論文要旨

Ensuring the sustainability of current society has been recognized as the hardest challenge of the 21st century. The role of catalysts that promote energy conversions and affect the efficiency of chemical processes is crucial to achieve this goal, and the functions required for sustainable catalytic processes become more and more sophisticated. For the development of highly functional catalysts, it is necessary not only to accurately design active sites but also to construct desirable reaction fields where the selective adsorption and concentration of reaction substrates can occur. So far, the former, accurate design of active sites, has been mainly researched in the area of homogeneous catalysis defined by coordination complexes, while the latter, design of reaction fields has been studied in the field of heterogeneous catalysis using metal oxides as representatives. However, recent focus has also been directed towards organic-inorganic hybrid materials with both these characteristics. Among them, metal–organic frameworks (MOFs) built from organic linkers coordinated to inorganic clusters to form three dimensional nanoporous structures have attracted worldwide attention as platform for catalyst design. In addition to their high specific surface areas, their ordered geometrical arrangement of organic and inorganic parts can be tuned based on a bottom-up approach via self-assembly; therefore, MOFs are expected to be key materials for realizing advanced catalyst design at the

molecular level.

Methodologies for catalyst design based on MOFs mainly consist of the following three categories, (1) Construction of active sites on organic linkers, (2) Utilization of metal-oxo clusters as active sites and (3) Application as catalyst precursors. Method (1) aims at the integration of organo- or organometallic-catalysts into MOFs through a post-synthetic modification (PSM) or post-synthetic exchange (PSE) of organic linkers, resulting in highly active heterogeneous catalysts. Method (2) lies in the use of the inorganic parts of MOFs as quantum-sized metal oxide in expectation of their unique photocatalytic properties due to the specific electronic structures as well as their novel acid/base catalytic reactivities originating from coordinatively unsaturated sites. On the other hand, method (3) is utilized in catalyst preparation, such as the facile formation of metal particles-embedded carbon materials, through the carbonization of MOFs. In this procedure, the unique MOF structures consisting of metal–organic composites influence the formation process of the active metal species, thus enabling metal-encapsulation in a highly dispersed state, which is hardly achievable by already reported methods.

In this thesis, efforts were devoted to the development of highly active catalysts by use of these three methods and their application to environmentally benign reactions in view of clean energy production. Moreover, the active site structures of the synthesized catalysts were elucidated by various spectroscopic techniques. Especially structural and optical factors contributing to the catalytic activity were investigated in detail. This thesis is a compilation of these results and consists of a total of 6 chapters.

Chapter 1 summarized the background surrounding this thesis and the purpose of the present study.

Chapter 2 detailed the immobilization of photocatalytically-active Pt(II) complexes on the linker of MOFs by a PSM technique, corresponding to method (1), and evaluation of their photocatalytic activity towards visible-light-driven water reduction reaction (WRR). To immobilize Pt complexes, a MOF built from Zr-oxo clusters and 2-aminoterephthalic acid, named UiO-66-NH$_2$, was chosen due to its exceptional chemical stability. The integration of Pt(II) complexes inside UiO-66-NH$_2$ was carried out by a one-pot PSM technique involving imine condensation of 2-pyridinecarboxaldehyde (2-formyl pyridine) and 2-aminoterephthalic acid to create a nitrogen-based bidentate anchor, 2-pyridylimine terephthalic acid (PTA), instantly followed by complexation of Pt(II) ion on it. The composite, Pt(PTA)@UiO-66-NH$_2$, acquired visible-light absorption corresponding to the LMCT transition of the prepared Pt(II) complexes. According to the results of XAFS and ^{1}H NMR analyses, the formed complexes are of square planar geometry and chelated by PTA ligand. Pt(PTA)@UiO-66-NH$_2$ exhibited WRR photoactivity under visible-light irradiation in aqueous solution in the presence of appropriate sacrificial electron donor, and efficient recyclability was achieved thanks to its heterogenous nature. The present procedure was found to be applicable on various MOFs wielding amino moieties and proved to be of great versatility in the development of

MOF materials with visible light responsivity and catalytic WRR activity.

Chapter 3 described the development of MOF photocatalysts for visible-light-driven water oxidation reaction (WOR) using photoexcitation of metal-oxo clusters based on the guideline of method (2). In the development of visible-light-responsive WOR photocatalysts, it is known that designing materials possessing narrow band gap and deep valence band position to oxidize water is of major importance. Considering the previous results reporting that bulk iron oxide exhibits visible-light-driven WOR activity, the use of iron-based MOFs having iron-oxo clusters (Fe-MOFs) as photocatalysts was considered promising. Among Fe-MOFs, MIL-101(Fe) was chosen owing to its large pore diameter and surface area and then applied for the visible-light-driven WOR from aqueous solution in the presence of appropriate sacrificial electron acceptor. The results demonstrated that MIL-101(Fe) can promote the reaction efficiently under visible light irradiation with wavelengths up to 600 nm, and moreover it evolved 10 times more oxygen than bulk iron oxide. Through activity comparison to other Fe-MOFs and their action spectrum analyses, it was found that the trinuclear clusters with coordinatively unsaturated sites within MOF act as photocatalytically active sites for highly efficient WOR activity. Thanks to the molecular-sized iron-oxo clusters, the diffusion distance for photo-formed holes to reach the coordinatively unsaturated active surface sites, where holes react with reactants, can be considerably shortened, thus leading to lower recombination rate on MIL-101(Fe) as well as its higher photocatalytic activity compared to bulk iron oxide. Furthermore, MIL-101(Fe) electrodes were prepared by a drop-casting method for photoelectrochemical WOR. In comparison to anodes made from bulk iron oxide, MOF electrodes exhibited 4 times higher photocurrent in intensity. Nyquist plot measurement ascertained that charge transfer at the interface between active sites and the electrolyte was largely lowered, which contributed as the crucial factor to achieve the high photoelectrochemical performance of MIL-101(Fe) photoanodes.

Chapter 4 described the approaches employed to enhance the photoactivity of Fe-MOFs. Photo-formed holes and oxygen reactive species with high oxidizing power created by iron-based MOFs during WOR can potentially react with the organic linker, which needs to be inhibited. Thereby, significant expectations are put on catalyst design strategies to enhance the chemical stability of the linkers and promote the main reaction between holes and reactants.

First, from a standpoint of improving chemical stability, nine Fe-MOFs based on MIL-88B(Fe) were prepared using terephthalic acid derivatives with different substituents as organic linkers. Fe-MOFs with electron donating groups ($-NH_2$, $-OH$, $-CH_3$) all exhibited lower activity towards visible-light-driven WOR than the conventional MIL-88B(Fe) consisting of pristine terephthalic acid, while efficient promotion of the reaction was attained when using MOFs with electron withdrawing moieties ($-F$, $-Br$, $-NO_2$). Among them, Fe-MOF synthesized from tetrafluoroterephthalic acid evolved 5 times more O_2 than MIL-88B(Fe). Hydroxyl radical, one of the reactive intermediates formed during WOR, has been known for its high reactivity with aromatic compounds and especially hydroxylation of terephthalic acid derivatives. By introducing electron withdrawing groups, the

electron density of the benzene ring in MOFs was lowered, which would suppress the hydroxylation reaction. The prevention of the side reaction was considered as one of the factors for the improvement of the activity.

Next, in order to selectively promote the main reaction between holes and H_2O, combining Fe-MOFs with cobalt oxide (CoO_x) known as highly active cocatalysts for WOR was inquired. The composite showed enhanced activity towards visible-light-driven WOR, the amount of evolved O_2 was increased by about 2 times at the maximum with 2 wt% in Co content. On the other hand, considering the fact that the rate of 2-propanol oxidation reaction, which is a two-electrons oxidation reaction, was hardly affected by CoO_x loading, it was revealed that CoO_x acts as a hole trapping site on Fe-oxo clusters and exhibits high performance for four-electrons reactions, like WOR.

Chapter 5 detailed the preparation of alloy nanoparticles-embedded porous carbons using MOFs as a precursor, based on catalyst design method (3), and evaluation of their electrocatalytic properties. Metal nanoparticles-embedded porous carbons (M@PC) have been intensively studied in the research field of electrocatalysis since they possess numerous active sites at the interface between metal species and carbon and high electrical conductivity. In recent years, the alloying effect on the catalytic properties of metal nanoparticles within M@PC, that is MM'@PC, has also been studied. Based on this perspective, focus was placed on Fe-oxo clusters within MOFs, since the metal elemental ratio (M/M') of Fe-oxo clusters within MOFs can be controlled. In the present study, MM'@PC were prepared by pyrolysis of MOFs composed of bimetal-oxo clusters (BMCs) containing Fe as a main component. As a result of TEM observations and XRD measurements, MM'@PC (M' = Co, Mn, Ni, Cr) were found to possess desired alloy nanoparticles embedded in a carbon matrix. Application to electrocatalytic WOR revealed that FeCo@PC was the most active materials, where a 210 mV cathodic shift of overpotential towards WOR was observed to achieve 10 mA cm^{-2} in comparison to pure Fe@PC. On the other hand, FeMn@PC was found to exhibit the highest activity for ORR with a reduced overpotential of 80 mV compared to other composites.

In Chapter 6, the results and conclusions of these various investigations were summarized and an overview of this thesis was presented.

審査結果の要旨

本論文は、金属–有機構造体（Metal–Organic Framework: MOF）の構造設計性を利用し、ナノレベルで構造制御された不均一系触媒の調製法の開拓を行うとともに、その上で誘起される各種環境調和型反応に対する触媒反応性を探索した研究をまとめたものであり、次のような成果を得ている。

(1) 光触媒機能を示す Pt 錯体の MOF への固定化において、MOF のリンカー中の芳香族アミンのイミン縮合を利用した窒素二座配位子の形成とその上での錯形成反応をワンポットで行う手法が汎用性の高い有効な手法であることを明らかにしている。また、得られた MOF 材料が可視光応答型の不均一系光触媒として安定的に水素生成反応を促進することを見出している。

(2) MOF の金属酸化物クラスターを光機能性部位とする材料開発指針の下、Fe 系 MOF の光触媒反応性の検討を行い、三核 Fe クラスターを有する Fe 系 MOF がバルク酸化鉄と比較して著しく高い活性で可視光酸素生成反応を促進できることを見出している。さらに、得られた MOF 材料の電極化に成功するとともに、光電気化学的な酸素生成反応への応用も実現している。

(3) 置換基の異なるテレフタル酸誘導体を有機リンカーとする九つの Fe 系 MOF の調製に成功するとともに、有機リンカー上の電子求引性基の存在が副反応としての有機リンカーのヒドロキシル化を抑制し、可視光酸素生成反応の活性を大きく向上させることを明らかにしている。さらに、Fe 系 MOF において、正孔と反応基質との速やかな反応を促す上で、コバルト酸化物との複合化が有効であることも見出している。

(4) MOF を前駆体とする設計指針の下、バイメタルクラスターを有する MOF 材料に炭化処理を施すことで、合金ナノ粒子内包多孔性カーボンの調製に成功している。また得られた材料が、電気化学的酸素発生反応と酸素還元反応に適用可能であることを見出している。

以上の成果は、MOF を利用した高機能不均一系触媒の開発に関する重要な知見を与えるとともに、環境調和型触媒プロセス分野の学術的・産業的発展に大きく貢献するものである。また、申請者が自立して研究活動を行うに必要な能力と学識を有することを証したものである。学位論文審査委員会は、本論文の審査ならびに学力確認試験の結果から、博士（工学）の学位を授与することを適当と認める。