

Reactivity of plasma-excited H₂O in CH₄/CO₂ reforming

○(D)Seigo KAMESHIMA^{1,2}, (M2)Ryo MIZUKAMI¹, (M1)Takumi YAMAZAKI¹,
(M2)Lukman Adi PRANANTO¹, (M1)Naoaki KODA¹, (B)Kenta SAKATA¹, and Tomohiro NOZAKI*¹

¹Dept. of Mechanical Engineering, Tokyo Institute of Technology,

²Japan Society for the Promotion of Science Research Fellow (DC1)

*E-mail: tnozaki@mech.titech.ac.jp

We investigate DBD and catalyst hybrid dry methane reforming^[1,2] (DMR; CH₄ + CO₂ → 2H₂ + 2CO), producing syngas (H₂ and CO) at relatively low temperature. Syngas is converted into liquid fuel^[3] whose energy density is much higher than solid state secondary batteries^[4]. Therefore DMR is highly expected as a greenhouse gas conversion technology^[5]. However, DMR is accompanied by serious coke deposition (CH₄ → C + 2H₂; 2CO → C + CO₂) which causes catalyst degradation. We found that plasma-excited H₂O plays an important role in hybrid DMR at low temperature: H₂O is excited by DBD to accelerate the oxidation of adsorbed CH_x which is a coke precursor produced via stepwise CH₄ dehydrogenation. As a result, coking was suppressed and higher yields of H₂ and CO were obtained.

Figure 1 shows a DBD and catalyst (φ3, 12 wt.%, Ni/Al₂O₃; Süd-chemie) hybrid reactor, consisting of a 20 mm i.d. and 1.5 mm thick quartz tube, 3 mm diameter inner electrode, and 60 mm long external electrode. Catalyst pellets were packed over 40 mm length and both ends of the catalyst bed were supported by metallic disks. The catalyst bed was heated under H₂ flow (500 cm³/min) at a constant heating rate of 5 °C/min (from 500 °C to 600 °C). Meanwhile, CH₄/CO₂ mixture was injected for 5 seconds at 2 min interval. The gas injection volume was 50 cm³ and CH₄/CO₂ ratio was 2. The applied voltage was 16 kV_{p-p} and 12 kHz. The discharge power was increased from 80 W to 110 W with temperature increase. Pressure was reduced to 5 kPa. To discuss the DBD effect, both of DBD-on and -off experiments were carried out.

Figure 2 shows CH₄ and CO₂ conversions and H₂ and CO yields. The H₂ and CO yields were clearly enhanced by DBD, although the CH₄ and CO₂ conversions were unchanged. The result implies that the CH₄ dehydrogenation (CH₄ → (CH_x + (4 - x)/2 H₂) → C + 2H₂) and the subsequent reverse water-gas shift reaction (CO₂ + H₂ → CO + H₂O) were not affected by DBD. On the other hand, plasma-excited H₂O enhanced CH_x oxidation (CH_x + H₂O → CO + (2 + x)/2 H₂), leading to increased selectivity of H₂ and CO. Moreover, the excited H₂O contributed to reduce the coke formation. Reaction enhancement induced by excited H₂O indicates that the reaction order of H₂O becomes not zero unlike conventional catalytic CH₄ reforming^[6].

Acknowledgement: This work was supported by the Japan Society for the Promotion of Science (JSPS): 16J09876. SK acknowledges the JSPS for providing Research Fellowship (DC1).

[1] S. Kameshima *et al.*, *Plasma Process. Polym.*, doi:10.1002/ppap.201600096 (*in press*); [2] S. Kameshima *et al.*, *Catal. Today*, **256** (2015) 67; [3] M. Stelmachowski and L. Nowicki, *Appl. Energy*, **74** (2003) 85; [4] A. Züttler *et al.*, *Phil. Trans. R. Soc. A*, **368** (2010) 3329; [5] M.-S. Fan *et al.*, *ChemSusChem*, **4** (2011) 1643; [6] J. Wei and E. Iglesia, *J. Catal.*, **224** (2004) 370.

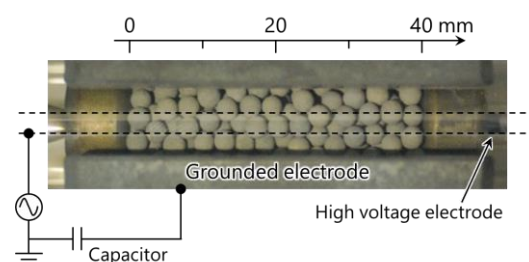


Fig. 1. DBD-Ni/Al₂O₃ catalyst hybrid reactor.

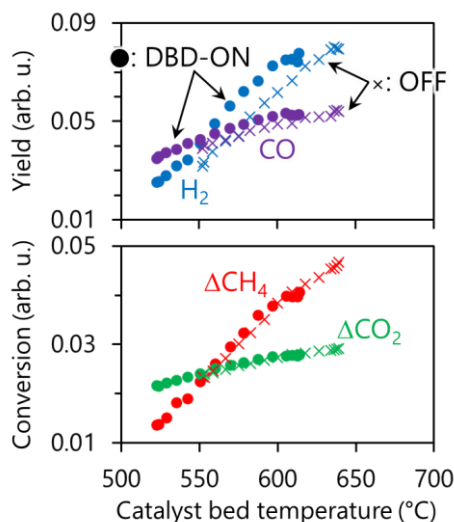


Fig. 2. Syngas production enhancement by DBD.