

氏 名 佐藤 宏祐

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学位論文題目 オペランド分光計測に基づく光触媒メタン転換反応の微視的
メカニズム解明

論文審査委員 主 査 齊藤 真司
機能分子科学専攻 教授
杉本 敏樹
機能分子科学専攻 准教授
横山 利彦
構造分子科学専攻 教授
倉持 光
構造分子科学専攻 准教授
斎藤 進
名古屋大学 学際統合物質科学研究機構 教授

(様式3)

博士論文の要旨

氏名 佐藤 宏祐

論文題目

オペランド分光計測に基づく光触媒メタン転換反応の微視的メカニズム解明

Methane, the main component of natural gas and a ubiquitous natural carbon resource, has the most robust C–H bonds and the highest activation barrier among the hydrocarbon species. Therefore, conversion of the most unreactive hydrocarbon of methane under mild reaction condition is challenging, remaining one of the globally important agendas for the development of a green society. Photocatalysis is a promising technology in which redox reactions are promoted by light; the endergonic steam reforming reaction of methane can be photocatalyzed at ambient conditions beyond thermodynamic limitations. In principle, the oxidation and reduction reactions are induced on the surface of photocatalysts by photogenerated holes and electrons, respectively. However, despite intensive research in the past, the microscopic redox reaction mechanism is not yet clear. The lack of an accurate and comprehensive understanding of the mechanism and reactive species obscures the design strategies of optimal reaction system for the photocatalytic conversion of methane.

For elucidating the microscopic redox reaction mechanism and the reactive species, I have addressed the challenge of the *operando* measurements on methane photocatalysis. The correlation between the result of *operando* measurements and the photocatalytic performance contains essential information on the reactive photogenerated species. Here, I briefly describe my work on (I) the reactive hole-derived species contributing to the oxidation reaction: methane activation and (II) the reactive electron species contributing to the reduction reaction: hydrogen formation.

(I) Critical role of interfacial water on photocatalytic methane oxidation

I employed three metal oxides as representative d^{10} (Pt/Ga₂O₃) and d^0 (Pt/NaTaO₃ and Pt/TiO₂) photocatalysts. The reaction activity of these photocatalysts exposed to methane gas was evaluated under dry ($P_{\text{H}_2\text{O}} = 0$ kPa) and wet conditions ($P_{\text{H}_2\text{O}} = 2$ kPa). The total methane conversion rates to carbon-containing products (CO₂, CO, and C₂H₆) under wet conditions were dramatically improved by typically more than 30 times at ambient temperatures (~300 K) and pressures (~1 atm) in comparison to dry conditions. Notably, ethane production was also enhanced for all photocatalysts owing to the presence of interfacial water, although water itself is not involved in the equation of methane coupling reaction ($2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$). This indicates that interaction of methane with interfacial water plays a key role in the photocatalytic C–H activation of methane ($\text{CH}_4 \rightarrow \cdot\text{CH}_3$), which is an independent feature of the d^{10} and d^0 photocatalyst materials.

To shed light on the role of interfacial water in the C–H cleavage process, I conducted *operando* infrared (IR) spectroscopy with isotope-labeled water (D₂O) for the three photocatalysts

under the reaction conditions. On the *operando* IR spectra, O–H stretching peaks derived from the hydrogen-bonded adsorbed HDO molecules emerged under UV irradiation and the peak growth rates of HDO have good correlations with the methane conversion rates. This indicates that the hydrogen abstraction process on catalyst surfaces by photoactivated interfacial water species ($\text{CH}_{4(\text{gas})} + \cdot\text{OD}_{(\text{ad})} \rightarrow \cdot\text{CH}_{3(\text{ad})} + \text{HDO}_{(\text{ad})}$) is the initial key step under wet conditions; the interfacial water species ($\cdot\text{OD}_{(\text{ad})}$) act as the reactive hole-derived species on methane photocatalysis. The $\cdot\text{OD}_{(\text{ad})}$ is preferentially formed via the oxidation of adsorbed water molecule by the surface-trapped holes ($\text{D}_2\text{O}_{(\text{ad})} + \text{h}^+ \rightarrow \cdot\text{OD}_{(\text{ad})} + \text{D}^+$). Moreover, kinetic advantage on water activation was clarified in the additional *ab initio* molecular dynamics simulation. These experimental and theoretical results indicate that the interfacial water kinetically plays crucial roles beyond the traditional thermodynamic concept of redox potential, in which oxidation of water by surface trapped holes is less thermodynamically favored than methane oxidation.

The microscopic properties of the initial methane activation ($\text{CH}_4 + \cdot\text{OH} \rightarrow \cdot\text{CH}_3 + \text{H}_2\text{O}$) directly affect the macroscopic reaction kinetics and optimal reaction conditions, as follows. The methyl radical ($\cdot\text{CH}_3$) intermediate undergoes multistep surface reactions to form C_2H_6 , CO, and CO_2 through multiple intermediates. I constructed a reaction model and estimated the stabilization energy of $\cdot\text{CH}_3$ intermediate (U) to be ~ 40 kJ/mol by curve fitting of the P_{CH_4} profile of photocatalytic methane conversion. The U value determines the threshold pressure of methane at which the methane conversion rate gets almost maximized. The threshold pressure becomes extremely high (~ 1000 atm) if the photocatalytic methane conversion is initiated by the molecularly physisorbed intermediate with an adsorption energy of ~ 15 kJ/mol; meanwhile, the value is comparable to or lower than 1 atm if the conversion is initiated by the dissociatively chemisorbed $\cdot\text{CH}_3$ intermediates with an adsorption energy of ~ 40 kJ/mol. Thus, the moderate stabilization of the $\cdot\text{CH}_3$ radical intermediate has direct consequences on the maximization of photocatalytic performance under ambient pressures (~ 1 atm).

Previous *ex-situ* observation methods have shown that photogenerated holes can be present on the surfaces of photocatalysts in various forms, such as holes trapped at surface lattice oxygen sites and holes trapped as surface hydroxyl radicals or ad-atom oxygen radicals derived from adsorbed water species. However, definitive identification of the reactive species in the methane activation has been difficult with the traditional *ex-situ* measurement techniques owing to the huge gap between the measurement and actual working conditions for methane photocatalysis. By combining real-time mass spectrometry and *operando* IR spectroscopy, this study expanded the molecular-level understanding of the photocatalytic C–H activation. I have shown that the methane activation is hardly induced by the direct interaction with the trapped hole at the surface lattice oxygen site; instead, activation is significantly promoted by hydrogen abstraction from methane by the photoactivated interfacial water species. The microscopic knowledge on methane activation provides a fundamental basis for the rational interface design of photocatalytic systems toward the sustainable utilization of methane under ambient conditions.

(II) Identification of reactive electron species for photocatalytic hydrogen evolution

After the water activation ($\text{H}_2\text{O}_{(\text{ad})} + \text{h}^+ \rightarrow \cdot\text{OH}_{(\text{ad})} + \text{H}^+$), hydrogen is produced through reduction reaction of the proton by the photogenerated electrons ($\text{H}^+ + \text{e}^- \rightarrow 1/2\text{H}_2$). Energetically, the photogenerated electrons are widely distributed at various trapped sites in the band gap of the semiconductor photocatalyst. A number of IR absorption measurements on photocatalysts have been conducted for observing photogenerated electrons using the characteristic IR absorption features of electron species. However, there remain fundamental problems in *operando* observation and identification of the "reactive" photogenerated electron species due to sample heating. Temperature of the catalysts inevitably rises upon irradiation of excitation light under the photocatalytic reaction. The faint spectroscopic signal derived from the reactive photogenerated electron species is typically obscured by the huge signal derived from non-reactive thermally excited electron species. It has thus been suggested that conventional *operando* spectroscopic measurements cannot extract the key information on the reactive species.

In this study, by modulating the excitation light intensity periodically and conducting *operando* IR spectroscopy in synchronization with the period, I succeeded in removing the thermal response and identifying the reactive photogenerated electron species for hydrogen evolution on photocatalytic steam reforming of methane. On the *operando* absorbance change spectra from non-illuminated conditions (dark conditions) to illuminated conditions (reaction conditions) for Pt/Ga₂O₃ exposed to methane gas and water vapor, broad absorption bands attributed to various electron species were detected. Among the observed absorption bands in broad infrared region (1000–5500 cm⁻¹), the only band with a peak at ~2100 cm⁻¹ declined in clear response to the enhancement of the hydrogen formation rate. This correlation indicates that the electrons shallowly trapped at the in-gap states of Ga₂O₃ ~0.26 eV below the conduction band minimum are the reactive electrons involved in photocatalytic hydrogen evolution.

Furthermore, this *operando* IR measurement clarified the reservoir role of the shallowly trapped states. Previous studies assert that noble metal cocatalysts serve as electron sinks. If the Pt cocatalysts on Pt/Ga₂O₃ photocatalysts serve as electron sinks, the absorption band derived from the electrons in Pt cocatalysts should correlate to the hydrogen formation rate. Nevertheless, the only band of ~0.26 eV shallowly trapped electrons declined in response to the photocatalytic activity. This indicates that the states of the Pt cocatalysts are almost fully occupied under working conditions and the shallowly trapped states serve as a reservoir for reactive electron species instead of Pt cocatalysts. This reservoir role was rationally described based on the kinetic model analysis.

The kinetic analysis indicates that ~40% of photogenerated electrons are still available under working conditions. For consuming the reserved reactive electrons more efficiently and enhancing the performance of photocatalytic hydrogen evolution, to increase the density of photoactivated water species on catalyst surfaces is of utmost importance because methane is activated by the interfacial water species. Thus, further knowledge on the photocatalytic activation of interfacial water and surface engineering strategies based on the microscopic knowledge are required in the future.

In summary, I have revealed the microscopic redox reaction mechanism on photocatalytic steam reforming of methane comprehensively. On oxidation side (methane activation), the interfacial water species play a crucial role as the hole-derived species. On reduction side (hydrogen formation), the electrons shallowly trapped at the in-gap states of Ga_2O_3 ~ 0.26 eV below the conduction band minimum act as the reactive electron species. To design optimal photocatalytic system and enhance the photocatalytic performance, it is also required to spatially identify where the reactive species are present. For tackling this challenge, I would like to extend the *operando* spectroscopic methodology to microscopic measurements as my future work.

博士論文審査結果

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Title
論文題目 オペランド分光計測に基づく光触媒メタン転換反応の微視的メカニズム解明

出願者は、水分子が吸着・凝集している無機酸化物半導体光触媒によって室温でメタンの C-H 結合が開裂した結果誘起される水素生成反応やメタンの酸化反応、及び非酸化カップリング反応の活性評価及び赤外分光測定を系統的に行い、非熱的にメタンを活性化させる際の反応律速過程や反応メカニズムに関する研究を行っている。また、周期的な紫外光照射に同期させて赤外スペクトルを測定し、光触媒反応の駆動力の根源である光誘起電子活性種の起源に迫る実験研究を行っている。

第一章では、本研究の背景と位置付けについて纏めている。

第二章では、様々なバンドギャップを有する酸化物光触媒試料の概要や金属助触媒の担持方法、それらの試料の電子顕微鏡観測及び紫外可視吸収スペクトルの評価について記載されている。

第三章では、光触媒の反応場をありのままにその場観測するために出願者が構築したオペランド拡散反射赤外分光実験装置の構成と概要について記載されている。

第四章では、拡散反射分光法で得られたデータを解析するために必要となる吸光度・クベルカムンク理論、ならびに室温の水蒸気雰囲気下で水分子の吸着量を制御するために必要となる Brunauer-Emmett-Teller (BET) モデルについて記載されている。

第五章では、Pt を担持させた $\text{Ga}_2\text{O}_3 \cdot \text{NaTaO}_3 \cdot \text{TiO}_2$ 光触媒を試料とし、吸着水分子の存在下の室温環境でメタンの C-H 結合が開裂し、その結果誘起される水素生成反応やメタンの酸化反応、非酸化カップリング反応の活性増大メカニズムに迫る実験研究について記載されている。特に、圧力を制御したメタンガスや水蒸気の雰囲気下で活性評価を系統的に行い、水素や二酸化炭素、エタンなどの種々の分子種の生成レートの圧力依存性に対する速度論的解析を詳細に行うことで、反応活性の圧力依存性の根源となるメチルラジカル反応中間体種の生成エネルギーを解明することに成功している。また、得られたエネルギー値が第一原理分子動力学シミュレーションの結果とよく一致することを検証しており、実験結果並びに理論計算結果との比較考察から、非熱的にメタンを活性化させる際の反応律速過程や反応メカニズムに関する知見を獲得することに成功している。

第六章では、本学位論文のもう一つの主要な研究結果である光触媒的還元反応の活性種となる光誘起電子種の正体に迫る実験研究について記載されている。特に、ミリ秒スケールで紫外光励起変調を行うことにより、光照射時の温度上昇を 0.5°C 程度にまで抑制することに成功し、熱励起電子による赤外光吸収を大幅に抑制して光誘起電子活性種由来の微弱なスペクトルを検出することに成功している点は特筆すべき事項である。その結果、Pt を担持させた Ga_2O_3 試料について、複数の赤外吸収成分の中で 2000cm^{-1} 近傍にピーク

を持つ電子の存在量が還元反応の活性と相関することを見出し、その電子種が Ga_2O_3 試料の伝導体から 0.26eV 程度浅い表面準位にトラップされたものであることを突き止めている。これまで、金属助触媒は光誘起電子を蓄積して還元反応の活性創出に作用すると想定されてきたが、本研究により、金属助触媒そのものではなく、その周辺の酸化物光触媒側にトラップ・蓄積される電子が還元反応の活性創出に本質的に重要な寄与を果たしているという新たな知見を得ることに成功している。

第七章では、本研究の総括を行い、さらに、光触媒性能を向上させるために活性種が存在する場所を高い空間精度で特定するオペランド顕微測定に関する展望・課題について述べている。

以上のように、本学位論文では、系統的な反応活性評価とオペランド赤外分光計測により、反応メカニズムの解明及び光触媒反応の更なる高活性化に資する微視的知見を獲得することに成功しており、博士論文にふさわしい価値を有している。本学位論文の一部は、既に第一著者として査読付き国内学術誌に 1 報、並びに査読付き国際学術誌に 1 報報告されている。

以上の理由により、審査委員会は、本論文が博士（理学）の学位授与に値すると判断した。