed the asymmetric 1,4-addition of various arylboronic acids to cyclic or linear enones in water under batch conditions to give the corresponding  $\beta$ -arylated carbonyl compounds in excellent yields and with excellent enantioselectivity. The catalyst was readily recovered by simple filtration and reused 10 times without loss of its catalytic activity and enantioselectivity. Moreover, a continuous-flow asymmetric 1,4-addition in a flow reactor containing PS–PEG–diene\*–Rh proceeded efficiently at 50 °C with retention of high enantioselectivity. Long-term continuous-flow asymmetric 1,4-addition during 12 hours readily gave the desired product on a ten-gram scale with high enantioselectivity.



**Figure 4.** Asymmetric 1,4-addition of aryl boronic acids to enones in the presence of a PS–PEG resin-supported homochiral rhodium complex.

### References

- 1) T. Osako, K. Torii, S. Hirata and Y. Uozumi, *ACS Catal.* **7**, 7371–7377 (2017).
- 2) D. Roy and Y. Uozumi, *Adv. Synth. Catal.* **360**, 602–625 (2018).
- 3) G. Hamasaka, S. Ichii and Y. Uozumi, *Adv. Synth. Catal.* **360**, 1833–1840 (2018).
- 4) G. Shen, T. Osako, M. Nagaosa and Y. Uozumi, *J. Org. Chem.* **83**, 7380–7387 (2018).