$Al_{(1-x)}B_2$ for the Realization of Hydrocarbons From Methane

The Center for Initiatives in STEM · DUKE ENERGY

Jose C. Berger,[a] Emma E. Blanco[a], Elan M. Marrero[a], Katerina L.Chagoya[b], and Richard G. Blair[a]

[a]Florida Space Institute, University of Central Florida Orlando, FL USA

[b]Department of Mechanical and Aerospace Engineering, University of Central Florida Orlando, FL USA

FLORIDA SPACE INSTITUTE · Blair Group

ABSTRACT

Methane is an extremely harmful greenhouse gas, contributing to the recent climate crisis. In order to rechannel the damaging effects of methane on the environment into more practical and lucrative applications (valorization), the catalyst Etched Aluminum Diboride (AlB_2) has been studied for the development of higher-order hydrocarbons from methane, which would ultimately result in lower energy costs and reduce greenhouse gas emissions for a cleaner environment. Using this catalyst in a plug-flow reactor , we have been able to realize olefins such as propene continuously for 17 hours at temperatures greater than 400°C.

INTRODUCTION

Hexagonal boron nitride (h-BN) is 2-D material that has recently been identified as a metal free catalyst for olefin hydrogenation (hydrogenation of compounds containing a C=C dbond) under reductive conditions (e.g. in the presence of hydrogen gas)[1], and dehydrogenation under oxidative conditions (e.g. in the presence of air)[2].

Methane has recently been oligomerized (consisting of similar or identical repeating units) to ethane over oxidized hexagonal boron nitride(h-BN) through oxidative methane coupling (OMC)[3].

The BN structure is not essential for catalytic activity. Of special interest in dealing with methane are reactive borides based on the AlB_2 structure, which consists of planar sheets of boron stabilized by metals with etched -OH functionality. Such structure offers the opportunity for the production of higher-order hydrocarbons, which would generate capital and provide new feedstock for polypropylene producers. This catalyst could also be implemented in coal gasification for cleaner-burning fuels.

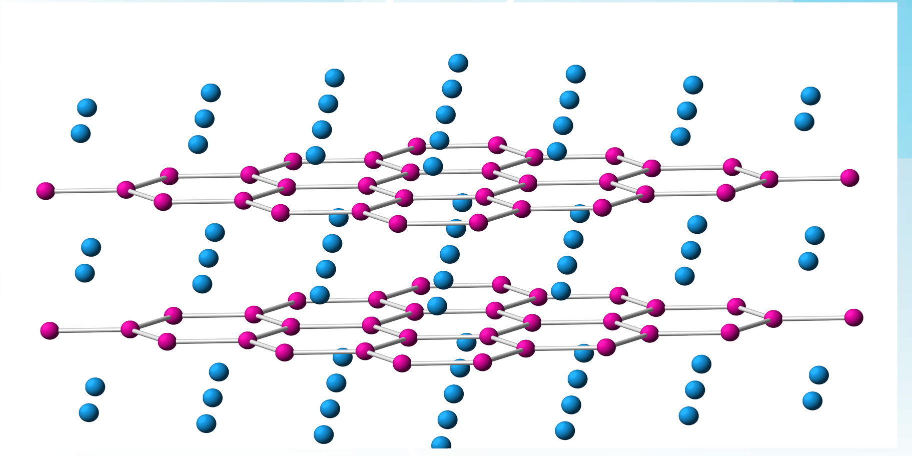

FIGURE 1. Side View of AlB_2 Structure.

METHODS

1) Approximately 0.500-1.00 g of boron catalyst were loaded into a coated glass tube, which was consecutively loaded into a stainless steel tube; the peripheries of both containers were blocked with insulating material.

2) Reaction vessel was placed in an insulated furnace and connected to the rest of the reactor.

3) Rate flows were set. Argom (bypass): 00.99 SCCM; Argon (reaction vessel): 13.00 SCCM; Methane: 09.73 SCCM; Oxygen: 01.01 SCCM.

4) At 308.2 kPa, experiments were performed at 19, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475, and 500 °C.

5) At desired temperature, gas chromatograph-mass spectrometer's (GC-MS) sequence was commenced; a sample was taken every hour for 17 hours.

6) Catalyst post-plug-flow was analyzed with TGA.

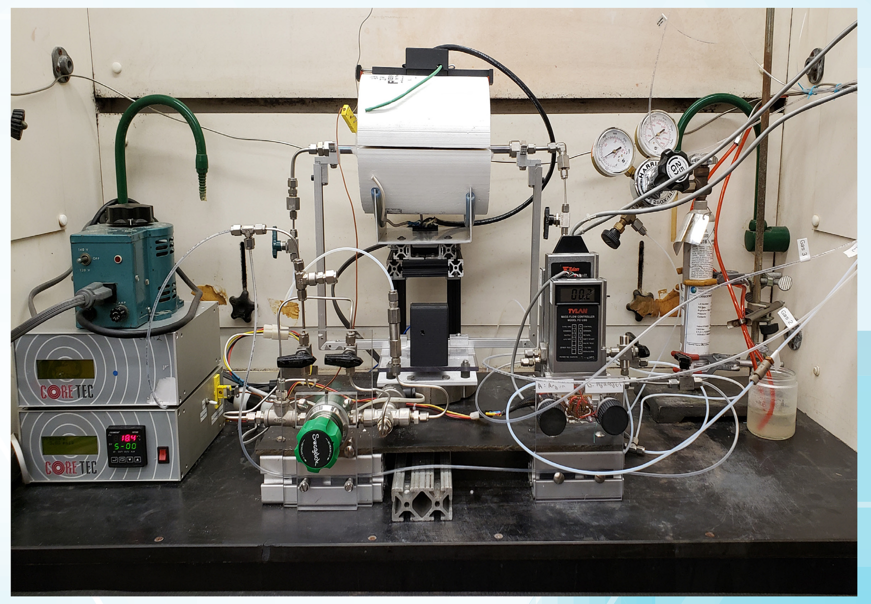

FIGURE 2. Plug-Flow (PF) Reactor.

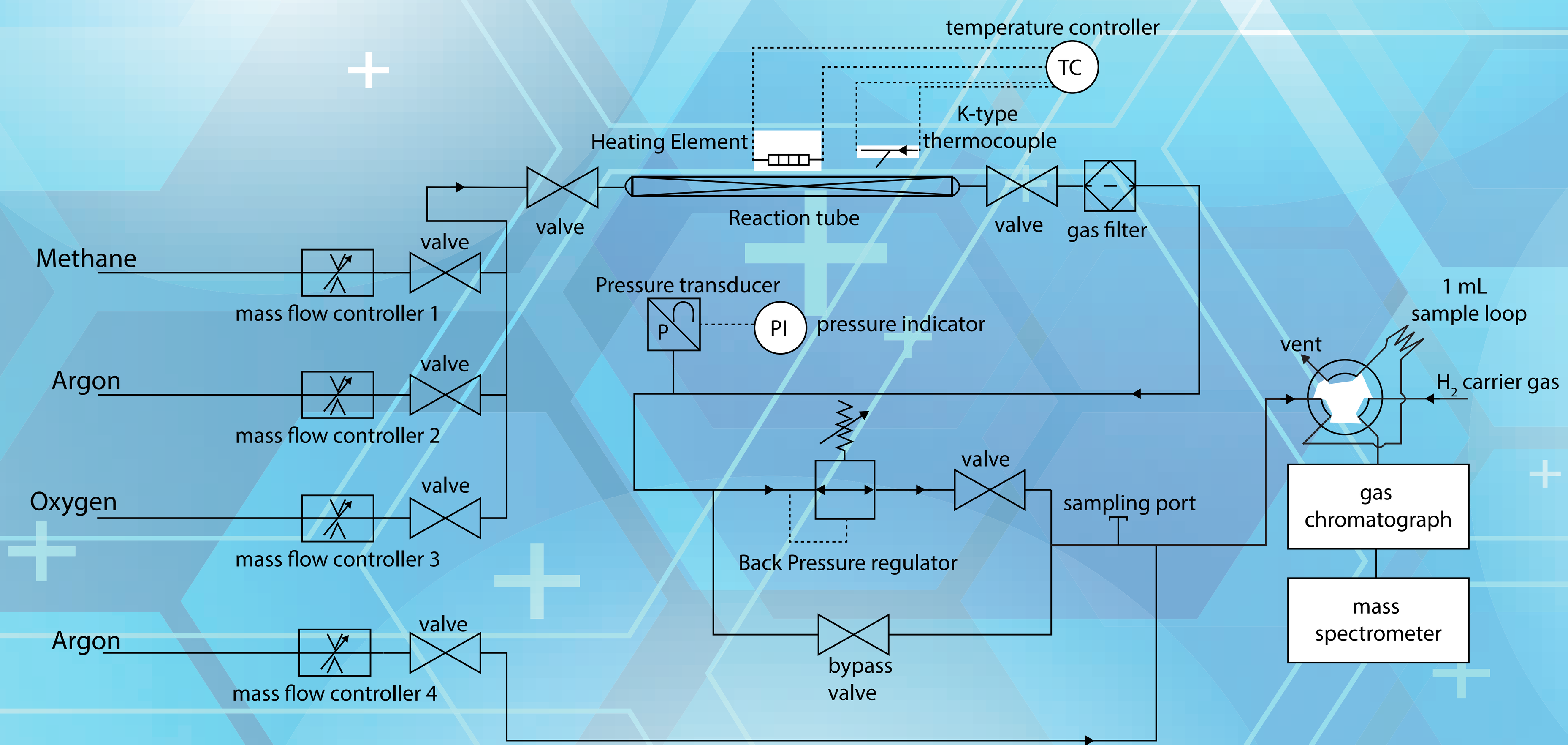

FIGURE 3. Plug-Flow Reactor block flow diagram.

RESULTS

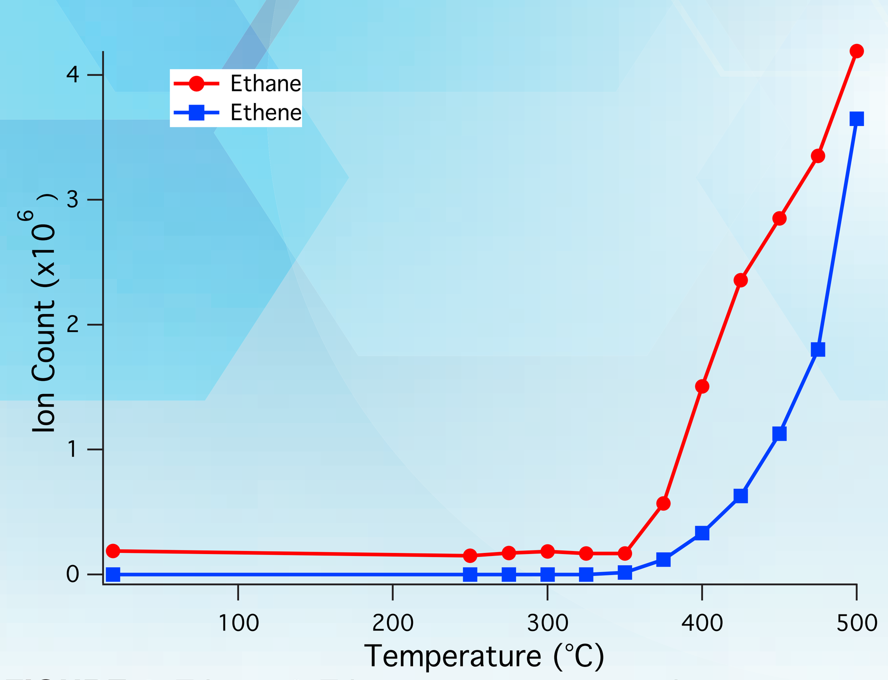

FIGURE 4. Ethane & Ethene temperature study.

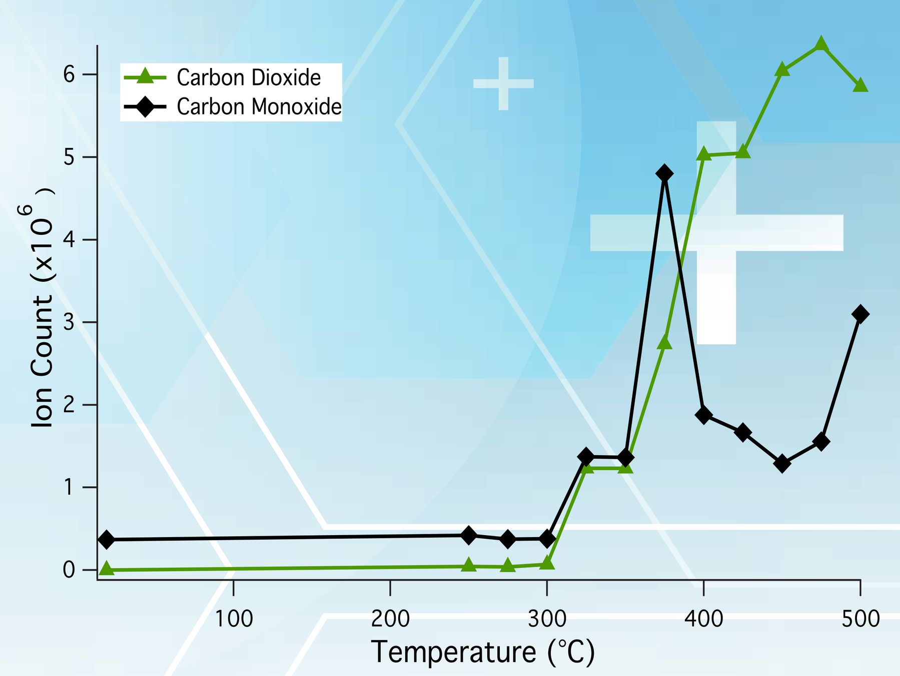

FIGURE 5. Carbond Dioxide & Carbon Monoxide temperature study.

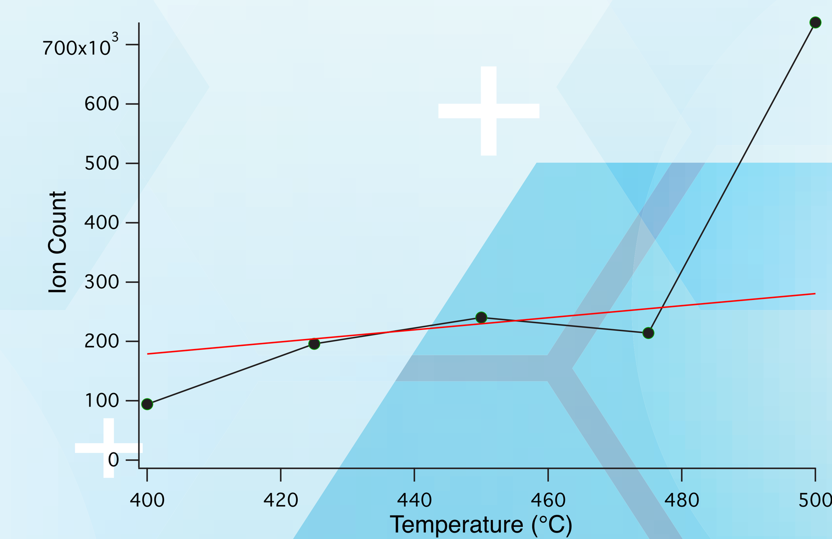

FIGURE 6. Propene temperature study.

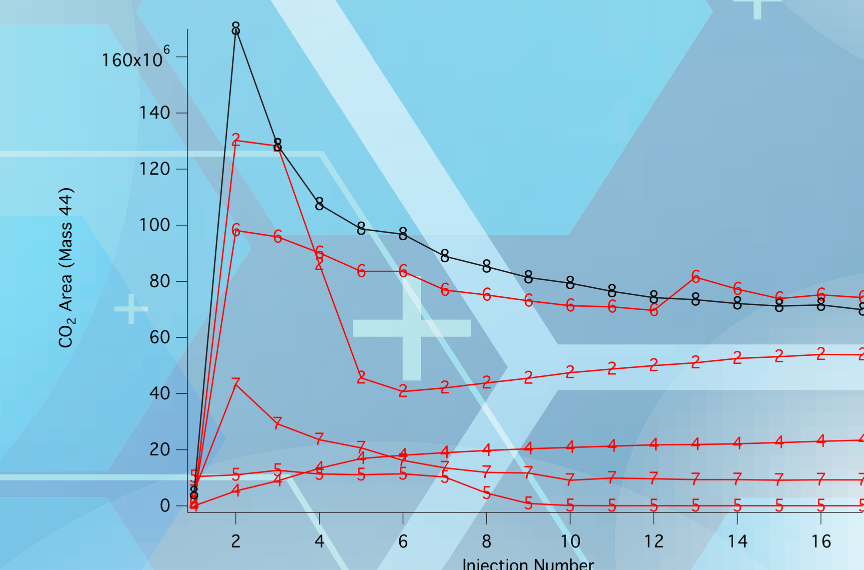

FIGURE 7. Catalytic activity of samples with distinct percentage of Al content.

DISCUSSION

•Presence of:

—CO and CO_2 indicative of incomplete and complete combustion, respectively.

—Hydrocarbons other than methane (e.g., ethane) indicative of Fischer-Tropsch-like chemistry; likely presence of synthesis-gas ($CO + H_2$) and thus, steam methane reformation reaction.

—Ethene and propene indicative of oxidative dehydrogenation reaction.

•Catalytic activity under ~308 kPa observed and as low as 19 °C (incomplete combustion and oxidative methane coupling), 250 °C (complete combustion), and 400 °C (oxidative dehydrogenation).

$$3CH_4 + O_2 + H_2O \longrightarrow 3CO + 7H_2 \quad \textbf{Steam Methane Reformation}$$

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O \quad \textbf{Incomplete Combustion}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \textbf{Complete Combustion}$$

$$H_2 + CO \longrightarrow C_2H_6,\ C_3H_8,\ C_4H_{10} \quad \textbf{Fischer-Tropsch}$$

$$2C_3H_8 + O_2 \longrightarrow 2H_2O + 2C_3H_6 \quad \textbf{Oxidative Dehydogenation}$$

FIGURE 8. Potential Chemical Equations Ocurring at the Catalyst's Surface.

•On average, the higher the percent of aluminum removed, the higher the activity of the catalyst.

CONCLUSION

Etched AlB_2 has demonstrated to be capable of producing both saturated and unsaturated hydrocarbons from CH_4, a greenhouse gas with no apparent practical employment. Such products have been observed at significantly lower pressures than those required by Fe or Co catalysts in Fischer-Tropsch chemistry (Fischer-Tropsch process traditionally oberserved at ~2000 kPa). Oxidative methane coupling has been suggested as potential pathway facicilitated by the catalyst. Although etched AlB_2's light-off temperature has been estimated to be 350 °C, the catalysts displayed activity at room temperature for the incomplete combustion of CH_4. Above all, the catalyst has the potential of replacing traditional catalysts mainly based on metal for the production of higher-order hydrocarbons and/or the valorization of CH_4 for the potential development of a circular economyand a renewable feedstock.

REFERENCES

1. Nash, D. J.; Restrepo, D. T.; Parra, N. S.; Giesler, K. E.; Penabade, R. A.; Aminpour, M.; Le, D.; Li, Z.; Farha, O. K.; Harper, J. K.; Rahman, T. S.; Blair, R. G., Heterogeneous Metal-Free Hydrogenation over Defect-Laden Hexagonal Boron Nitride. *ACS Omega* **2016**, *1* (6), 1343-1354.

2. Grant, J. T.; Carrero, C. A.; Goeltl, F.; Venegas, J.; Mueller, P.; Burt, S. P.; Specht, S. E.; McDermott, W. P.; Chieregato, A.; Hermans, I., Selective oxidative dehydrogenation of propane to propene using boron nitride catalysts. *Science* **2016.**

3. Wang, Y.; Zhao, L.; Shi, L.; Sheng, J.; Zhang, W.; Cao, X.-M.; Hu, P.; Lu, A.-H., Methane activation over a boron nitride catalyst driven by in situ formed molecular water. *Catalysis Science & Technology* **2018,** *8* (8), 2051-2055.

ACKNOWLEDGEMENTS

I would love to express my immense gratitude towards the Lord, Dr. Richard Blair, Dr. Katerina Chagoya, Macey Fancher, Emma Blanco, Elan Marrero, the Excel Program, the Center for Initiaves in STEM, Duke Energy, the University of Central Florida, and my family. Thank you for all of your kindness.