Boron-Rich Catalysts for Metal-Free Methane Valorization

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Abstract

Small hydrocarbon molecules such as methane and ethane are considered low-value compounds based on the current market and cost of transport. However, their efficient utilization would enhance the energy and chemical independence of the United States . Of these compounds, methane is an underutilized resource that, if properly exploited, could improve local and national job prospects. Valorization of methane by converting it to aromatic products through dehydroaromatization would be a viable path toward utilization of this resource. We have developed a long lived. boron-based catalysts that has good dehydroarmatization activity. The catalyst long-life is due to reduced coking. This long lived catalysts will finally allow exploitation of methane sources in a responsible manner.

Introduction

Methane itself has relatively low-value and is often flared at sites to convert to CO_2 which has a lower global warming potential (GWP). Through dehydroaromatization (DHA) methane can be converted to the higher value compound benzene with hydrogen production as well. States-of-the-art catalysts are plagued by deactivation through coking. This coking is attributed to Brønsted acid sites on the catalyst. Implementation of catalysts that lack

$$2CH_4 \rightarrow H_2C{=}CH_2 + 2H_2$$

$$6CH_4 \rightarrow \bigcirc + 9H_2$$

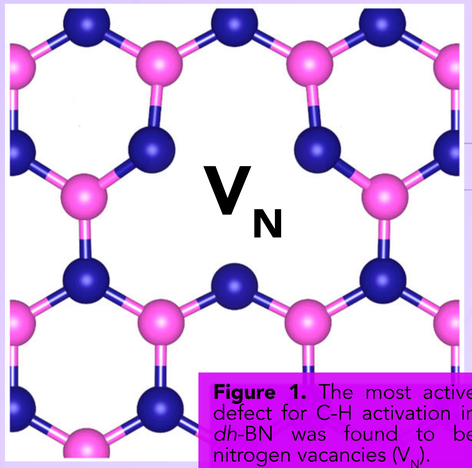


Figure 1. The most active defect for C-H activation in *dh*-BN was found to be nitrogen vacancies (V_N).

these sites should exhibit enhanced lifetimes. Brønsted acid-free catalysts can be realized through the introduction of vacancies in hexagonal boron nitride (*dh*-BN) These introduce acceptor states in the BN band structure allowing harvesting of light and transfer of energy to adsorbed molecules and breaking of C-H bonds[1] without the production of CO or CO_2.

Results

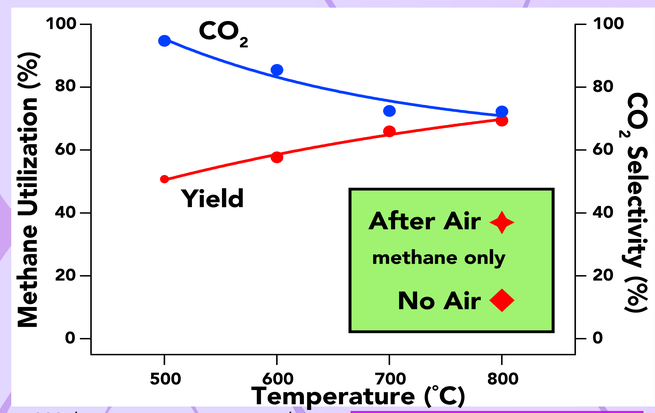


Figure 2. An air/methane mixture shows steady increase in yields with temperature similar to traditional zeolite-based catalysts. When air is removed, product yields are much higher with an initial air activation.

With no pretreatment, the prepared catalyst showed some activity for hydrocarbon formation from methane. Methane utilization was significantly improved with an activation step using a reducing mixture of air and methane.

Yields of hydrocarbons were increased by 400%. During activation the amount of CO_2 produced steadily decreased indicating oligomerization and aromatization pathways were becoming more accessible.

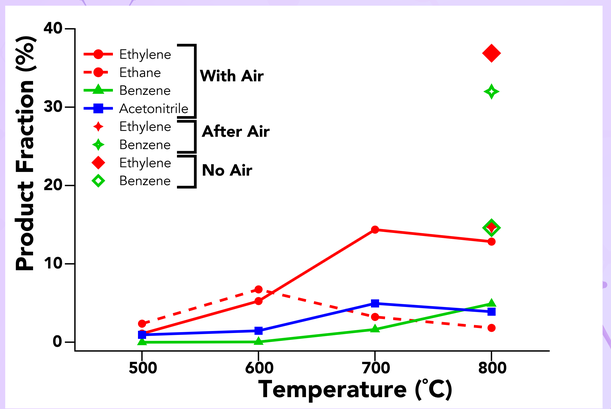


Figure 3. With a methane/air mix benzene selectivity increased with temperature. Air activated catalyst showed high benzene selectivity. Catalyst exposed to methane alone showed higher ethylene selectivity.

The air activated material produced a significantly different product distribution with benzene formation favored over ethylene formation. The majority fraction of the product stream was composed of unsaturated hydrocarbons. After 17 hours on stream no loss of catalytic activity was observed.

Methods

dh-BN

Defect-laden boron nitride was prepared from hexagonal Boron Nitride (Saint-Gobain Grade PCTF5) that had been dried under dynamic vacuum (30 mtorr) at 400 ˚C for 12 hours.

Two grams of this material produced by grinding in a SPEX mixer mill vial composed of zirconia (ZrO_2) with (1) 19 mm zirconia ball for 1 hour.

Upon milling the white h-BN became brownish due to the introduction of point defects

Investigation of Catalytic Activity

The reaction tube was packed with 0.2g of catalyst and 1.3 g of mullite support. The catalyst was studied at 800 ˚C with and without air activation. Air activation was performed by flowing a mixture of methane (3 sccm) and air (7 sccm) over the catalyst.

The reactor temperature was ramped from 500 ˚C to 800 ˚C over 10 hours and held at 800˚C for 7 hours. DHA activity was evaluated with a flow of methane (3 sccm) at 40 psig and 800˚C.

Activation and DHA product composition was analyzed by GC-MS (Agilent 6890N and 5973N). The product stream was automatically sampled once an hour with a gas sample valve.

Quantitation was performed by integrating the resulting chromatographs and normalizing to the ionization cross section of each species.

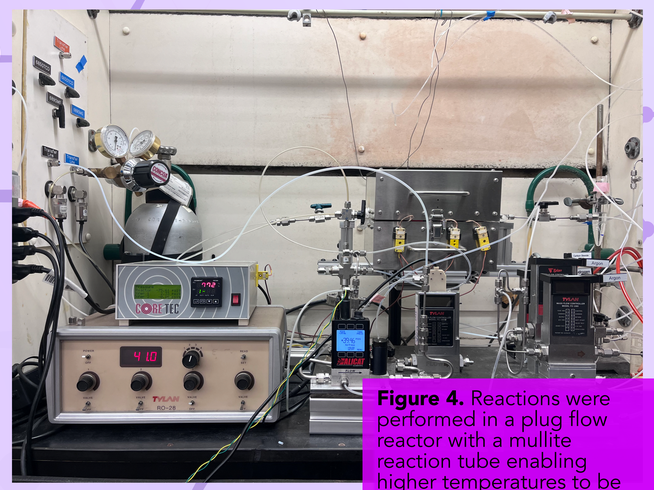
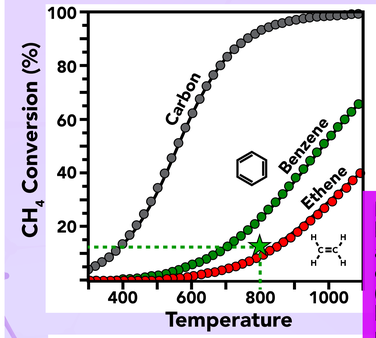


Figure 4. Reactions were performed in a plug flow reactor with a mullite reaction tube enabling higher temperatures to be studied. Mass balance was determined by measuring the flow in and out.

Coking



No coking was evident on the catalyst even though exposure to light was observed to lead to coking.[2]

Figure 5. Zeolite-based DHA catalysts are predicted to favor carbon formation (coking). The observed benzene yield is on par with zeolite catalysts.[3]

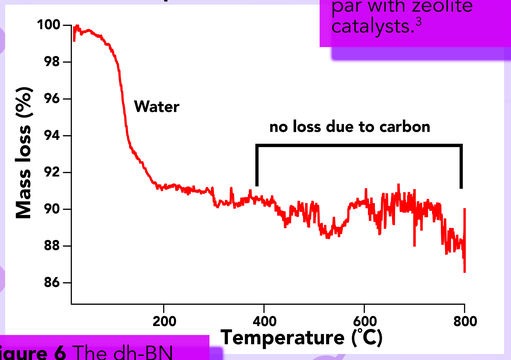


Figure 6 The dh-BN DHA catalysts shows no coking after 17 hours on stream.

Conclusion

Activation of *dh*-BN under a reducing mixture of air and methane resulted in a long-lived DHA catalysts with good selectivity and yield. The exceptional lifetime (17 hrs) of the catalyst can be attributed to the lack of coking observed on the spent catalyst. Without a coking pathway, hydrocarbon yields will increase. The role of air activation must be further studied to realize a relevant catalyst.

References

1. 2. 3.

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Acknowledgments

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