

Elucidating plasma-surface interaction mechanism for CO₂ conversion toward decentralized low carbon technology

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Conversion of carbon dioxide to useful chemicals using low-carbon energy sources attracts keen attention. The use of renewable electricity to operate catalytic conversion of CO₂ is being recognized as a promising decarbonizing technology [1,2]. First, a chemical reaction is activated electronically thus renewable electricity is utilized directly. Second, an electron-assisted reaction would decrease the reaction temperature that eliminates high-temperature processes with combustion of hydrocarbons. Electrochemistry, Photochemistry, and a combination of these principles are studied exclusively for this purpose. In addition, electrical heating with renewable electricity is considered as industrially applicable electrification technology for the decarbonization of chemical processes. However, high temperature is still needed within the scope of conventional thermal reaction regime: technological innovation may arise via efficient heat transfer and temperature management technology, such as selective heating of material, rapid heating, extreme high-temperature that the combustion can not achieve.

We propose nonthermal plasma-driven heterogeneous catalysis of CO₂ as a new concept of an electricity-driven chemical reaction control while utilizing renewable energy [3,4]. The catalytic surface reaction is modified by the plasma-generated reactive species, most likely vibrationally excited molecules, leading to much smaller activation energy than that of thermal catalysis [5,6]. In this study, DBD (dielectric barrier discharge) combined catalytic reaction was applied to reverse water gas shift reaction (CO₂ + H₂ = CO + H₂O ΔH = 41 kJ/mol, ΔG = 24 kJ/mol at 400 K). The CO₂ conversion exceeded the thermal equilibrium when Pd₂Ga/SiO₂ (10wt.%) alloy catalyst was used. The *in situ* transmission infrared (TIR) spectroscopy was employed while DBD was generated during the spectroscopy. The formation of monodentate formate (m-HCOO) was promoted by direct interaction between adsorbed hydrogen and vibrationally excited CO₂ via the Eley-Rideal pathway. Because bending mode vibration of CO₂ becomes an excellent electron acceptor and the reaction between adsorbed hydrogen on Pd, as an electron donor, is enhanced. Interestingly, the dissociation of m-HCOO, as a rate-determining step, was also promoted by DBD under hydrogen-rich conditions. Such unique reaction behavior was confirmed by the fluidized-bed DBD reactor [6-8], showing the activation energy of 75 kJ/mol for thermal catalysis and a drastic reduction to 43 kJ/mol for plasma catalysis. The individual role of DBD and alloy catalyst over the plasma-promotion effect is discussed comprehensively.

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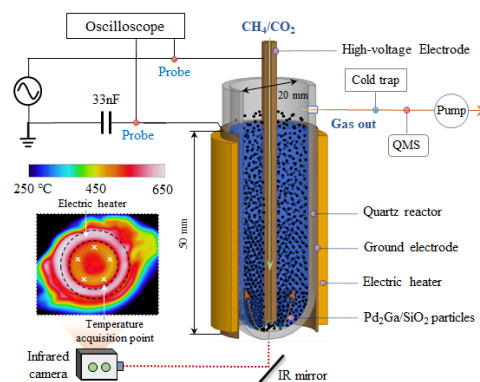


Figure 1. Schematic diagram of fluidized-bed DBD reactor

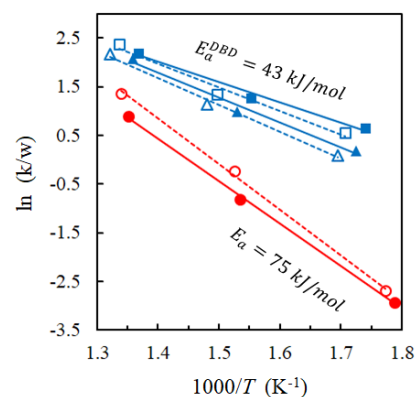


Figure 2. Arrhenius plot for the reverse water gas shift reaction in the fluidized-bed DBD reactor. ■ 10 wt.% (100 kHz), ▲ 10 wt.% (12 kHz), □ 3 wt.% (100 kHz), △ 3 wt.% (12 kHz), ● 10 wt.% (Thermal), ○ 3 wt.% (Thermal). Total flow rate = 200 cm³/min (STP), Power = 30 W, H₂/CO₂ = 3, WHSV = 3000 cm³/g/h (STP), Total pressure = 15 kPa, SEI = 220 kJ/mol. STP: standard temperature and pressure (101.3 kPa and 298 K).

References

- [1] A D N Kamkeng et al: *Chem. Eng. J.* **409** (2021) 128138
- [2] AI Stankiewicz and H Nigar: *React. Chem. Eng.* **5** (2020) 1005
- [3] A Bogaerts et al: *J. Phy. D: Appl. Phys.* **53** (2020) 443001
- [4] H-H Kim et al: *Int. J. Plasma Environ. Sci. Technol.* **15** (2021) e01004
- [5] Z Sheng et al: *Chem. Eng. J.* **399** (2020) 125751
- [6] D-Y Kim et al: *J. Am. Chem. Soc.* **144** (2022) 14140
- [7] X Chen et al: *J. CO₂ Util.* **54**, (2021) 101771
- [8] X Chen et al: *Plasma Process. Polym.* e2200207 (2023)