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学位論文題目 Development of metal-complex based catalysts for electro-
and photo-chemical CO₂ reduction

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Summary of Doctoral Thesis

Name in full Lee Sze Koon

Title Development of metal-complex based catalysts for electro- and photo-chemical CO₂ reduction

Catalytic CO₂ reduction into liquid fuels and commodity chemicals under benign condition has drawn tremendous attention, not only as a means to decrease the competition for limited fossil fuel reserves but also help to reduce the concentration of atmospheric CO₂. The conversion of CO₂ into small molecules such as carbon monoxide (CO) and formic acid (HCOOH) is economically desirable. This is because CO can be used to synthesize methanol (CH₃OH) with existing Fischer-Tropsch technology, while HCOOH represents as a promising reversible hydrogen carrier and other applications.

In this context, we are interested in exploring transition metal complexes containing redox-active ligand(s) as catalysts for CO₂ reduction. Redox-active ligands with extensive conjugated systems can store reducing electrons in their π -network and help to stabilize transition metals in low oxidation states. These features can suppress the purely metal-centered reduction that is usually energetically more demanding. In addition, transition metal centers of the complexes can adopt several oxidation states and act as active sites for CO₂ reduction. These metal complexes are also expected to exhibit selective CO₂ reduction activity over the competing proton reduction reaction. Therefore, this class of complexes should accumulate multiple reducing equivalents at as low a potential as possible, which is at least thermodynamically sufficient to catalyze the reaction, and can serve as excellent catalysts for CO₂ reduction.

In this doctoral thesis, after the General Introduction, the low-overpotential electrochemical CO₂ reduction by a phosphine-substituted Ru polypyridyl complex is reported in Chapter 1. In the previously reported electrocatalytic CO₂ reduction system based on Ru polypyridyl complexes, a large potential is applied in order to achieve a significant rate of the reaction. This large overpotential, which corresponds to an activation energy of the reaction, has been one of the drawbacks of the system. Therefore, the development of an electrocatalyst that can operate at low-overpotential is of utmost importance to improve the performance of the system. In this study, I have succeeded in developing a Ru complex that can promote electrocatalytic CO₂ reduction to CO (TOF = 4.7 s⁻¹) at low-overpotential (η = 0.4 V) by the introduction of a phosphine ligand at the position *trans* to the labile ligand. A Ru complex with a mixed phosphine-pyridine ligand, *trans*(*P*,*MeCN*)-[Ru(*tpy*)(*pqn*)(*MeCN*)]²⁺ (*pqn* = 8-

(diphenylphosphanyl)quinoline) was employed as a catalyst in this study. Detailed investigations including cyclic voltammetry, bulk electrolysis, spectro-electrochemical measurement, and DFT-calculation, were performed to shed light on the catalytic activity and the reaction mechanism, I also revealed that the σ -donation character of phosphine destabilizes the Ru–N(MeCN) bond, while π -back donation character of phosphine participates in stabilizing the Ru–C(CO₂) bond of CO₂ adduct. As a result, the Ru complex can bind CO₂ at the one-electron reduced state and catalyze CO₂ reduction with low-overpotential, which is different from conventional Ru polypyridyl complexes that bind CO₂ at its two-electron reduced state. DFT calculation supported that the electron is stored in the redox-active tpy ligand during the first reduction. The work provides a new strategy to reduce the overpotential of electrocatalyst for CO₂ reduction.

In Chapter 2, I extend the work in Chapter 1 to study the photocatalytic CO₂ reduction activity of the phosphine-substituted Ru polypyridyl complex. Generally, dye-sensitized photocatalytic CO₂ reduction has been widely reported using a combination of photosensitizer (light-absorbing unit) and catalyst (active center). In this regard, Ru polypyridyl complexes were commonly used as photosensitizer to drive photoreactions, and they were also known to active for CO₂ reduction. However, to our surprise, there have been no example of a non-sensitized mononuclear Ru complex that can function as both the photosensitizer and catalyst for CO₂ reduction. Non-sensitized photocatalyst exhibits several advantages over the dye-sensitized photocatalytic system because the non-sensitized photocatalyst require less component, lower cost, easier reaction optimization, and also reduces number of the intermolecular electron transfer events. In this study, I successfully developed the first example of non-sensitized mononuclear Ru photocatalyst for CO₂ reduction driven by visible-light. The key to success is the Ru polypyridyl scaffold that allows visible-light harvesting, ability to bind CO₂ upon first reduction, and a monodentate labile site for substrate binding and product dissociation. This Ru photocatalyst showed excellent stability and activity as compared to current-best-in-class counterparts. I also found that the selectivity of the product can be tuned depending on the acidity of the reaction media. Under slightly acidic condition, >94 % of CO was selectively produced, while >99 % of HCOOH was selectively formed under slightly basic environment. I have successfully isolated and characterized an essential catalytic intermediate, carbonyl-coordinated Ru complex, and proposed the plausible catalytic mechanism. This novel non-sensitized Ru photocatalyst open new avenues for photoelectrochemical cell and other photocatalysis application.

In Chapter 3, I demonstrate the visible-light driven CO₂ reduction by Ni complexes containing redox-active ligands. The construction of molecular catalysts based on abundant and cheap first-row transition metals is beneficial for economically viable application. In nature, Ni-containing carbon monoxide dehydrogenase (CODH) can carry out selective CO₂ reduction to CO, which is assisted by a precisely positioned redox-active ferredoxin unit. As inspired by CODH and results from Chapters 1 and 2, I newly designed Ni complexes with redox-active iminopyridine moieties in order to promote multi-electron CO₂ reduction. These Ni complexes exhibit two reversible redox waves within -2.0 V vs. ferrocene/ferrocenium that is attributed to the Ni center and iminopyridine-based reduction. The complexes could promote selective photocatalytic CO₂ reduction to produce CO under visible-light irradiation with the assistance of Ru photosensitizer, [Ru(dmb)₃]²⁺ (dmb = 4,4'-dimethyl-2,2'-dipyridyl). Previously, Ni complexes containing redox-active iminopyridine moieties showed poor faradaic efficiency for electrochemical CO₂ reduction to CO and no photochemical study has been reported. Current work showed for the first time that redox-active iminopyridine ligand can assist Ni complex for selective photochemical CO₂ reduction to produce CO under visible-light.

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博士論文審査結果

Name in Full 氏名 Lee Sze Koon

論文題目 Development of metal-complex based catalysts for electro- and photo-chemical CO₂ reduction

我々人類が直面するエネルギー枯渇・環境破壊・地球温暖化といった深刻な問題を解決するための一つの方策として、太陽光エネルギーを化学エネルギーへと変換可能な人工光合成反応が大きな注目を浴びている。とりわけ、二酸化炭素 (CO₂) 還元反応はクリーンなエネルギー源の創製と CO₂ 排出量の抑制とを同時に達成できる点で非常に魅力的である。本学位論文では、電気化学的或いは光化学的に二酸化炭素を還元する金属錯体触媒の開発をその目的とし、種々の金属錯体の触媒活性ならびにその反応機構に関する研究について報告している。以下に概要を示す。

序論に続き、第 1 章では、ルテニウム単核錯体を用いた電気化学的 CO₂ 還元反応についてまとめている。本研究では、リン原子の導入による反応性の向上を期待し、含リン原子配位子を有したルテニウム錯体 (RuP) を触媒として選択した。RuP の触媒活性について各種電気化学測定により評価を行い、RuP が低過電圧で CO₂ を一酸化炭素 (CO) へと選択性良く還元できることを見出した。また、分光電気化学測定ならびに量子化学計算に基づいた触媒反応機構の解明にも成功している。その結果、金属錯体中に導入したリン原子がルテニウムイオンと基質 (CO₂) の結合を促進することで、良好な触媒活性が発現することが明らかとなった。

第 2 章では、光化学的 CO₂ 還元触媒の開発について報告している。光化学的 CO₂ 還元では、触媒反応の進行に必要な 2 つの反応 (光反応および化学反応) を、1 つの分子 (機能統合型触媒) で担うことができれば、良好な触媒の開発が可能となる。このような観点に基づく触媒の開発はこれまでもなされてきたが、光を効率的に吸収し、大きな速度で CO₂ 還元反応を進行させ、長期間にわたり安定な触媒の開発は達成されていない。本研究では、可視域に強い吸収を示す RuP の光化学的 CO₂ 還元触媒としての評価を行った。その結果、RuP がこれまでに報告された機能統合型 CO₂ 還元触媒の中で最も大きな反応速度ならびに触媒回転数を示すことが明らかになった。更に各種条件での分光測定ならびに反応中間体の単離を行い、詳細な反応メカニズムを提唱している。

第 3 章では、酸化還元活性な配位子を有するニッケル錯体の CO₂ 還元能について報告している。自然界においてはニッケル錯体を有する金属酵素、carbon monoxide dehydrogenase (CODH) が酸化還元活性なタンパク質と共同的に作用することで CO₂ 還元反応を進行させることが知られている。そこで本研究では、酸化還元活性なイミノピリジン部位を有するニッケル錯体を新規に開発し、その触媒能について検討を行った。得られた錯体については単結晶 X 線構造解析により構造を明らかにした。また電気化学測定を行ったところ、金属中心並びに配位子部位に由来する酸化還元波が観測され、錯体が多電

子移動能を有することが判明した。更に、光増感剤の存在下で CO₂還元能について検討した結果、触媒反応が進行し、反応生成物として CO が選択的に得られることが明らかとなった。

以上のように、本学位論文では、金属錯体を用いた新たな二酸化炭素還元触媒の創出に成功した、また触媒反応の機構に関しても詳細に調査されており、その学術的意義は大きいと認められる。以上より、博士(理学)の学位を与えるのにふさわしい学位論文であると審査員全員一致で判断した。

(備考)

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