論文 / 著書情報
Article / Book Information

題目(和文)	流動層プラズマによるCO2転換プロセスの電化
Title(English)	Electrification of CO2 Conversion Processes by Fluidized-bed Plasma
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12526号, 授与年月日:2023年9月22日, 学位の種別:課程博士, 審査員:野崎 智洋,末包 哲也,近藤 正聡,笹部 崇,高橋 秀治
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12526号, Conferred date:2023/9/22, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（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 ）

The thesis aims to achieve an efficient electrification of CO_2 conversion.

In Chapter 1, motivation and background, we explained the importance of electrification of CO_2 conversion and the superiorities of plasma catalysis. Meanwhile, we highlight, unlike thermal catalysis where simply a catalyst plays the main role, plasma catalysis is more complex; besides surface catalytic analysis, the rarely studied plasma characteristics and dynamic plasma–catalyst interaction are equally important, posing the key obstacles to its development. In Chapter 2, we focus on the plasma–catalyst interaction behaviors, comparatively analyzing the properties of both plasma and catalyst bed in each representative system, and conclude the fluidized-bed dielectric barrier discharge (FB-DBD) reactor is the ideal candidate. In Chapter 3, in CO_2-to-CO conversion via Langmuir-Hinshelwood (L-H) mechanism using CO_2–CH_4 reforming as a model, we proposed FB-DBD and experimentally verified its superiorities over packed-bed DBD (PB-DBD) in plasma catalytic synergism (PCS). We analyzed the forward catalysis behavior, heat transfer, discharge properties and reverse reaction; the forward CO_2 conversion was selectively promoted to reach the thermal equilibrium. In Chapter 4, CO_2 was further co-reacted with more reactive H_2 via the representative Eley-Rideal (E-R) pathway; FB-DBD decreased the apparent activation energy from 75 kJ/mol of thermal catalysis to 43 kJ/mol and CO_2 conversion well beyond the thermal equilibrium. Meanwhile, we obtained the criterion of DBD for maximizing the PCS: low electron energy and high electron concentration by increasing streamer amount, instead of streamer size. In Chapter 5, we focus on converting CO into solid carbon using Boudouard reaction as a model. We initially confirmed the Mars-van Krevelen (MvK) mechanism; FB-DBD and H_2 jointly contributed to an efficient CO conversion and so far, the best production of carbon nanofiber with unique spiral structure. The details are as follows:

Chapter 1: Motivation and background

The electrification means converting renewable energy, such as solar and wind, into electricity and then driving the chemical reactions. The main processes include electric heating, like MW heating, which has been well established. The high-temperature heat can be provided without CO_2 emission. In addition, there are electro catalysis, photo catalysis and plasma catalysis, which enable the CO_2 conversion at decreased temperatures. Electro and photo catalysis have witnessed the main advancements in hydrolysis; however, the domain of CO_2 conversion remains in its nascent stage and faces challenges of low energy efficiency. Comparatively, plasma catalysis, offers distinct flexibilities in feed gas (not only CO_2, but also i.e., CO, CH_4, N_2, and H_2O), energy source, active species and operation, which fulfills the precise requirements for the global CO_2 utilization.

Nonetheless, plasma catalysis is still in its infancy; the CO_2 conversion and energy efficiency are predominantly far from the industrial implementations owing to the weak PCS. In this regard, similar to thermal catalysis, the new catalyst design and characteristics have garnered the most attention. However, it is worth noting that, unlike thermal catalytic surface reaction, plasma–catalyst coupling is significantly more challenging but rarely studied: (1) plasma is neither generated nor diffused in catalyst micropores; (2) plasma generation and catalyst-oriented interaction are determined by numerous factors, i.e., discharge type, catalyst bed, electric field, gas, discharge power and frequency; (3) there is a timeliness for plasma–catalyst interaction as most plasma-generated reactive species feature short lifetime; (4) the heat generated by plasma could increase the catalyst temperature, particularly the hotspot, which may deviate the reaction path, or even lead to a catalyst sintering. (5) there is a thermodynamic equilibrium limitation: both the forward and reverse reactions are possible to be promoted by plasma. To this end, the plasma, catalysis and plasma–catalyst interaction must be synthetically considered for an efficient PSC.

Chapter 2: Development of fluidized-bed DBD reactor

We firstly focus on the dynamic plasma–catalyst coupling mode, considering both plasma characteristics (i.e., discharge pattern, ionization degree, active species) and catalyst bed (i.e., gas gap, surface area, heat and mass transfer) and comparatively analyzing which type of plasma, catalyst bed is the most promising. We summarized the representative plasma catalytic systems with their characteristic features and highlight how the FB-DBD showed intrinsic capability to maximize the plasma–catalyst interaction. We further reviewed the ongoing research on fluidized-bed plasma catalysis, based on which we critically evaluated the superiority of FB-DBD to other candidates,

especially the most widely used PB-DBD. Finally, we discussed the perspectives of FB-DBD, involving challenges and development potential.

Chapter 3: Verification of fluidized-bed DBD in dry CH_4 reforming (Langmuir-Hinshelwood (L-H) mechanism)

The representative CO_2–CH_4 reforming (DMR) via L-H mechanism was studied in FB-DBD. The DBD-induced synergistic effect as well as discharge behaviors (electron concentration, energy and electron collision kinetics) were compared with those of PB-DBD. The forward DMR was promoted dramatically when DBD was generated in the FB reactor due to an extended surface area of powdered catalysts and their interaction with plasma-generated reactive species. Moreover, enhanced heat and mass transport, as well as longer residence time, in the FB reactor contribute the significant enhancement of DMR performance. Reaction promotion in the thermal FB reactor (without DBD) was quite marginal, verifying that extended surface area in the FB reactor is not effective unless the rate-determining step, known as C–H bond breaking, is promoted via vibrational excitation by DBD. Moreover, the reverse reaction of DMR was studied in FB-DBD. The reverse DMR was not influenced by DBD at all; the forward DMR is promoted selectively by DBD. The chemical composition reached but was limited by the thermal equilibrium.

Chapter 4: Kinetic analysis of reverse water gas shift reaction (Eley-Rideal (E-R) mechanism)

Dramatic promotion of CO_2-to-CO conversion by FB-DBD via E-R mechanism was experimentally verified in reverse water gas shift (RWGS) reaction as well. We observed plasma catalysis yielded more than doubled CO_2 conversion compared to thermal catalysis with identical temperature. Reaction can be further promoted by augmenting frequency (from 12 to 100 kHz), where the CO_2 conversion over 10wt％ Pd_2Ga/SiO_2 surprisingly well beyond the thermal equilibrium. Interestingly, increasing discharge power (from 30 to 60 W), on the contrary, contributes little to PCS. Arrhenius plots indicated the FB-DBD yielded a decreased activation energy from 75 kJ/mol of thermal to 43 kJ/mol, independent from both discharge frequency and power. Lissajous plots further revealed that the most active 100 kHz plasma features large discharge current and low sustain voltage and charge, suggesting a decreased electron energy and single streamer size; the increased streamer amount in time scale can simultaneously promote the density and coupling flux of electron. Comparatively, increasing electron concentration by enhancing the shrinking streamer size in 60 W plasma is not work. Electron collision kinetics depicted vibrationally excited CO_2 dominated electron activation channel, which can be facilitated by decreasing electron energy to a certain extent.

Chapter 5: Application to Boudouard reaction (Mars-Van Krevelen (MvK) mechanism)

In this chapter, we focus on CO-consumed processes using FB-DBD for higher value-added utilization of CO_2. In this sense, another representative catalytic mechanism, that is MvK mechanism, will be involved due to the reducibility of CO. The challenging and poorly touched gas-to-solid CO disproportionation to carbon was studied as a model, which is promising for the negative CO_2 emissions and green carbon-based industries. The spiral or spring-like carbon nanofiber with a yield of 121.0 gram_C/gram_Fe and production rate of 20.2 gram_C/gram_Fe/h was achieved without catalyst deactivation and reactor clogging, which is by far the best performance using a practical technology in the reported plasma-enhanced Boudouard processes. Fe_3O_4, instead of Fe, was identified as the key active site for carbon deposition; the vibrational excitation of CO by plasma and in situ reduction of Fe_3O_4 by H_2 via the MvK mechanism jointly contributed to an efficient CO-to-C conversion. Heat self-sustaining of Boudouard reaction and integrating the CO_2-to-CO and Boudouard processes in a single reactor are underway, which is promising for promoting the negative CO_2 emission and green carbon industries.

Chapter 6: Summary and future work