International Research Center for Elements Science – Organometallic Chemistry –

http://om.kuicr.kyoto-u.ac.jp/en/index.html

Prof
OHKI, Yasuhiro
(D Eng)

Assist Prof
TANIFUJI, Kazuki
(D Sc)

Assist Prof
HIGAKI, Tatsuya
(Ph D)

Program-Specific Res
IZU, Hitoshi
(D Sc)

PD (JSPS)
JAYAKUMAR, Sanjeevi
(Ph D)

Assist Techn Staff

FUJISAKI, Yoshie

Students

KATO, Itsuki (M1)
MATSUOKA, Yuto (M1)
TANAKA, Kanata (M1)
SHIMOYAMA, Sayaka (UG)
SUNAMI, Kohei (UG)
HOSHI, Yutaro (UG)

Scope of Research

Developing efficient energy storage systems and innovative material production processes is a significant challenge for chemists to contribute to a sustainable society. We plan to approach these problems by using *transition metal clusters* of which multiple metal atoms work together as catalysts and functional materials. Our laboratory focuses explicitly on creating a new method to synthesize the clusters with atomic precision and applying the obtained clusters to difficult reactions such as the reduction of CO_2 and N_2.

KEYWORDS

Transition Metal Clusters
Homogeneous Catalysis
Nitrogen Fixation
Bioinorganic Chemistry

Recent Selected Publications

Ohki, Y.; Munakata, K.; Matsuoka, Y.; Hara, R.; Kachi, M.; Uchida, K.; Tada, M.; Cramer, R. E.; Sameera, W. M. C.; Takayama, T.; Sakai, Y.; Kuriyama, S.; Nishibayashi, Y.; Tanifuji, K., Nitrogen Reduction by the Fe Sites of Synthetic [Mo_3S_4Fe] Cubes, *Nature,* **607,** 86-90 (2022).

Lee, C. C.; Kang, W.; Jasniewski, A. J.; Stiebritz, M. T.; Tanifuji, K.; Ribbe, M. W.; Hu, Y., Evidence of Substrate Binding and Product Release via Belt-Sulfur Mobilization of the Nitrogenase Cofactor, *Nat. Catal.*, **5,** 443-454 (2022).

Tanifuji, K.; Sakai, Y.; Matsuoka, Y.; Tada, M.; Sameera, W. M. C.; Ohki, Y., CO Binding onto Heterometals of [Mo_3S_4M] (M = Fe, Co, Ni) Cubes, *Bull. Chem. Soc. Jpn.*, **95,** 1190-1195 (2022).

Tanifuji, K.; Jasniewski, A. J.; Villarreal, D.; Stiebritz, M. T.; Lee, C. C.; Wilcoxen, J.; Ohki, Y.; Chatterjee, R.; Bogacz, I.; Yano, J.; Kern, J.; Hedman, B.; Hodgson, K. O.; Britt, R. D.; Hu, Y.; Ribbe, M. W., Tracing the Incorporation of the "Ninth Sulfur" into the Nitrogenase Cofactor Precursor with Selenite and Tellurite, *Nat. Chem.*, **13,** 1228-1234 (2021).

Tanifuji, K.; Ohki, Y., Metal-Sulfur Compounds in N_2 Reduction and Nitrogenase-Related Chemistry, *Chem. Rev.*, **120,** 5194-5251 (2020).

Catalytic N_2 Silylation by the Fe Sites of Cuboidal $[Mo_3S_4Fe]$ Clusters

Biological N_2 fixation is conducted by nitrogenase that employs a unique Fe/Mo-S-C cluster as its catalytic site (FeMoco, [(*R*-homocitrate)$MoFe_7S_9C$]). Synthetic counterparts of the FeMoco, metal-sulfur clusters, demonstrated capturing N_2 on rare occasions; nevertheless, the catalytic conversion of this stable molecule has not been achieved despite its relevance to the biological N_2 fixation. This study focuses on capture, activation, and catalytic conversion of N_2 by an Fe atom incorporated into our $[Mo_3S_4]$ incomplete-cubane platform bearing bulky Cp ligands. Treatment of these clusters with excess Na and $ClSiMe_3$ under a N_2 atmosphere gave $N(SiMe_3)_3$ with up to 248 eq. per cluster. This work exemplifies the N_2-reducing capability of Fe atoms in a S-rich environment, which biological systems have selected to achieve a similar purpose. Further studies are ongoing to unveil the effect of an incorporated metal atom (Fe vs Co or Ni) on catalytic N2 silylation.

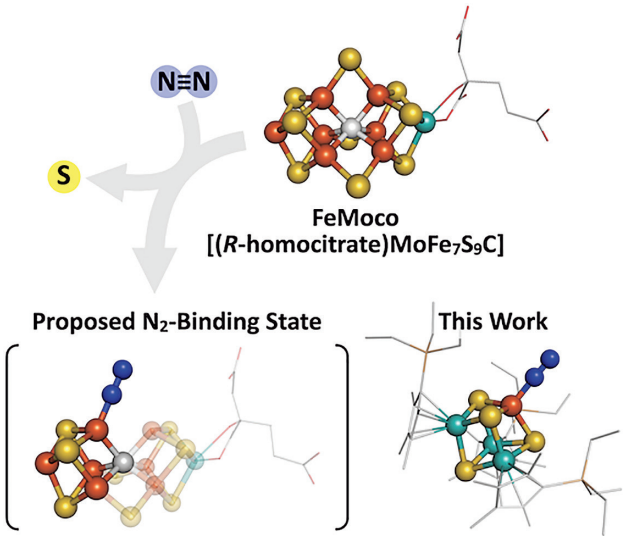

Figure 1. Proposed N_2 binding state of FeMoco and a N_2-bound Mo-Fe-S cluster.

Tracing the S Incorporation into the Nitrogenase Cofactor Precursor

FeMoco is arguably one of the most complex metallocofactors in Nature. Its biosynthetic pathway is correspondingly complicated and remains unclear, which hampers applications of this enzyme toward artificial N_2 fixation. In this study, we investigated an enzymatic process by which FeMoco precursor (L-cluster, $[Fe_8S_9C]$) is generated from two $[Fe_4S_4]$ clusters on the protein by using a *semi-synthetic* approach. The study revealed that this process includes a S atom uptake from SO_3^{2-} and that the S atom is replaceable with homologous elements (Se, Te). Moreover, we succeeded in selective observation of the incorporated elements and theoretical simulations supporting the reactions' feasibility. These results show that nitrogenase requires an S source as an external substrate for its function.

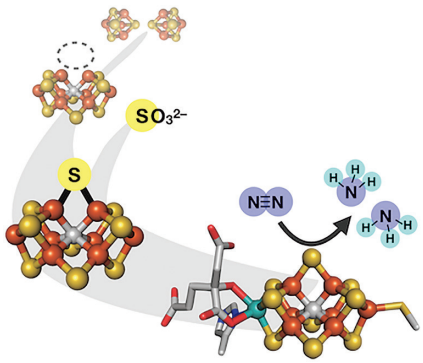

Figure 2. Schematic description of a sulfur uptake from sulfite (SO_3^{2-}) in the biosynthetic pathway of FeMoco.