

Partial Methane Oxidation to Methanol at Plasma-Catalyst-Liquid Interfaces

James Ho¹, Matthew Hershey², Wesley D. Beck², and Dayne F. Swearer²

¹Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL, USA

²Department of Chemistry, Northwestern University Evanston, IL, USA

Abstract: Plasma assisted partial oxidation of methane to methanol was performed using nanosecond pulse discharges in water to generate plasma bubbles. High liquid selectivity of methanol (>97%) was achieved by tuning the plasma electron energy and by partitioning copper oxide between the plasma and liquid states within fritted gas dispersion tubes. We propose this direct plasma-catalyst-liquid interface is critical towards radical stabilization.

1. Introduction

Plasma-liquid interactions have shown effective for transforming hydrocarbons into liquid oxygenates, but specific product selectivity is challenging in the absence of catalyst.^[1] When a catalyst is integrated into these systems, it is usually dispersed into the liquid,^[2] minimizing catalyst-plasma interactions due to mass transport limitations and short lifetimes of plasma species.

In this work, we experimentally demonstrate the importance of mass transfer of plasma-activated species and their interactions with catalysts in liquid environments. By constructing a direct catalyst interface between plasma and water, we demonstrate a one-step method for ambient pressure and room temperature partial oxidation of methane (POM) to methanol.

2. Methods

Copper oxide (CuO) catalysts were dropcast into commercially available gas dispersion tubes to create the plasma-catalyst-liquid interface (**Fig. 1A**). POM was carried out using nanosecond pulse discharges in these catalytic membranes to create plasma bubbles. Liquid oxygenated products were quantified by ¹H NMR and gas product distribution were determined by gas chromatography. The role of plasma-catalyst-liquid interactions on methanol selectivity was investigated by changing the frit pore size and gas flowrate. Plasma discharge properties such as electron energy were also modified by increasing the applied voltage and concentration of argon gas.

3. Results and Discussion

Fig. 1B compares the liquid oxygenate distribution given different methods of catalyst integration. The methanol selectivity and overall production rate of liquid oxygenates increases when CuO is integrated directly into the frit compared to when CuO is dispersed into solution, illustrating the significance of plasma-catalyst-liquid interactions. **Fig. 1C** shows that at greater frit pore sizes, the production rate of oxygenated products increases but the methanol selectivity decreases. The increase in production rate with increasing pore size is consistent with a larger electron density available within the pore channels, allowing for increased plasma-liquid interactions. While smaller pores resulted in fewer liquid oxygenated products, we hypothesize the increase in surface area and proximity-dependent interactions between active plasma species and

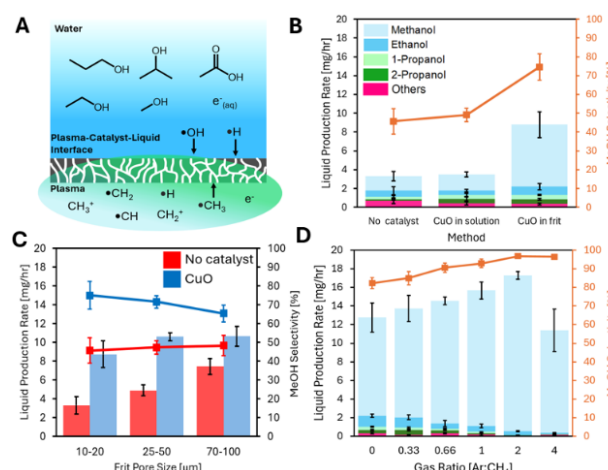


Fig. 1. (A) Schematic of plasma-catalyst liquid interface. POM optimization experiments by varying (B) catalyst integration method (C) frit pore size and (D) argon concentration

catalyst helps stabilize key radical species toward methanol selectivity. By increasing the argon concentration (**Fig. 1D**), we further increase the selectivity of methanol to upwards of 97%, which we attribute to argon dilution which inhibits gas-phase recombination of $\bullet\text{CH}_3$ to C_2 + hydrocarbons.

4. Conclusion

By controlling the plasma environment and mass transport interactions between the plasma and catalyst, we significantly improve methanol selectivity and production rate, where the addition of the direct plasma-catalyst-liquid interface yielded the greatest improvements. Beyond methane oxidation, our investigations tailoring plasma-catalyst-liquid interactions holds promise towards for other organic oxidation reactions in liquid environments.

Acknowledgements

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References

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