

Membrane Reactors for Catalytic Conversion of Methane to Fuels and Petrochemicals

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Indirect processes for the conversion of methane to petrochemicals and liquid fuels involve the formation of synthesis gas via steam reforming or partial oxidation. The introduction of O₂ using dense oxygen anion conductors into a CH₄/H₂O stream can combine air separation with reforming/oxidation reactions. These processes can significantly reduce the cost of synthesis gas production, but have not been implemented in practice. The direct conversion of methane to fuels and petrochemicals remains an even more formidable challenge. Oxidative coupling to form C₂ hydrocarbons on metal oxides and catalytic pyrolysis of CH₄ to alkenes on cation-exchanged H-ZSM5 give desired products with limited yields because of sequential reactions or thermodynamic constraints. O₂ co-reactants in oxidative conversion routes lead to direct and sequential pathways for CO_x formation, which limit C₂ yields to ~20%. Non-oxidative pyrolysis yields are restricted to aromatic products and to ~10% benzene yields because of equilibrium constraints and the unselective formation of large organic deposits. The higher temperatures required to increase yields lead to loss of selectivity and to structural collapse of zeolite channels required for shape selectivity.

Here, we couple shape-selective MoC_x/H-ZSM5 catalysts for methane pyrolysis with thin films of electronic-proton conductors that selectively remove H₂ from the catalyst bed at reaction temperatures^[1, 2]. These studies led to novel procedures for the synthesis of membranes as supported thin films and to detailed structural and mechanistic characterization of catalysts and of heterogeneous-homogeneous pathways involved in methane reactions at high temperatures. These strategies led to high temperature requirements in previous studies because thin membrane films and effective catalysts were unavailable and to low reaction rates and selectivities and insufficient H₂ transport rates. Dense SrCe_{0.95}Yb_{0.05}O_{3-α} thin films (~2 μm) were used to remove H₂ during methane pyrolysis on Mo/HZSM-5 to overcome kinetic and thermodynamic constraints imposed by H₂^[3]. At 950 K, these films removed

only a small fraction of the H₂ produced and hydrocarbon synthesis rates were unaffected by H₂ removal. Higher temperatures led to a modest increase in CH₄ conversion rates, but also to slightly lower C₂-C₁₂ hydrocarbon selectivities and to higher catalyst deactivation rates. These undesired effects were eliminated by the addition of small amounts of CO₂ to the CH₄ reactants. The combination of dense SrCe_{0.95}Yb_{0.05}O_{3-α} thin films, chain limiting pyrolysis reactions on Mo/H-ZSM5 catalysts, and CO₂ co-reactants led to modestly higher hydrocarbon synthesis rates than in conventional reactors and to stable catalyst performance.

The improvements achieved by continuous H₂ removal are in agreement with the predictions of rigorous reaction-transport simulations in tubular reactors with permeable walls^[4]. These detailed models including homogeneous CH₄ pyrolysis pathways, chain-growth reactions to undesired polyaromatic hydrocarbons, surface-catalyzed C-H activation of CH₄ and C₂H₆, and C₂H₄ aromatization on acid sites. They also include rigorous descriptions of hydrogen permeation through mixed conducting membrane in various operating modes based on non-equilibrium thermodynamic formalisms, which account for the influence of the contacting gas phase on the concentrations of all charge carriers within the membrane. Simulations indicate that H₂ removal from homogeneous pyrolysis reactors increase CH₄ conversions, but C₂-C₁₀ yields are low because of competing chain growth pathways leading to carbon. The introduction of catalytic sites that merely initiate pyrolysis by forming methyl radicals gives higher CH₄ conversion rates, but does not influence C₂-C₁₀ yields. Sites that form and convert C₂ species via surface reactions without significant carbon formation increase C₂-C₁₀; they are required to exploit the effects of H₂ removal in practical systems. Simulations of H₂ removal through SrCe_{0.95}Yb_{0.05}O_{3-x} membrane films 10-100 μ films at 1000 K indicate that high C₂-C₁₀ yields (90%) are possible, but depend critically on the ability of catalytic sites to restrict chain growth via spatial constraints or other mechanisms of chain termination.

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