

論文 / 著書情報  
Article / Book Information

題目(和文)	非平衡プラズマにおける振動励起CO2の触媒表面反応に関する反応機構の研究
Title(English)	Mechanistic study on the catalytic surface reaction of vibrationally-excited CO2 in nonthermal plasma
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論文要旨

THESIS SUMMARY

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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words )

<p>CO<sub>2</sub> hydrogenation using green H<sub>2</sub> produced by renewable energy can lead to various products. However, the efficient and economical high-value conversion of CO<sub>2</sub> is a challenge facing the scientific and industrial community. Various approaches, such as electrocatalysis and photocatalysis, are working towards the high-value conversion of CO<sub>2</sub>, but they are still expensive and energy-consuming. Therefore, it is necessary to develop breaking through technologies that can efficiently convert CO<sub>2</sub> based on the electrification of chemical processes.</p> <p>In recent years, nonthermal plasma (NTP) assisted catalysis has received great attention as a new technology for CO<sub>2</sub> valorization. NTP is characterized by having abundant vibrationally-excited molecules with various active species including ions, radicals, and free electrons which arise due to inelastic collisions between high-energy electrons and ground state molecules. This effectively makes thermodynamically challenging reaction possible by removing the thermal equilibrium limitations experienced in thermal catalysis. Moreover, the NTP process offers the advantage of integrating with renewable energy with high variabilities of energy production, such as solar and wind power, as it operates instantaneously and provides the flexibility to be switched on/off quickly as needed. In the NTP conditions, vibrationally-excited molecules are dominant channels because of their low energy threshold compared with ionization or dissociation. This point is particularly important as unique reaction pathways arise. However, an understanding of the catalytic surface reaction dynamics of vibrationally-excited molecules is still lacking. In this thesis, I present an elucidation of the microscopic mechanisms of NTP-assisted catalysis, especially the reaction on the catalytic surface of vibrationally-excited molecules.</p> <p>In Chapter 1 (Introduction), I explain research motivation in terms of the interaction between vibrationally-excited molecules and the catalytic surface.</p> <p>In Chapter 2 (Cooperative catalysis of vibrationally-excited CO<sub>2</sub> and alloy catalyst breaks the thermodynamic equilibrium limitation), I explored the reaction promotion of NTP-activated catalysis by vibrationally-excited CO<sub>2</sub> via Eley-Rideal mechanism. I investigate the CO<sub>2</sub> hydrogenation in intermetallic Pd<sub>2</sub>Ga/SiO<sub>2</sub> catalysts and compared to thermal conditions. I chose Intermetallic Pd<sub>2</sub>Ga as the catalyst because this material has been reported to be active for CO<sub>2</sub> conversion. I first present the kinetic study. Although both thermal and NTP conditions showed close to 100% CO selectivity, it is worth emphasizing that when activated by NTP, CO<sub>2</sub> conversion not only improves more than 2-fold under thermal conditions but also breaks the thermodynamic equilibrium limitation. Mechanistic insight into NTP-activated species and intermetallic Pd<sub>2</sub>Ga/SiO<sub>2</sub> catalyst surface were investigated by using <i>in situ</i> transmission infrared (TIR) spectroscopy, where catalyst surface species were identified during NTP irradiation. Moreover, in <i>in situ</i> X-ray absorption fine-structure analysis under reaction conditions, the catalyst under NTP conditions not only did not undergo restructuring affecting CO<sub>2</sub> hydrogenation but also could clearly rule out catalyst activation by heating. <i>In situ</i> characterizations of the catalysts during CO<sub>2</sub> hydrogenation depict that vibrationally-excited CO<sub>2</sub> significantly enhances the catalytic reaction. the agreement of</p>
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approaches combining experimental studies and density functional theory (DFT) calculations substantiates that vibrationally-excited CO<sub>2</sub> reacts directly with hydrogen adsorbed on Pd sites (via Eley–Rideal type mechanism) while accelerating formate formation due to neighboring Ga sites. Moreover, DFT analysis deduces the key reaction pathway that the decomposition of monodentate formate is promoted by NTP-activated hydrogen species. I believe that the understanding and insights in this work enables the high designability of CO<sub>2</sub> hydrogenation catalysts toward value-added chemicals based on the electrification of chemical processes via NTP.

In Chapter 3 (*In situ* infrared absorption probing of plasma catalysis: vibrationally-excited species induced Mars–van Krevelen type mechanism), I focused on the reaction promotion of NTP-assisted catalysis by vibrationally-excited CO via Mars–van Krevelen mechanism. I was able to unambiguously identify vibrationally-excited CO species with *in situ* TIR diagnostics performed in a catalyst free environment. The rotational temperature of CO remained unchanged at room temperature (ca. 300 K) at various NTP powers, while the vibrational temperature was increased from 1000 K to 1300 K with NTP power, showing that CO is excited into the vibrational quantum number of three. The effect of NTP, or vibrationally-excited CO, was studied using surface reaction over wurtzite ZnO. A comparative study with ground state CO by *in situ* TIR spectroscopy suggests that vibrationally-excited CO over the wurtzite ZnO surface promotes thermodynamically limited CO oxidation at room temperature. The spectral evidence shows that vibrationally-excited CO exhibits an unusual CO adsorption band due to strong binding energy with Zn<sup>2+</sup>, which improves the CO oxidation by activating the reaction with adjacent lattice oxygen in the wurtzite ZnO via the Mars–van Krevelen type mechanism at room temperature. The present findings provide new possibilities for achieving low temperature CO oxidation based on the electrification of chemical processes through NTP. Furthermore, in additions to the Langmuir–Hinshelwood and Eley–Rideal type mechanisms, the findings support the utility of the Mars–van Krevelen type mechanism, which is one of the three basic catalytic surface reaction mechanism of vibrationally-excited molecules in NTP-assisted catalysis

In Chapter 4 (Summary and future work), I present summary and outlook for future work.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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