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# 論文 / 著書情報
# Article / Book Information

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（博士課程）
Doctoral Program

# 論 文 要 旨

THESIS SUMMARY

| 系・コース： Department of, Graduate major in | Mechanical Engineering 系 コース | 申請学位（専攻分野）： Academic Degree Requested | 博士 Doctor of (Engineering) |
|---|---|---|---|
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）


In plasma-enhanced $CO_2$ methanation reaction, as nonthermal plasma can provide both heat and radical effect, auto-methanation under nonthermal plasma treatment becomes possible. This thesis aims to demonstrate the feasibility of the above process on different types of catalysts. To this end, plasma-enhanced catalytic performance in the packed-bed dielectric barrier discharge (PB-DBD) reactor was confirmed at first (Chapter 2). *In situ* diffuse reflectance infrared Fourier-transform spectroscopy experiment was conducted to understand reaction mechanism (Chapter 2). Auto-methanation was designed when discharge power was sufficient for reactor to reach the initial reaction temperature (Chapter 3). DBD plays important roles as 'ignition' and 'promotion' once highly reactive species can well interact with catalyst surface.

Chapter 1 provides the introduction to $CO_2$ methanation and nonthermal plasma. $CO_2$ methanation is considered as one promising way to produce synthetic renewable methane at high yield by using renewable hydrogen. However, this reaction is affected by slow conversion speed at low temperatures. Applying nonthermal plasma can solve this problem because it can lower reaction barrier by generating more vibrationally excited $CO_2$ molecules. Nonthermal plasma is generated by applying high voltage between two parallel electrodes. In this process it is possible for gas temperature to maintain close to room temperature while temperature for electrons is relatively high.

In Chapter 2, DBD-assisted pulsed methanation was developed to suppress the rapid catalyst temperature increase due to the exothermic nature of $CO_2$ methanation

reaction. As a result, the catalyst heating effect was minimized and the role of DBD was highlighted. The low-temperature $CO_2$ methanation was improved on Ru-based multi-metallic catalyst and by applying DBD to the reaction. Because La promotes adsorption of $CO_2$ via vibrational excitation. Besides, increasing the frequency from 12 kHz to 100 kHz at constant power can improve reaction performance because high-frequency operation enhances generation of vibrationally excited $CO_2$, further accelerating carbonate formation on catalysts. To better understand reaction mechanism in DBD environment, *in situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was employed under the presence of DBD.

From *in situ* DRIFTS results, it was found that reaction is more likely to follow "*$CO_2$ associative route*" in which formation of carbonate species plays an important role in DBD-enhanced methanation reaction. Besides, the role of adding Ru and La into catalyst is also confirmed. It proves our catalyst can present a good catalytic performance and DBD environment can further promote it at a lower temperature. However, the role of formyl in the formation of $CH_4$ under the presence of DBD remains unclear. Because neither formate nor CO is identified as intermediate species in this study, the reaction pathway is hard to track from the DRIFTS observation.

As nonthermal plasma is applied to promote catalytic performance, both heat and radicals generated by discharge are considered as impact factors. However, it is always hard to distinguish them. Thermodynamically, $CO_2$ methanation is an exothermic reaction, which is highly dependent on the temperature. The proper management of exothermic energy generated during methanation is critical to developing the $CO_2$ conversion system on an industrial scale. To avoid thermal runaway from reactor, a better insulation system needs to be developed. Radicals promoting excited $CO_2$ generation has been reported in many methanation studies. It has great significance for achieving a higher $CO_2$ conversion with discharge at a much lower energy than reaction heat.

Methanation with nonthermal plasma treatment could efficiently produce methane even without external heating. This is one process intensification technique to improve the methanation process which usually requires heating at approximately 250-300 °C, which imparts a significant advantage to the process operation from an economic viewpoint. This also implies realization of auto-methanation becomes possible.

In Chapter 3, this study realized auto-methanation on 4 types of catalysts including Ru-modified La-Ni/$Al_2O_3$, La-modified Ni/$Al_2O_3$, Ru/$TiO_2$ and Ru/$Al_2O_3$. As scaling up the reactor is another target in this chapter, 2 different diameter reactors were used (i.d. 20 mm & i.d. 30 mm). $CO_2$ conversion behaviors in a vertical packed-bed dielectric barrier discharge reactor at 80 kPa were investigated. Besides, whether self-sustained reaction is feasible or not after DBD-OFF was also observed. The low-temperature $CO_2$ methanation can be improved on Ru(La-Ni)/$Al_2O_3$ and La-Ni/$Al_2O_3$ by applying DBD to the reaction while DBD has no promotion effect on Ru/$TiO_2$ and Ru/$Al_2O_3$. With only DBD treatment, DBD heating can help increase catalyst temperature to reaction temperature. However, self-sustained reaction only occurs on both monometallic Ruthenium catalysts due to their good catalytic activities around 200 °C. DBD in this process plays important role as ignition (on Ru/$TiO_2$ & Ru/$Al_2O_3$) or even promotion (on Ru(La-Ni)/$Al_2O_3$ & La-Ni/$Al_2O_3$). However, it should be pointed that long-term stability test on the catalyst is further needed. It's worthwhile to find an appropriate catalyst whose activity can be well promoted by DBD. If so, DBD can be well used in auto-methanation with a lower power consumption. To scale up the reactor, the type of catalyst and prevention from heat loss prove 2 most significant factors.

Chapter 4 provides conclusion and outlook for the 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 1copy of 800 Words (English).

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