アカデミックプログラム［Ｂ講演］｜09. 錯体化学・有機金属化学：口頭Ｂ講演

2024年3月19日(火) 15:55 ~ 17:15 F1232(12号館 [3階] 1232)

[F1232-2vn] 09. 錯体化学・有機金属化学

座長：亀尾 肇、小林 厚志

英語

15:55 ~ 16:15

[F1232-2vn-01]

Photocatalytic CO_2 Reduction Using Binary Metal-Porphyrins as Photosensitizer and Catalyst Units

〇Sunghan Choi[1], Sebastian Nybin Remello[1], Osamu Ishitani[1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

英語

16:15 ~ 16:35

[F1232-2vn-02]

Electrocatalytic Reduction of Low Concentration CO_2 by Iron Porphyrins

〇Sebastian Nybin Remello[1,3], Osamu Ishitani[1,2] (1. Tokyo Institute of Technology , 2. Hiroshima University, 3. Cochin University of Science and Technology)

日本語

16:35 ~ 16:55

[F1232-2vn-03]

鉄ジシリル錯体を用いた炭素−ヘテロ二重結合切断反応

〇菅 雄翔[1]、砂田 祐輔[1,2] (1. 東大院工、2. 東大生研)

英語

16:55 ~ 17:15

[F1232-2vn-04]

An Iron Porphyrin-Based Framework Catalyst for Highly Efficient Photocatalytic CO_2 Reduction

〇XIANJUN LI[1], Kento KOSUGI[2], Maho IMAI[2], Yutaka SAGA[2], Tetsuya KAMBE[2], Shigeyuki MASAOKA[2], Mio KONDO[1,2,3] (1. Tokyo Institute of Technology, 2. Osaka University, 3. JST PRESTO)

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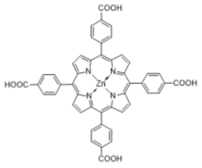
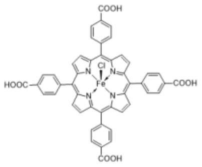
Title: Photocatalytic CO_2 Reduction Using Binary Metal-Porphyrins as Photosensitizer and Catalyst units

Sunghan CHOI, Sebastian Nybin Remello, Osamu Ishitani*

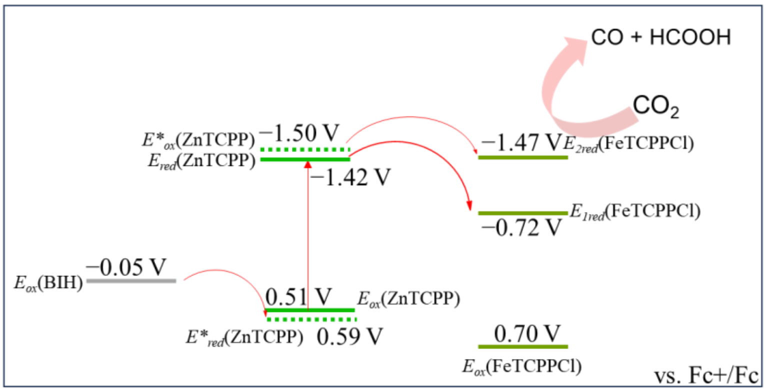
Photocatalytic CO_2 reduction consisting of both ZnTCPP and FeTCPP efficiently proceeded due to optimized electron transfer within their close distance. Furthermore, employing a metal-organic framework (MOF) containing ZnTCPP, FeTCPP linkers, and ZrO clusters exhibited substantial CO_2 reduction capabilities.



ZnTCPP



FeTCPP



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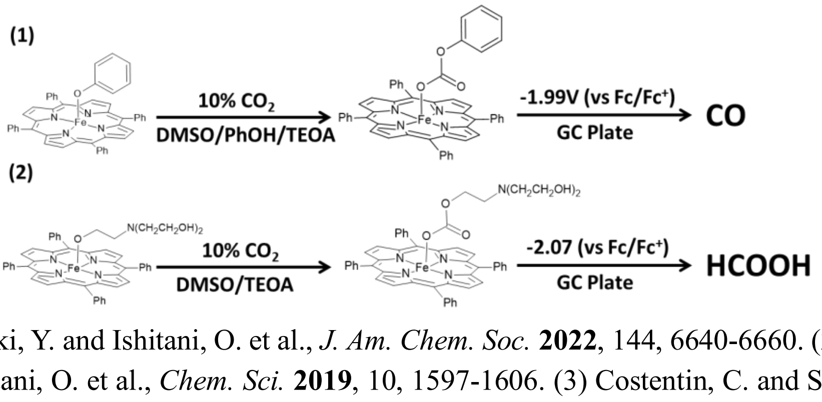
Electrocatalytic Reduction of Low Concentration CO_2 by Iron Porphyrins

([1]*Tokyo Institute of Technology*, [2]*Hiroshima University,* [3]*Cochin University of Science and Technology*) ○Sebastian Nybin Remello,[1,3] Osamu Ishitani[1,2]

Keywords: Low Concentration CO_2 Reduction; Iron Porphyrin; Electrocatalytic reaction

Transition Metal Complexes are one of the effectively utilized systems for the selective conversion of CO_2 with high efficiency, and most of these catalyst systems can function effectively under electrochemical and photochemical conditions. For the practical realization of these systems for the direct conversion of CO_2 in the flue gas, the catalyst should work under low concentrations of CO_2.[1] The Re(I) complexes with a deprotonated triethanolamine are efficient catalysts for direct reduction of low-concentration CO_2; the versatility of this system is attributed to the fast CO_2 insertion reaction to the Re-O bond.[2] However, considering the elemental strategy, we should identify other efficient catalysts based on earth-abundant elements that can work under low CO_2 concentrations.

Porphyrin complexes of iron are efficient catalysts for CO_2 reduction under electrochemical and photochemical conditions. Selective electrochemical reduction of CO_2 to CO is observed in most iron porphyrin-based catalyst systems under pure CO_2 atmosphere when a Brønsted acid is employed as an additive or prepositioned near the catalyst by ligand modification.[3] In this report, we could successfully observe CO formation using the commercially available iron porphyrin catalyst Fe(III) tetraphenyl porphyrin (FeTPP), under 10% CO_2 concentration with a 91% faradic yield and 23 TON in the presence of phenol and TEOA (trace,) indicating the possibility phenyl carbonate formation with FeTPP-Phenol system (eq. 1). The formation of Fe-CO_2-OPh was confirmed using FTIR by observing the C=O stretching upon CO_2 bubbling to the FeTPP-OPh complex. Another aspect is the possibility of low-concentration CO_2 reduction in the presence of triethanolamine (TEOA); the reaction produced HCOOH as the major product with a 52% faradic yield and 12 TON, in this case also, the CO_2 inserted complex, Fe-CO_2TEOA was observed using FTIR (eq. 2).



(1) Yamazaki, Y. and Ishitani, O. et al., *J. Am. Chem. Soc.* **2022**, 144, 6640-6660. (2) Kumagai, H. and Ishitani, O. et al., *Chem. Sci.* **2019**, 10, 1597-1606. (3) Costentin, C. and Savéant J. M. et al., *Science* **2012**, 338 (6103), 90-94.

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鉄ジシリル錯体を用いた炭素–ヘテロ二重結合切断反応

（東大院工 [1]・東大生産研 [2]）　○菅　雄翔 [1]・砂田　祐輔 [1,2]

Cleavage of Carbon–Heteroatom Double Bonds by Iron Disilyl Complexes

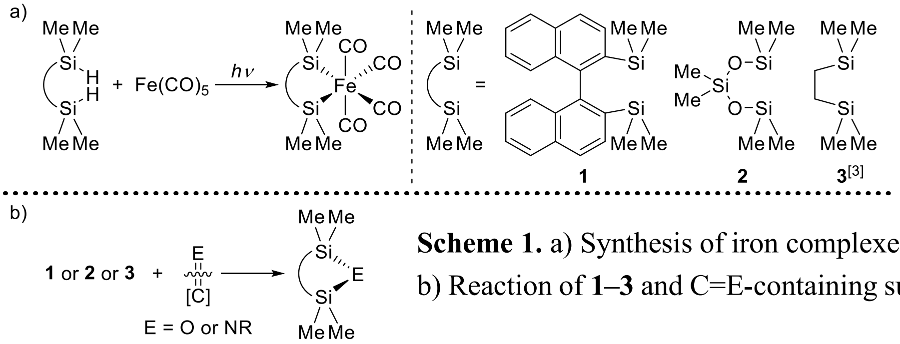
([1]*Graduate School of Engineering and* [2]*Institute of Industrial Science, The University of Tokyo*)
○Yuto Suga[1], Yusuke Sunada[1,2]

Transition metal complexes bearing organosilyl ligands exhibit unique reactivity reflecting the chemical properties of silicon moieties. For instance, coordinatively unsaturated and electron-rich metal complexes could be facilely synthesized by introducing the organosilyl ligands due to their strong electron donating properties as well as strong *trans*-influence. In addition, oxophilic property of silicon moiety led to the effective activation of oxygen-containing molecules such as carbonyl compounds.[1]

Herein, we synthesized a series of iron complexes **1**–**3** bearing bridging disilyl ligands (Scheme 1-a). We found that **1**–**3** could cleave the C=E (E = O, NR) double bonds of the substrates to afford cyclic compounds bearing silicon–heteroatom bonds (Scheme 1-b). A similar reaction using **3** was previously reported by Nakazawa and Gladysz, but the applicable substrates were limited to aldehydes.[2] In contrast, both ketones and imines could be used in our system. For instance, C=O double bond of cyclopropenone was facilely cleaved by iron complexes, giving cyclic siloxane in good yield. It should be emphasized here that an iron complex bearing cyclopropenyl-1-ylidene ligand could also be isolated.

Keywords : Iron, Silicon, Carbene, Double Bond Cleavage

有機ケイ素配位子を持つ遷移金属錯体は、ケイ素配位子の強い電子供与性や親酸素性などの特性を反映した種々の興味深い性質を示す[1]。今回我々はまず、架橋ジシリル配位子を有する鉄錯体 **1**–**3** (Scheme 1-a) を合成した。さらに、**1**–**3** が基質の C=E (E = O, NR) 二重結合を切断し、環状 Si–E–Si 化合物を与えることを見出した (Scheme 1-b)。同様の反応が Nakazawa, Gladysz らによって報告されているが、基質はアルデヒドに限られている[2]。一方、我々の系ではケトンやイミンも基質として適用可能であった。さらに、シクロプロペノンを基質として用いた際には、環状ジシロキサンに加えてシクロプロペニリジン配位子を有する鉄錯体が得られた。



Scheme 1. a) Synthesis of iron complexes **1**–**3**.
b) Reaction of **1**–**3** and C=E-containing substrates.

[1] M. T. Whited, B. L. H. Taylor, *Comments Inorg. Chem.* **2020**, *40*, 217.
[2] H. Nakazawa, D. L. Johnson, J. A. Gladysz, *Organometallics* **1983**, *2*, 1846.
[3] L. Vancea, W. A. G. Graham, *Inorg. Chem.* **1974**, *13*, 511.

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An Iron Porphyrin-Based Framework Catalyst for Highly Efficient Photocatalytic CO_2 Reduction

([1]*Tokyo Institute of Technology*, [2]*Osaka University*, [3]*JST PRESTO*) ○Xianjun Li[1], Kento Kosugi[2], Maho Imai[2], Yutaka Saga[2], Tetsuya Kambe[2], Shigeyuki Masaoka[2], Mio Kondo[1,3]

Keywords: CO_2 Reduction; Photochemical Reaction; Iron Porphyrin; Self-Assembly; Heterogeneous catalyst

To address both challenges of global warming and energy scarcity, visible-light driven CO_2 reduction (e.g., $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$) can be a viable solution, and the development of catalytic systems for the reaction is widely studied.

In this work, we aimed to construct a novel catalytic system for photochemical CO_2 reduction. An iron porphyrin complex bearing carboxyl groups (-COOHs) at its peripheral positions (Fe(III) meso-tetra(4-carboxyphenyl) porphyrin chloride), **[FeCl(H_4P)]**, Figure 1) was employed as the basic unit.

Self-assembly of **[FeCl(H_4P)]** afforded a framework catalyst, **[Fe(H_2P)]$_n$** (Figure 2), which possesses fixed carboxylate groups and free carboxyl groups with a multifunctional environment. **[Fe(H_2P)]$_n$** shows very high catalytic activity for a photocatalytic CO_2 reduction to form CO at under visible-light irradiation in a CO_2-saturated acetonitrile (MeCN) solution containing $Ir(ppy)_3$ (Hppy = 2-phenylpyridine, 20 μM) as a photosensitizer, 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH, 0.2 M) as a sacrificial electron donor, and trifluoroethanol (TFE, 0.2 M) as a proton source. During a 3-hours of photocatalytic experiment, the amount of CO increased extremely fast while H_2 evolution was negligible (Figure 3). An average production rate of CO reached 1.8×10^6 /μmol g^{-1} h^{-1} with 100% of selectivity. This rate is new record among molecule-based heterogeneous photocatalytic systems for CO_2 reduction to produce CO reported up to now.

In the presentation, we will also show the detailed results of robustness tests, gas adsorption results and investigation of proton conductivity.

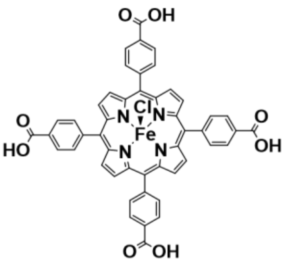

Figure 1. Chemical structure of **[FeCl(H_4P)]**

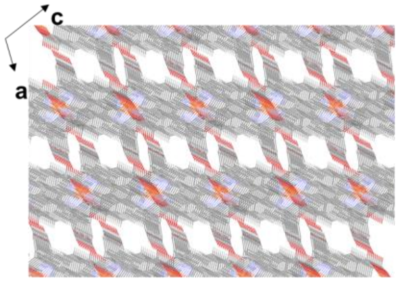

Figure 2. Crystal packing structure of **[Fe(H_2P)]$_n$**

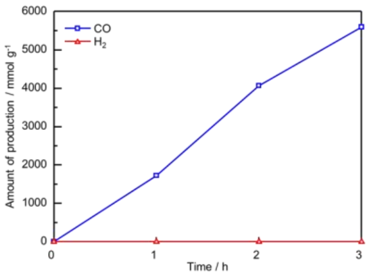

Figure 3. Production amounts of CO and H_2 generated from CO_2 saturated MeCN solution, which contained 16 μg **[Fe(H_2P)]$_n$**, 20 μM $Ir(ppy)_3$, 0.2 M BIH and 0.2 M TFE, being irradiated with a Xe lamp (400 ≤ λ ≤ 750 nm) over 3 h at 20 °C.

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