

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)

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, Prize for Science and Technology

Member

Assistant Professor
OSAKO, Takao
HAMASAKA, Go
Post-Doctoral Fellow
NAGAOSA, Makoto
PAN, Shiguang
Graduate Student
KOBAYASHI, Noboru
SAKURAI, Fumie
TSUJI, Hiroaki
YAN, Shuo
Technical Fellow
TORII, Kaoru
TAZAWA, Aya
Secretary
SASAKI, Tokiyo
FUKUSHIMA, Tomoko

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.

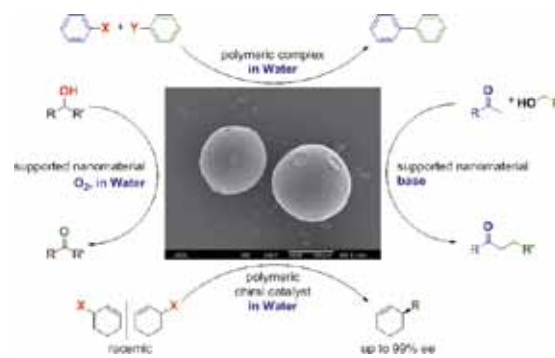


Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

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 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. A Palladium-Nanoparticles and Silicon-Nanowire-Array Hybrid: A Platform for Catalytic Heterogeneous Reactions¹⁾

We report the development of a silicon nanowire array-stabilized palladium nanoparticle catalyst, SiNA-Pd. Its use in the palladium-catalyzed Mizoroki-Heck reaction, the hydrogenation of an alkene, the hydrogenolysis of nitrobenzene, the hydrosilylation of an α,β -unsaturated aldehyde, and the C–H bond functionalization reactions of thiophenes and indoles achieved a quantitative production with high reusability. The catalytic activity reached several hundred-mol ppb of palladium, reaching a TON of 2,000,000.

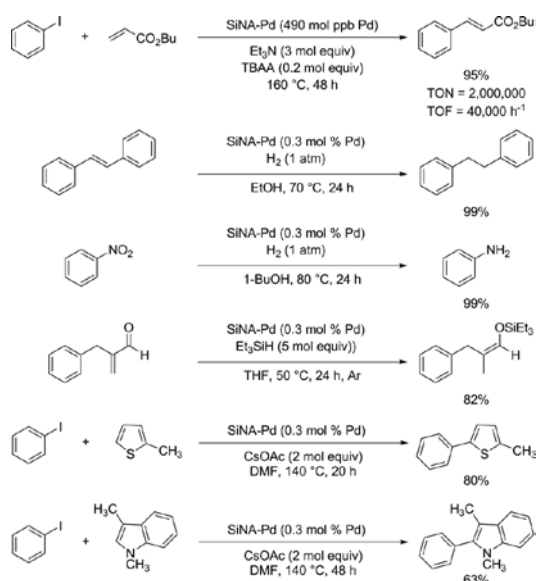


Figure 2. The Mizoroki-Heck reaction, the hydrogenation of an alkene, the hydrogenolysis of nitrobenzene, the hydrosilylation of an α,β -unsaturated aldehyde, and the C–H bond functionalization reactions of a thiophene and an indole catalyzed by SiNA-Pd.

2. Direct Dehydrative Esterification of Alcohols and Carboxylic Acids with a Macroporous Polymeric Acid Catalyst²⁾

A macroporous polymeric acid catalyst was prepared for the direct esterification of carboxylic acids and alcohols that proceeded at 50–80 °C without removal of water to give the corresponding esters with high yield. Flow esterification for the synthesis of biodiesel fuel was also achieved by using a column-packed macroporous acid catalyst under mild conditions without removal of water.

Award

UOZUMI, Yasuhiro; The Commendation for Science and Technology by the Minister of MEXT, Prize for Science and Technology (2014).



Figure 3. Direct dehydrative esterification of alcohols and carboxylic acids with a macroporous polymeric acid catalyst.

3. Asymmetric Sonogashira Coupling with a Chiral Palladium Imidazoindole Phosphine Complex³⁾

The asymmetric Sonogashira coupling of 1-(2,6-dibromophenyl)naphthalene or 4,16-dibromo[2,2]paracyclophane with various terminal alkynes was carried out with a palladium complex of a homochiral imidazoindole phosphine, a derivative of a (3*R*,9*aS*)-2-aryl-[3-(2-dialkylphosphanyl)phenyl]tetrahydro-1*H*-imidazo[1,5*a*]indol-1-one, to give the corresponding axially chiral monoalkynylated biaryl products with up to 72% enantiomeric excess.

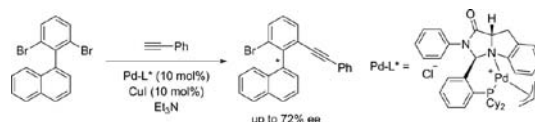


Figure 4. Asymmetric Sonogashira coupling with a chiral palladium imidazoindolephosphine complex.

References

- 1) Y. M. A. Yamada, Y. Yuyama, T. Sato, S. Fujikawa and Y. Uozumi, *Angew. Chem., Int. Ed.* **53**, 127–131 (2014).
- 2) M. Minakawa, H. Baek, Y. M. A. Yamada, J. W. Han and Y. Uozumi, *Org. Lett.* **15**, 5798–5801 (2013).
- 3) H. Zhou and Y. Uozumi, *Synlett* **24**, 2550–2554 (2013).