

# Theoretical Studies of Hydrocarbon Oxidation Catalyzed by Iridium- and Ruthenium-Oxo Complexes in the Coexistence of Water

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(水共存下におけるイリジウムおよびルテニウムオキソ錯体による炭化水素の酸化に関する理論的研究)

区 分 : 甲

## 論文内容の要旨

Oxidation of hydrocarbons having inert C-H bond such as methane and benzene is an important chemical and catalytic process in the modern industrial chemistry. The current commercial process converting methane and benzene into methanol and phenol, respectively, requires high temperature and pressure with multi-step reaction and the formation of by-product. Additionally, the currently reported catalytic hydroxylation of these compounds are performed in harmful solvents with sacrificial agents such as  $\text{H}_2\text{O}_2$ . In this thesis the author proposes new catalyst that can solve these problems, especially, reactions proceed in aqueous solution without sacrificial agents. Herein the author proposes the methane hydroxylation catalyst for light-driven fuel cell and benzene hydroxylation catalyst in aqueous solution. General introduction of this thesis is given in Chapter 1.

In Chapter 2-4 a light-driven methane fuels cell has been proposed (Figure 1). This is the fuel cell that convert methane into methanol driven by the visible light irradiation for anode consists of an iridium-aqua complex  $[\text{Ir}^{\text{III}}(\eta^5\text{-C}_5\text{Me}_5)\{\text{bpy}(\text{COOH})_2\}(\text{H}_2\text{O})]^{2+}$  ( $\text{bpy}(\text{COOH})_2 = 2,2'$ -bipyridine-4,4'-dicarboxylic acid) over  $\text{WO}_3$ . This anode electrode was developed by Ogo and coworker for the light-driven fuels cell catalyzing water splitting via an iridium-oxo complex  $[\text{Ir}^{\text{V}}(\eta^5\text{-C}_5\text{Me}_5)\{\text{bpy}(\text{COOH})_2\}(\text{O})]^{2+}$ . In Chapter 2 the catalytic cycle of  $\text{H}_2\text{O}$  oxidation has been clarified that the formation of the iridium-oxo complex reacting with  $\text{H}_2\text{O}$  to form O-O bond is an important step for the  $\text{H}_2\text{O}$

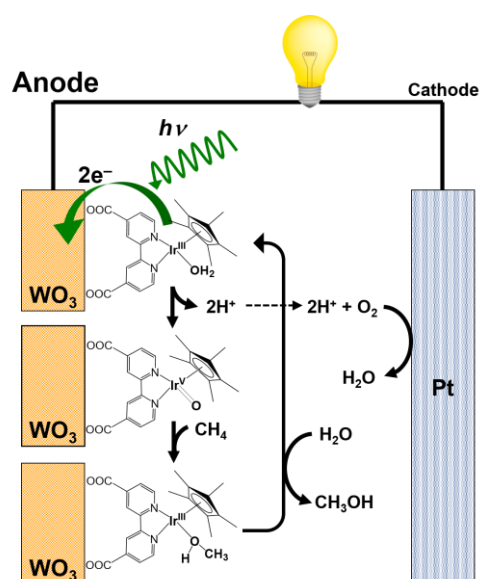
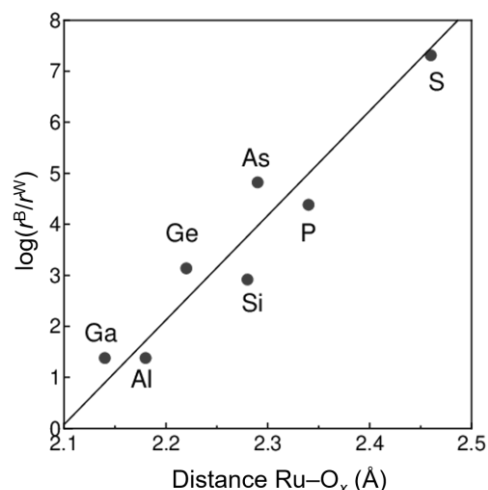


Figure 1. Proposed light-driven methane fuel cell.

oxidation. The detail reaction mechanism of the formation of the iridium–oxo complex has been investigated by using a cluster model that iridium complex is over a  $(\text{WO}_3)_{40}$  cluster with the coordination of carboxylate group to W atom in Chapter 3. By performing time-dependent DFT (TD-DFT) and DFT calculations, it has been demonstrated that deprotonation reactions from aqua and hydroxyl ligand, leading to the activation of Ir  $5d$  orbitals, play an essential role for visible-light irradiation. The catalytic methane hydroxylation by iridium–oxo complex has been proposed in Chapter 4 by employing DFT calculations. DFT calculations show that the methane hydroxylation by the iridium–oxo complex proceed with relatively low energetical barrier. Moreover, intrinsic bond orbital analysis has provided the possibility of decreasing the activation energy for C–H bond by introducing appropriate ligand.

The author has also proposed a high-performance catalyst for benzene hydroxylation in aqueous solution in Chapter 5. Ru-substituted Keggin-type polyoxometalate **RuOX**  $[\text{Ru}^{\text{V}}(\text{O})\text{XW}_{11}\text{O}_{39}]^{n-}$  ( $3 \leq n \leq 6$ ) ( $\text{X} = \text{Al}, \text{Ga}, \text{Si}, \text{Ge}, \text{P}, \text{As}, \text{and S}$ ) is used for a model catalyst. Computed results demonstrated the activation free energy for benzene hydroxylation is decreased as the elongation of distance in  $\text{Ru}-\text{O}_x$  while the that for water oxidation is not. The reaction rate ratio between benzene hydroxylation and water oxidation reaction ( $r^{\text{B}}/r^{\text{W}}$ ) is calculated by using the Arrhenius-like equation. A good liner correlation between the  $\log(r^{\text{B}}/r^{\text{W}})$  (Figure 2) and bond distance in  $\text{Ru}-\text{O}_x$  has been observed. The calculated values lead to the conclusion that  $[\text{Ru}^{\text{V}}(\text{O})\text{SW}_{11}\text{O}_{39}]^{3-}$  is a candidate high-performance benzene hydroxylation catalyst even low concentration of benzene in aqueous solution.



**Figure 2.** Relationship between  $r^{\text{B}}/r^{\text{W}}$  and distance in  $\text{Ru}-\text{O}_x$ .

General conclusion has been shown in Chapter 6. In this thesis the development of methane and benzene hydroxylation catalysts by performing DFT and TD-DFT calculations has been presented. Both catalysts are performed in the coexistence of  $\text{H}_2\text{O}$ , where  $\text{H}_2\text{O}$  act as not only oxygen source for transition metal–oxo active species but also solvation of proton. It has also shown the guideline for the development of high-performance catalysts that oxides hydrocarbon. The author provides an excellent milestone for chemistry of catalyst from the viewpoint of theoretical chemistry. Also, the author contributes to further understanding or the catalytic fashion of hydrocarbon hydroxylation in the coexistence of water.