

Non-thermal Plasma Conversion of Methane to Methanol with Water and Heterogenous Catalysts

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Abstract: This work explores the conversion of methane to methanol in atmospheric pressure plasma catalytic systems (AC driven gas phase DBD and liquid water reactor). Heterogenous catalysts of active metals on metal oxides are explored in conjunction with plasma to enhance selectivity through selective $\cdot\text{OH}$ formation and C-H cleavage.

1. Introduction

Methanol (MeOH) is an important precursor for chemicals and fuels that can be converted from CH_4 , a major greenhouse gas (GHG) source. Currently MeOH is commercially produced from energy intensive steam reforming of fossil natural gas, with associated high GHG impact¹. Alternative approaches aim to electrify this process, to lower GHG impacts using renewable energy sources and improve carbon efficiency through high selectivity of MeOH production. In this regard, low-power non-thermal plasmas offer an efficient partial oxidation approach towards high selectivity CH_4 conversion to MeOH . While the current TRL of plasma partial oxidation technologies is low (1-2)², plasma catalytic technologies are considered promising due to their relatively high conversion and scalability possibilities.

This work focuses on the development of a non-thermal plasma bubbling reactor aimed at converting CH_4 into higher value MeOH with liquid water. It is hypothesized that MeOH can be produced with high selectivity through the reaction of methyl radicals ($\cdot\text{CH}_3$) and hydroxyl radicals ($\cdot\text{OH}$), while over-oxidation can be reduced by rapidly transferring the MeOH to the aqueous phase³. In plasma-liquid systems, high radical concentrations lie in the gas phase and in the vicinity of the gas-liquid interface. Thus, having a high concentration of CH_4 to form $\cdot\text{CH}_3$ and a high concentration of H_2O to form $\cdot\text{OH}$ is desired to maximize yield of MeOH . Heterogenous catalyst inclusion of metals supported by photo-catalytic oxides are utilized in the reactor with the goal of promoting C-H activation and $\cdot\text{OH}$ production at the plasma-liquid interface.

2. Methods

Conversion is explored with an AC driven gas phase dielectric barrier discharge (DBD) plasma with and without metal oxide photocatalysts and H_2O vapor oxidant. Important catalyst surface mechanisms are deduced with an in-situ DRIFTS measurement system⁴. The inclusion of a liquid surface is used to explore the hypothesis of enhanced selectivity due to the trapping of gas phase MeOH in the liquid. Gas phase reactivity is compared to the plasma liquid system for otherwise similar plasma conditions (power, gas phase composition, etc.).

3. Results and Discussion

Gas phase conversion of MeOH is shown in Figure 1 in an empty DBD reactor operating at various plasma conditions and CH_4 admixtures. The molar ratios of CH_4 to H_2O vary as 8:1, 34:1, and 59:1. Generally, it is observed

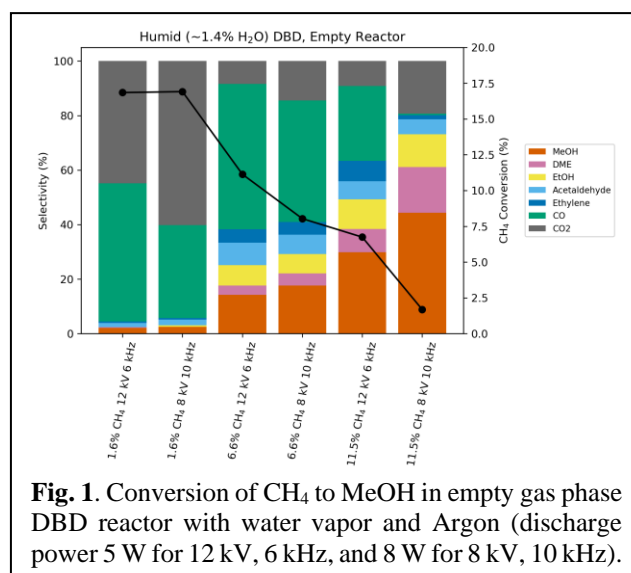


Fig. 1. Conversion of CH_4 to MeOH in empty gas phase DBD reactor with water vapor and Argon (discharge power 5 W for 12 kV, 6 kHz, and 8 W for 8 kV, 10 kHz).

that as the concentration of CH_4 increases, conversion decreases from around 17% to around 2%, but selectivity for MeOH increases from < 5% to nearly 40%. Higher CH_4 concentrations in this system are expected to prevent the over-oxidation of CH_4 into undesirable products (i.e. CO_2).

4. Conclusion

CH_4 conversion to MeOH is demonstrated in plasma catalytic systems, using only gas and gas-liquid reactor systems. Results demonstrate conversion and selectivity comparable to literature, and ongoing work aims to improve selectivity and yield using a liquid reactor and heterogenous catalysts.

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