

Euro Petrochemistry 2019: Conversion of CH₄ into Value-added Chemicals by Plasma-Catalysis-Yanhui Yi-Dalian University of Technology

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Abstract

Methane (CH₄), the main component of natural gas and shale gas, has a large reservation and wide distribution in the world, and thus it has been considered as an alternative energy source for oil. However, due to high stability (439 kJ/mol C-H bond energy), negligible electron affinity and low polarizability of CH₄ molecule, catalytic conversion of CH₄ into value-added chemicals is considered the “holy grail” of catalytic chemistry, and thus effective utilization of CH₄ has attracted much attention. Herein, we report a CH₄/NH₃ plasma reaction promoted by Pt and Cu catalysts for synthesis of hydrocyanic acid (HCN) at low temperature (400 °C). HCN, an important chemical in organic chemistry, is widely used in pesticide, medicine, metallurgy, fuel and polymer, but it is currently produced through Andruddow process (1000-1100 °C, Pt-Rh alloy gauze catalyst), the reaction of CH₄, NH₃, and O₂, or BMA process (1300 °C, Pt mesh catalyst), the reaction of CH₄ and NH₃ at atmospheric pressure. That is, the plasma catalysis technology has dramatically lowered the reaction temperature for HCN synthesis. We also report a CH₄/O₂ plasma reaction promoted by Ni/Al₂O₃ catalysts for production of CH₃OH. Under the conditions of 85°C, 2:1 CH₄/O₂ molar ratio, 0.393 s residence time and 30 W discharge power, 66.6 % methanol selectivity is achieved with 6.4 % methane conversion. The Ni/Al₂O₃ catalysts were characterized by TPR, XRD, XPS and HRTEM, and the results show that the production of CH₃OH is mainly attributed to the highly dispersed NiO phase which has a strong interaction with Al₂O₃ support. In addition, 0D modelling (ZD-Plaskin) results show that CH₃OH is mainly produced through the radical reactions CH₄ + O(1D) → CH₃O + H, CH₃O + H → CH₃OH and CH₃O + HCO → CH₃OH + CO

Chemical transformations of CO₂ into value-added chemicals and fuels have been regarded as a key element for creating a sustainable low-carbon economy in the chemical and energy industry.

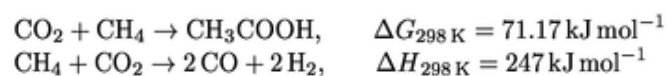
A particularly significant route that is currently being developed for CO₂ utilization is catalytic CO₂ hydrogenation. This process can produce a range of fuels and chemicals, including CO, formic acid, methanol, hydrocarbons, and alcohols; however, high H₂ consumptions (CO₂+3 H₂→CH₃OH+H₂O) and high operating pressures (ca. 30–300 bar) are major challenges associated with this process.

Instead of using H₂, the direct conversion of CO₂ with CH₄ (dry reforming of methane, DRM) into liquid fuels and chemicals (e.g., acetic acid) represents another promising route for both CO₂ valorization and CH₄ activation. CH₄ is an ideal H supplier to replace H₂ in CO₂ hydrogenation as CH₄ has a high H density and is available from a range of sources (e.g., natural gas, shale gas, biogas, and flared gas). Moreover, it is an inexpensive carbon source that can increase the atom utilization of CO₂ hydrogenation owing to the stoichiometric ratio of C and O atoms, as well as reduce the formation of water.

Recently, Ge and co-workers investigated the direct C–C coupling of CO₂ and CH₄ to form acetic acid on a Zn-doped ceria catalyst by density functional theory (DFT) modeling;¹ this is an attractive route as the direct conversion of CO₂ and CH₄ into acetic acid is a reaction with 100 % atom economy [Equation 1]. However, this reaction is thermodynamically unfavorable under practical conditions. The conventional indirect catalytic process often proceeds through two steps (Scheme 1): 1) DRM to produce syngas (CO and H₂) at high temperatures (>700 °C), and 2) conversion of syngas into liquid fuels and chemicals at high pressures. This indirect route for CO₂ valorization and CH₄ activation is inefficient as the DRM process for syngas production is highly endothermic and requires high temperatures and energy input [Equation 2]. Catalyst deactivation due to carbon deposition is another challenge impacting the use of this reaction on a commercial scale.

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It is almost impossible to directly convert two stable and inert molecules (CO₂ and CH₄) into liquid fuels or chemicals in a one-step catalytic process bypassing the production of syngas. A stepwise method was proposed to convert CO₂ and CH₄ into acetic acid over Cu/Co-based catalysts,² Pd/C, Pt/Al₂O₃,³ Pd/SiO₂, and Rh/SiO₂⁴ by heterogeneous catalysis. The catalyst was first exposed to CH₄, forming CH_x species on the catalyst surface. Subsequently, the feed gas was changed from CH₄ to CO₂, and acetic acid was formed through the reaction of CO₂ with CH_x over the catalyst. This indirect process is complicated by the periodic change of reactants and the product collection.⁵



In conclusion, the one-step room-temperature synthesis of liquid fuels and chemicals from the direct reforming of CO₂ with CH₄ has been achieved by using a novel atmospheric-pressure DBD reactor. The total selectivity for liquid chemicals was approximately 50–60 %, with acetic acid as the major product. The CH₄/CO₂ molar ratio and the type of catalyst can be used to manipulate the production of different oxygenates. These results clearly show that non-thermal plasmas can be used to overcome the thermodynamic barrier for the direct transformation of CH₄ and CO₂ into a range of strategically important platform chemicals, especially for the production of acetic acid with 100 % atom economy. Additionally, combining the DBD with noble-metal catalysts produced formaldehyde, which cannot be generated in the same plasma reaction without a catalyst. This finding suggests that new research should be directed at designing a catalyst with high selectivity towards a desirable product.

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