Innovative Catalysis Development Based on Radiant Right Spectroscopy

Division of Advanced Molecular Science
(Department of Photo-Molecular Science, Photo-Molecular Science III)

TAKAYA, Hikaru
Associate Professor
(Cross Appointment)
[takaya@ims.ac.jp]

Education
1993 B.S. Osaka University
1995 M.S. Osaka University
1998 Ph.D. Osaka University

Professional Employment
1995 JSPS Research Fellow
1998 Assistant Professor, Osaka University
2002 Guest Scientist, Scripps Research
2008 Associate Professor, Kyoto University
2019 Associate Professor (Cross Appointment), Institute for Molecular Science

Awards
2001 N.E. CHEMCAT Award in Synthetic Organic Chemistry, Japan
2008 The 22nd Special Young Lecturer in the 88th CSJ Annual Meeting
2012 Theme Chemistry Journal Award
2015 BCSJ Award, The Chemical Society of Japan
2019 BCSJ Award, The Chemical Society of Japan

Member
Secretary
HAGIWARA, Hisayo

Keywords Organometallic Catalyst, Peptide-Based Material, X-Ray Spectroscopy

For future sustainable development, we promote research development of advanced catalysts based on element strategy criteria. Non-precious metal such as iron, nickel, cobalt, and cupper catalysts are investigated for synthetic transformation of various organic molecules related to pharmaceutical and photoelectronic materials. To elucidate the precise catalytic properties and mechanism, X-ray absorption spectroscopy (XAS) and various radiant right spectroscopies provided at UVSOR are used, where development of a solution-phase in situ XAS spectroscopic techniques and system will be intensively conducted for the study of homogeneous organometallic catalysts. Multidisciplinary research covered on DFT and XAS spectroscopy is also conducted to achieve an efficient structural determination technique being never accessible by the conventional XAS-based structural analysis. Using these cutting-edge spectroscopic technologies, we aim to promote innovative catalyst research which enable us highly efficient transformation of extremely unreactive organic molecules such as simple aromatic compounds, CO_2, and biomass into valuable functional materials.

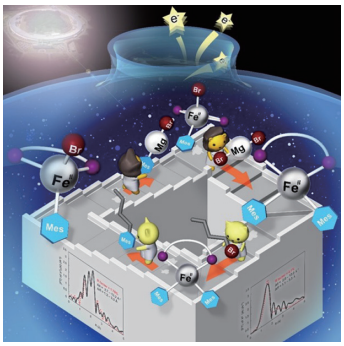


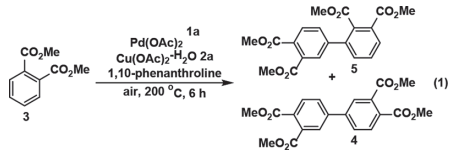
Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

Selected Publications

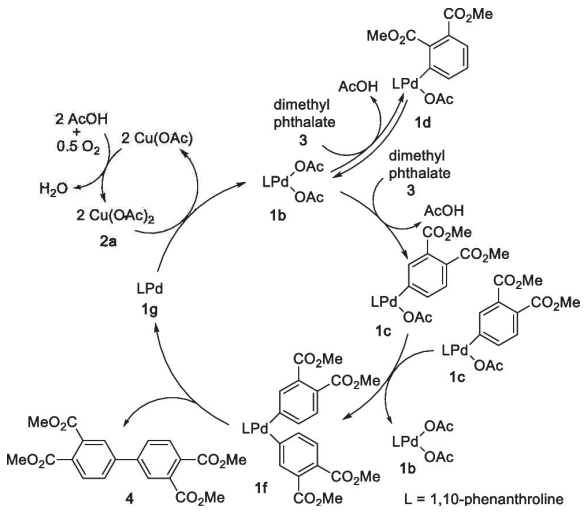
- R. N. Dhital, A. Sen, T. Sato, H. Hu, R. Ishii, D. Hashizume, H. Takaya, Y. Uozumi* and Y. M. A. Yamada, "Activator-Promoted Aryl Halide-Dependent Chemoselective Buchwald-Hartwig and Suzuki-Miyaura Type Cross-Coupling Reactions," *Org. Lett.* **22**, 4797–4801 (2020).
- L. O. Benjamin, H. Takaya and T. Uemura, "Polymer Guest Directing the Solid-State Conversion of a Metal-Organic Framework," *J. Am. Chem. Soc.* **141**, 14549–14553 (2019).
- R. Agata, H. Takaya, T. Iwamoto, T. Hatakeyama, K. Takeuchi, N. Nakatani and M. Nakamura, "Iron-Catalyzed Cross Coupling of Aryl Chlorides with Alkyl Grignard Reagents: Synthetic Scope and Fe^{II}/Fe^{IV} Mechanism Supported by X-Ray Absorption Spectroscopy and Density Functional Theory Calculations," *Bull. Chem. Soc. Jpn.* **92**, 381–390 (2019).
- H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagi, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi and M. Nakamura, "Investigation of Organoiron Catalysis in Kumada–Tamao–Corriu-Type Cross-Coupling Reaction Assisted by Solution-Phase X-Ray Absorption Spectroscopy," *Bull. Chem. Soc. Jpn.* **88**, 410–418 (2015).

1. DFT-XAS-Based Mechanistic Investigation of Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate[1,2)]

Pd-catalyzed oxidative coupling reaction of phthalate esters is a well-known industrial process for the production of biphenyl compounds which can be readily converted into biphenyl tetracarboxylic dianhydride (BPDA), being an important monomer of polyimides. Equation 1 shows a typical



procedure of the oxidative coupling, where dimethyl phthalate **3** readily couples in the presence of catalytic amounts of $Pd(OAc)_2$ **1a** and $Cu(OAc)_2$ **2a** to afford the corresponding biphenyls **4** and **5**. Despite the widespread use of this process, the precise reaction mechanism had still remained unclear due to the severe reaction condition and the complex Pd/Cu heterobimetallic catalyst system including paramagnetic Cu(II) species, both which hamper the conventional analysis based on solution-phase NMR. To solve such problems in mechanistic study of homogeneous catalysis, we conducted to use XAS which enables element specific analysis to determine the oxidation state and the geometry of catalytic species.[3,4)] Recently, we have succeeded to elucidate the mechanism of Pd/Cu-catalyzed oxidative coupling of dimethyl phthalate as shown in Scheme 1. The oxidation states and the local coordination geometries of catalytic intermediates **1d**, **1c**, and **2a** were determined under the stoichiometric conditions of each reaction path. DFT- and single crystal X-ray structural analysis adequately provided the precise molecular structure of these intermediates. This research is first to provide a clear answer to the long-term debate on the reaction mechanism in the last three decades and demonstrated that XAS is the powerful tool for the mechanistic study on homogeneous transition-metal-catalyzed reactions, being difficult by means of the conventional solution-phase NMR analysis.



Scheme 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAFS analysis.

2. XAFS-Based Structural Study on Flexible Organometallic Systems[5–7)]

Generally, organometallics bearing highly flexible molecular structure make it difficult to prepare a single crystal with sufficient size and quality for X-ray crystallography. We conducted DFT-XAS-based structural analysis of such flexible molecule. Recently, Prof. Uemura and Benjamin found a flexible MOF prepared from $[Zn_2(BDC)_2(DABCO)]_n$ and polystyrene which has a polymer-threaded multi-layered structure after removing the DABCO pillar ligand. The polymer-threaded extremely flexible molecular scaffolds showed no clear diffraction pattern except for a broad peak. To determine the molecular structure of this flexible MOF system, we carried out Zn K-edge and O K-edge XAS. A DFT-based simulation of both XAS spectra clearly demonstrated that $[Zn_2(BDC)_2]_n$-monolayer was preserved well in the turbostratic phase without DABCO pillar.

Another successful application was achieved in the structure determination of rotaxane-linked iron porpyrin dimer in which two units of iron-porpyrin or phtalocyanine were interlocked through highly flexble quadruplet axials. Fe K-edge XAS-based structural analysis supproted with DFT-MD-based simulation succefully provides the precise local coordionation geometry of iron centers in highly flexible supramolecular system.

References

1) H. Masafumi, K. Sano, Y. Kanazawa, N. Komine, Z. Maeno, T. Mitsudome and H. Takaya, *ACS Catl.* **8**, 5827–5841 (2018).
2) Y. Kanazawa, T. Mitsudome, H. Takaya and M. Hirano, *ACS Catal.* **10**, 5909–5919 (2020).
3) Y. Aoki, T. Toyota, H. Kawasaki, H. Takaya, A. K. Sharma, K. Morokuma and M. Nakamura, *Asian J. Org. Chem.* **8**, 1–6 (2019).
4) Y. Tanaka, Y. Kitamura, R. Kawano, K. Shoji, M. Hiratani, T. Honma, H. Takaya, H. Yoshikawa, T. Tsuruoka and D. Tanaka, *Chem. –Eur. J.* **26**, 1–9 (2020).
5) L. O. Benjamin, H. Takaya and T. Uemura, *J. Am. Chem. Soc.* **141**, 14549–14553 (2019).
6) N. Mihara, Y. Yamada, H. Takaya, Y. Kitagawa, K. Igawa, K. Tomooka, H. Fujii and K. Tanaka, *Chem. –Eur. J.* **25**, 3369–3375 (2019).
7) N. Mihara, Y. Yamada, H. Takaya, Y. Kitagawa, S. Aoyama, K. Igawa, K. Tomooka and, K. Tanaka, *Chem. –Eur. J.* **23**, 7508–7514 (2017).