

Plasma-derived atomic hydrogen promotes CO₂ methanation at low temperature through the Eley–Rideal mechanism

Dae-Yeong Kim¹, Shinya Furukawa², Tomohiro Nozaki¹

¹*Department of Mechanical Engineering, Institute of Science Tokyo, Tokyo, Japan*

²*Division of Applied Chemistry, Osaka University Osaka, Japan*

Abstract: We developed a plasma catalysis system that supplies atomic hydrogen directly from the gas phase, enhancing CO₂ methanation over Ni/Al₂O₃. Through kinetic studies, in situ plasma characterization, and theoretical calculations, we demonstrated that plasma-derived atomic hydrogen lowers the energy barrier of bidentate formate hydrogenation by shifting from the Langmuir–Hinshelwood to the Eley–Rideal mechanism.

1. Introduction

Plasma catalysis, which utilizes nonthermal plasma in catalytic processes, has gained significant attention due to the synergistic interactions between the plasma and catalyst surfaces. Numerous studies have been reported on plasma catalysis in hydrogenation reactions such as CO₂ hydrogenation and ammonia synthesis, and it has been shown that reaction is significantly enhanced compared to thermal catalysis [1-2]. However, understanding the dynamics and mechanisms of plasma-activated gaseous species on catalytic surfaces remains limited. Additionally, the properties and reactivity of plasma-derived atomic hydrogen (PDAH) are still not well understood.

We investigated plasma-catalytic CO₂ methanation over Ni/Al₂O₃, uncovering the unique reaction behavior of plasma-activated hydrogen aligned with the Eley–Rideal (E–R) mechanism. We examined how PDAH efficiently catalyzes CO₂ methanation. Compared to thermal conditions, the high energy and translational freedom of PDAH activate the E–R mechanism, lowering the energy barrier for the rate-determining step of CH₄ formation.

2. Results and Discussion

CO₂ methanation performance of Ni/Al₂O₃ was evaluated in packed-bed dielectric barrier discharge (DBD) reactor. Compared to thermal conditions, CO₂ conversion is enhanced under DBD conditions at temperatures below 300 °C while maintaining a high CH₄ selectivity of >98%. Under thermal conditions, the activation energy is 82.1 kJ/mol, whereas under DBD conditions, it is reduced to 58.6 kJ/mol, indicating that plasma lowers the energy barrier for CH₄ formation. Under thermal conditions, CO₂ and H₂ show nearly zero-order dependence, suggesting the reaction proceeds according to the Langmuir–Hinshelwood (L–H) mechanism. Under DBD conditions, the reaction order for CO₂ decreases, suggesting faster adsorption due to plasma-activated CO₂ [3]. Notably, a first-order dependence for H₂ is observed under DBD conditions, indicating that plasma-activated H₂ promotes CO₂ methanation. Meanwhile, atomic hydrogen, easily generated through electron collisions, is the most abundant radical in plasma-activated hydrogen. The zero-order reaction of CO₂ under both thermal and plasma conditions suggests high intermediate surface coverage derived from

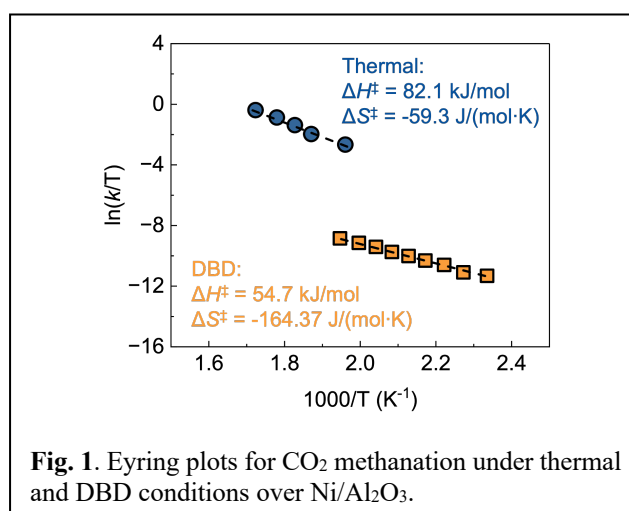


Fig. 1. Eyring plots for CO₂ methanation under thermal and DBD conditions over Ni/Al₂O₃.

CO₂. Under DBD conditions, the catalyst surface is likely covered with CO₂-derived intermediates, and CH₄ formation occurs via direct reaction with PDAH, consistent with the E–R mechanism. Meanwhile, E–R mechanism shows a large negative entropy change due to the loss of high translational freedom during the surface reaction. Activation parameters estimated via the Eyring plot (Fig. 1) reveal that both activation enthalpy (ΔH[‡]) and entropy (ΔS[‡]) decrease under DBD conditions compared to thermal conditions. The significant drop in ΔS[‡] supports a shift in the rate-determining step from L–H to E–R mechanism.

3. Conclusion

Overall, this study underscores the role of PDAH in catalytic CO₂ hydrogenation and its significance. Moreover, these findings may extend to other types of catalytic hydrogenation, such as methanol, hydrocarbon production, and ammonia synthesis.

Acknowledgement

This study was supported by JSPS KAKENHI (24K17036 and 24H00199) and JST CREST (JPMJCR19R3).

References

- [1] A. Bogaerts et al., *J. Phys. D: Appl. Phys.*, **53**, 443001 (2020).
- [2] T. Nozaki et al., *Jpn. J. Appl. Phys.*, **63**, 12 (2024).
- [3] D.-Y. Kim et al., *J. Am. Chem. Soc.*, **144**, 14140 (2022).