

論文 / 著書情報
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Type(English)	Summary

論文要旨

THESIS SUMMARY

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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Methane dry reforming (MDR: $\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{H}_2 + 2 \text{CO}$) is a promising reaction for biogas upgrade towards valuable chemicals. This thesis presents the experimental study of nonthermal plasma-enabled MDR, aiming for providing deep insight into nonthermal plasma-catalyst interfacial physicochemical phenomena. The DBD (dielectric barrier discharge) provides vibrationally excited species (e.g. CO_2^v and CH_4^v) by low-energy electron impact in nonthermal plasma-enabled MDR. Two kinds of nickel-based catalysts were employed to investigate the CO_2 -Ni and CO_2 -La interaction, respectively. DBD-activated CO_2 shows enhancement for oxygen-contained species uptake over Ni and La respectively, which further influence the coke formation behavior and the oxidation of adsorbed CH_4 fragments (CH_x^*), respectively. The low and high frequency DBD were employed to reveal the influence of the electrical properties on overall reforming behavior by Lissajous plot analysis and electron-molecule collisions theory. The kinetic analysis was carried out to reveal the DBD-enhanced CH_4 activation over the Ni surfaces. This current work provides a fundamental discussion towards nonthermal plasma-enabled MDR based on microscopic surface chemistry, and macroscopic electrical and kinetic analysis. Six chapters are involved in this thesis.

Chapter 1 (Introduction) provides an introduction to MDR and the role of nonthermal plasma when it is combined with heterogeneous catalysis. The research motivation is explained by the thermodynamic and kinetic aspects.

In Chapter 2 (Oxidation behavior of Ni/ Al_2O_3 catalyst), the oxidation behavior of Ni/ Al_2O_3 catalyst (spherical 3 mm mean diameter) by DBD-activated CO_2 was investigated compared with CO_2 thermal oxidation, aiming for providing new insight into oxidation-reduction cycle of nonthermal plasma-enabled MDR. Quantitative analysis of reaction spectrometry reveals plasma oxidation is much stronger than thermal oxidation. The distribution of NiO over the cross-section of catalyst pellets was analyzed by Raman spectroscopy. When specific energy input (*SEI*) is sufficiently small, direct oxidation by DBD-activated CO_2 (i.e. CO_2^v) is the main oxidation route which significantly oxidizes Ni to NiO, where oxidation amount was much higher than corresponding thermal oxidation. Because NiO thin layer was formed in the external surface during plasma oxidation with the thickness of ca. 20 micrometers, both DBD generation and DBD-activated species penetration into the internal pores are inhibited. Due to the formation of NiO, catalyst uptakes oxygen beyond thermal equilibrium. The NiO thin layer drives the oxidation-reduction cycle in the plasma-enabled catalysis of MDR, where ground state CH_4 is dehydrogenated almost fully within the 20 micrometers NiO shell before further diffusion into internal pores.

In Chapter 3 (CO_2 activation behavior over La-Ni/ Al_2O_3 catalyst), La-modified Ni/ Al_2O_3 was employed to investigate surface carbonates formation behaviors under CO_2 treatment. In-situ plasma-DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) and ex-situ CO_2 -TPD (temperature programmed desorption) study were carried out to understand the interaction between

DBD-activated CO₂ and catalyst. DBD can enhance CO₂ activation on La by vibrational excitation, leading to more surface carbonate species formation than that in thermal treatment. Moreover, bicarbonate and bridge carbonate can be generated by DBD-activated CO₂ treatment. Due to the characteristics of the neighboring distribution on the atomic scale Ni and La, the CO₂-La-derived carbonate species, oxidize CH_x^{*} on Ni to generate syngas. The synergism of nonthermal plasma-enabled MDR is explained by the DBD-enhanced surface carbonate generation: DBD-enhanced carbonate species accelerate surface reaction with CH_x^{*} species. Regeneration of active sites for following CH₄ chemisorption is promoted towards a higher CH₄ conversion.

In Chapter 4 (Electrical properties of dielectric barrier discharge), the basic property of MDR was presented based on low and high frequency packed bed DBD reactor. The discharge behaviors by Lissajous plot and electron collision kinetics were investigated comprehensively. The 100 kHz DBD leads the highest reactant conversion and product yield, followed by 12 kHz DBD, and both of DBD hybrid reforming show a significant enhancement than thermal reforming. The power-determining parameters are decoupled into plasma sustain voltage (U_{sus}) and mean discharge current ($I_{\text{p-p}}$). 100 kHz DBD is operated in the low U_{sus} and high $I_{\text{p-p}}$ regime, while 12 kHz DBD is operated high U_{sus} and low $I_{\text{p-p}}$ regime. The increase in $I_{\text{p-p}}$ is critically important to emerge DBD-induced synergism, while an increase in U_{sus} (or mean electron energy) seems to be a minor effect. Generation of vibrationally excited species are the dominant electron-molecule collision pathways. Production rate of CH₄^v are correlated well with the net increase in CH₄ conversion.

In Chapter 5 (Kinetic study on methane dry reforming), a kinetic analysis of MDR was investigated to elucidate the reaction promotion mechanism enabled by DBD-catalyst interaction. Reaction order for CH₄ and CO₂ were determined respectively as 0.68 and -0.17, which were kept unchanged by DBD, indicating the surface coverage of CH₄ and CO₂ was not influenced by nonthermal plasma. The Arrhenius plot for forward CH₄ rate constant revealed that 12 kHz DBD hybrid reaction is characterized as *mixed catalysis* where plasma and thermal catalysis are not decoupled. In contrast, 100 kHz DBD is regarded as *pure plasma catalysis* where DBD-activated species dominates surface reaction, contributing to a decrease of activation energy from 91 kJ/mol to 45 kJ/mol. Such result is well correlated with molecule beam study where activation energy via vibrationally excited CH₄ ranges 42–69 kJ/mol on various Ni surfaces, illustrating vibrationally excited CH₄ plays the key role in *pure plasma catalysis* towards activation energy decrease.

Chapter 6 (Conclusion and future work) provides conclusion 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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