

International Research Center for Elements Science – Organometallic Chemistry –

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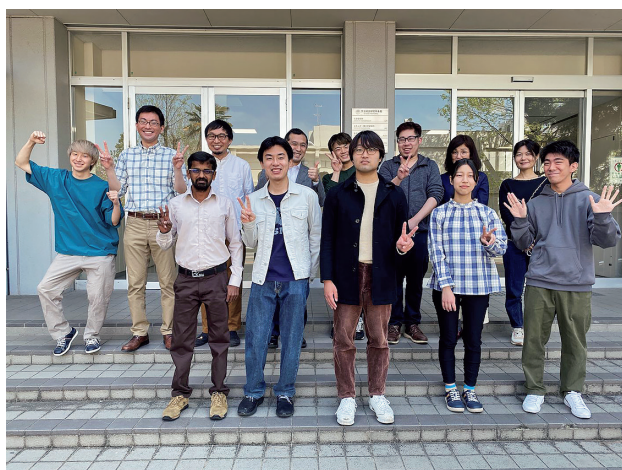
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Scope of Research

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 CO₂ and N₂.

KEYWORDS

Transition Metal Clusters
Homogeneous Catalysis
Nitrogen Fixation
Bioinorganic Chemistry



Recent Selected Publications

Izu, H.; Bhave, D. G.; Matsuoka, Y.; Sameera, W. M. C.; Tanifuji, K.; Ohki, Y., Synthesis, Characterization, and Catalytic Activity of a Cubic [Mo₃S₄Pd] Cluster Bearing Bulky Cyclopentadienyl Ligands, *Eur. J. Inorg. Chem.*, **26**, e202300399 (2023).

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 [Mo₃S₄Fe] Cubes, *Nature*, **607**, 86-90 (2022).

Lee, C. C.; Kang, W.; Jasiewski, 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 [Mo₃S₄M] (M = Fe, Co, Ni) Cubes, *Bull. Chem. Soc. Jpn.*, **95**, 1190-1195 (2022).

Tanifuji, K.; Ohki, Y., Metal-Sulfur Compounds in N₂ Reduction and Nitrogenase-Related Chemistry, *Chem. Rev.*, **120**, 5194-5251 (2020).

Catalytic N₂ Silylation by the Fe Sites of Cuboidal [Mo₃S₄Fe] Clusters

Biological N₂ fixation is conducted by nitrogenase that employs a unique Fe/Mo-S-C cluster as its catalytic site (FeMoco, [(*R*-homocitrate)MoFe₇S₉C]). Synthetic counterparts of the FeMoco, metal-sulfur clusters, demonstrated capturing N₂ on rare occasions; nevertheless, the catalytic conversion of this stable molecule has not been achieved despite its relevance to the biological N₂ fixation. This study focuses on capture, activation, and catalytic conversion of N₂ by an Fe atom incorporated into our [Mo₃S₄] incomplete-cubane platform bearing bulky Cp ligands. Treatment of these clusters with excess Na and ClSiMe₃ under a N₂ atmosphere gave N(SiMe₃)₃ with up to 248 eq. per cluster. This work exemplifies the N₂-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.

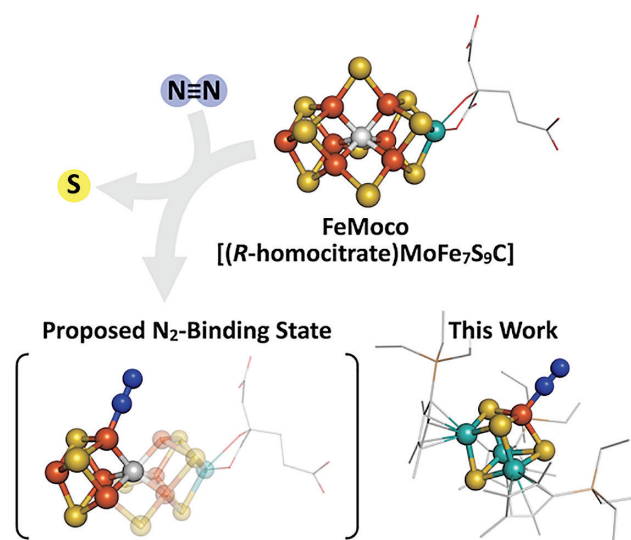


Figure 1. Proposed N₂ binding state of FeMoco and a N₂-bound Mo-Fe-S cluster.

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 N₂ fixation. In this study, we investigated an enzymatic process by which FeMoco precursor (L-cluster, [Fe₈S₉C]) is generated from two [Fe₄S₄] clusters on the protein by using a *semi-synthetic* approach. The study revealed that this process includes a S atom uptake from SO₃²⁻ 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.

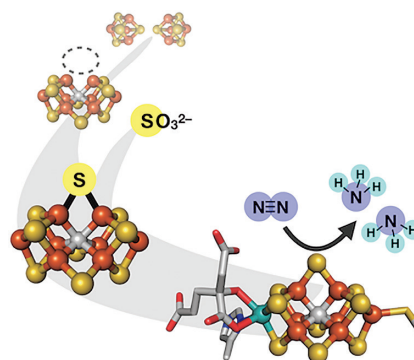


Figure 2. Schematic description of a sulfur uptake from sulfite (SO₃²⁻) in the biosynthetic pathway of FeMoco.