

Innovative C1 Chemistry by Plasma-Catalyst Hybrid Reaction

プラズマ触媒反応による革新的なC1ケミストリーの創成

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This paper describes dry methane reforming (*DMR*) using Ni catalysts and DBD hybrid reactor, aiming for efficient conversion of greenhouse gas into syngas and contribute to innovative C1 chemistry. Both CH₄ and CO₂ are vibrationally excited through low-energy electron collision, which is the efficient energy transfer pathways between molecules and electrons. Subsequently, vibrationally excited molecules are absorbed onto the catalyst surface with much smaller threshold energy than that of ground state molecules. Therefore, material and energy conversion efficiency is expected to increase in the hybrid operations, enabling energy efficient and low-temperature greenhouse gas conversion. Low temperature gas conversion is critically important because high temperature thermal energy, which is produced through combustion of initial feed, is eliminated: Overall exergy loss through the reforming process is greatly minimized.

DBD is produced in 20 mm inner diameter quartz tube packed with Ni-Al₂O₃ catalyst pellets (3 mm sphere) over 20 mm length. 3 mm metallic rod was inserted into the center of quartz tube as a high voltage electrode. CH₄ dehydrogenation occurs on the catalyst surface (R1). Subsequently, CO₂ is reduced by H₂ which is known as the reverse-water gas shift reaction (R2). R1–R2 are so fast compared to de-coking reaction (R3), therefore, solid carbon is accumulated on the catalyst surface.



DBD is readily extinguished once solid carbon, or electrically conductive film, is formed on the pellet surface. Therefore, total pressure was reduced to 5–10 kPa so that DBD is generated independently of coking. Moreover, CH₄ was supplied intermittently, while CO₂ was continuously supplied: Solid carbon was removed during CH₄ flow is turned off. Carbon removal is determined by the Boudouard equilibrium at given catalyst temperature. The catalyst bed was heated by an external electric heater and the bed temperature was monitored by an infrared camera. Output gas (CO, H₂, CH₄, CO₂) was analyzed online by quadruple mass spectrometer, providing semi-quantitative information of reforming reaction. Time dependent change in gas components is provided in Fig. 1. Between A and C,

steady state was established by the thermal reaction. DBD is turned on at point C, *DMR* is enhanced, then H₂ and CO partial pressure increased: The bed temperature also increased slightly. Between D and E, CH₄ was turned off while DBD was kept running. This period is de-coking phase. Because endothermic enthalpy is small for this reaction, the bed temperature increased markedly. At point D, CO increases slowly via R3, showing the de-coking reaction is much slower than R1 and R3. CH₄ is introduced at point E again: The bed temperature decreased dramatically due to *DMR*: H₂ and CO abruptly increase. For further understanding of reaction mechanism, detailed analysis of reforming reaction and the electronic kinetics will be discussed at the symposium.

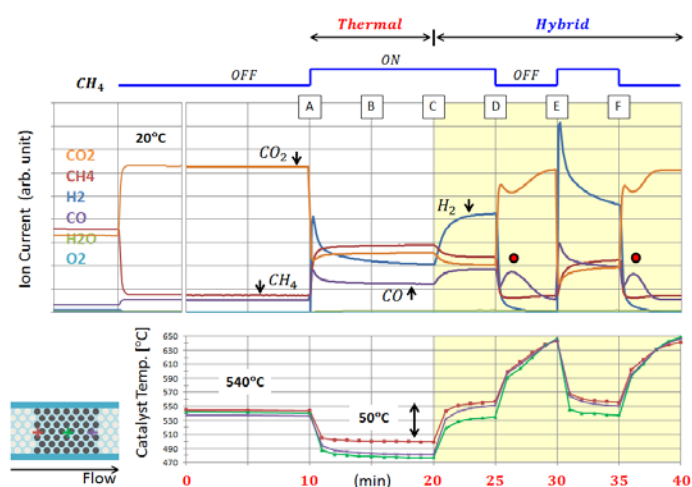


Fig. 1 Time dependent change in gas components and bed temperature: GHSV: 20600h⁻¹, 70W, SEI: 0.5J/cm³.