

Innovative Catalysis Development Based on Radiant Light Spectroscopy

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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 copper 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 light 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, CO₂, and biomass into valuable functional materials.

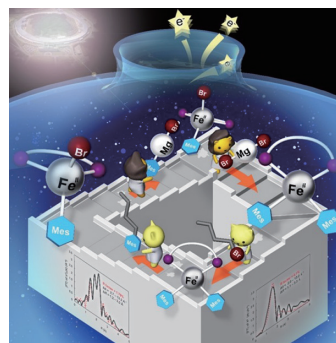


Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

Selected Publications

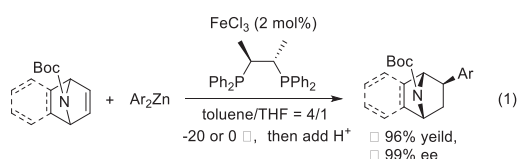
- H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagi, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi and M. Nakamura, "Investigation of Organoiron Catalysis in Kumada-Tamao-Corriu-Type Cross-Coupling Reaction Assisted by Solution-Phase X-Ray Absorption Spectroscopy," *Bull. Chem. Soc. Jpn.* **88**, 410–418 (2015).
- 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).
- Y. Kanazawa, T. Mitsudome*, H. Takaya* and M. Hirano*, "Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate: Synchrotron Radiation Sheds Light on the Cu Cycle Mechanism," *ACS Catal.* **10**, 5909–5919 (2020).
- L. Adak, M. Jin, S. Saito, T. Kawabata, T. Itoh, S. Ito, A. K. Sharma, N. J. Gower, P. Cogswell, J. Geldsetzer, H. Takaya, K. Isozaki and M. Nakamura*, "Iron-Catalysed Enantioselective Carbometalation of Azabicycloalkenes," *Chem. Commun.* **57**, 6975–6978 (2021).

1. DFT-XAS-based Mechanistic Investigation of Transition-Metal-Catalyzed Reaction in Homogeneous Phase¹⁻⁴⁾

Mechanistic study on transition-metal complex-catalyzed reaction in homogeneous phase mostly carried out by means of solution-phase NMR analysis. However, studies on base metal catalysts being essential for SDGs achievement often suffer from difficulties due to their paramagnetic property which provide unusual large paramagnetic shifts with significant peak broadening. To solve the problems in mechanistic study of base metal-catalyzed reaction, we conducted to use XAS which enables element specific analysis to determine the oxidation state and the geometry of catalytic species without interference from the paramagnetic property.

Recently, we have succeeded to elucidate the mechanism of Pd/Cu-catalyzed oxidative coupling of dimethyl phthalate where the oxidation states and the local coordination geometries of catalytic intermediates were determined under the stoichiometric conditions of each reaction path.^{1,2)} DFT- and single crystal X-ray structural analysis adequately provided the precise molecular structure of these intermediates. This research is the 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 paramagnetic transition-metal complex-catalyzed reactions being difficult by means of the conventional solution-phase NMR analysis.

Effectiveness of the DFT-XAS-based mechanistic study on paramagnetic transition-metal complex-catalyzed reaction was clearly demonstrated in iron-catalyzed enantioselective carbometallation of azabicycloalkenes (eq. 1).³⁾ In this study, formation of diphosphine ligand-coordinated tetrahedral iron species, which is a key species for chiral recognition of substrate, was successfully identified with the molecular structure in the reaction mixture.



2. XAFS-Based Structural Study on Flexible Organometallic Systems⁵⁻⁷⁾

Generally, organometallics bearing highly flexible molecular structure make it difficult to prepare a single crystal bearing 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.⁴⁾

Another successful application was achieved in the structure determination of double-decker type iron porphyrin/phtalocyanine dimer in which two units of iron-porphyrin or phtalocyanine were interlocked through highly flexible quadruplet axials or iron-oxo linkage.^{5,6)} Fe K-edge XAS-based structural analysis supported with DFT-MD-based simulation successfully provides the precise local coordination geometry of iron centers in highly flexible supramolecular system.

Another successful example of the DFT-XAS-based structural study was demonstrated by the molecular structure determination of an anionic homoleptic organo-transition metal complex of $[Li(12-crown-4)_2][MPh_6\{Li(thf)\}_2]$ (M = Rh and Ir) in THF solution which are the first examples of hexaaryl complexes of d6 metals with a partially contacted ion pair structure of $Ir^{2-}-Li^+$ in solution-phase.⁷⁾

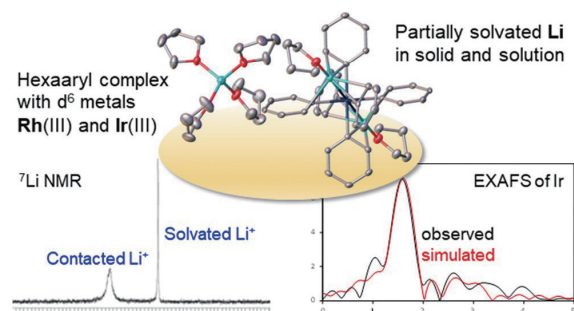


Figure 2. The molecular structure determination of $[Li(12-crown-4)_2][MPh_6\{Li(thf)\}_2]$.

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