The Topotactic Synthesis of Low-Dimensionality Boron

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Abstract

Borides, such as AlB_2, exist in layered structures compromised of alternating sheets of boron and a metal. By etching away the aluminum ion, an unstable boride structure is left behind which could be used as a catalyst to convert methane into higher-order hydrocarbons. Different etchants, such as sodium hydroxide solution and ion exchange resin, were used to synthesize the boron structure. Using x-ray fluorescence, it was found the ion exchange etchant was able to remove most of the aluminum. In addition, the resulting boron product was shown to successfully upgrade methane to propene.

Introduction

Hexagonal boron nitride (*h*-BN) is a solid chemical substance that is inert under normal conditions, but when subjected to high-energy ball milling, random boron or nitrogen molecule or ejected leaving a vaccancy in the crystal structure. This defected structure is known as defect-laden boron nitride (*dh*-BN). Previous research showed that *dh*-BN material can convert CO_2 into methanol and formic acid by hydrogenation, but it undetermined which vacancies catalyze the reaction. The ability to synthesize a 2-D structured boron material from borides in order to study the behavior of the nitrogen vaccanies in *dh*-BN.

Borides, such as AlB_2, exist in layered structures comprised of alternating sheets of boron and metal atoms (Figure 1). Versions of these compounds can be obtained by chemically etching away the metal atoms, leaving behind an unstable boron structure (Figure 2). In this research, new way of synthesizing of 2-D boron sheets using a mixture of mechanochemistry and wet chemistry.

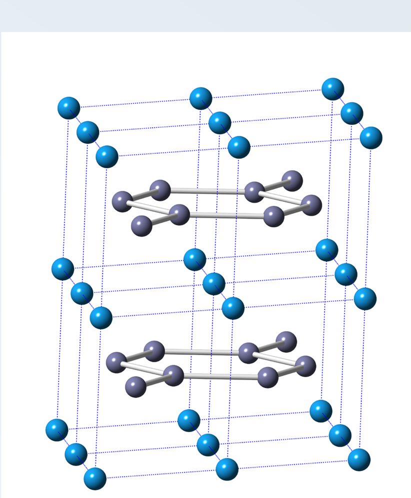

Figure 1- AlB_2 Crystal Structure

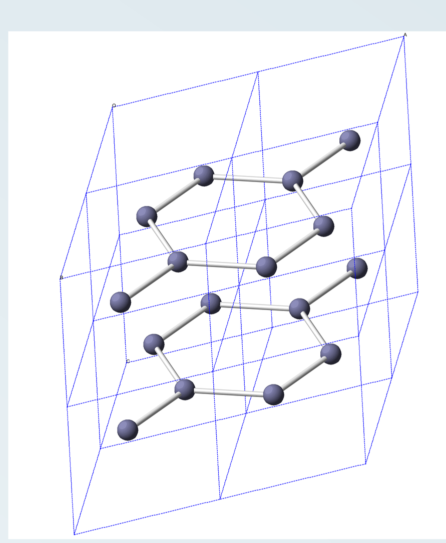

Figure 2- Boron Crystal Structure

Objective

This research proposes a new method of synthesizing both 2-D and 3-D boron containing vacancies by chemically etching aluminum dodecaboride (AlB) in order to produce a catalyst for the carbonylation of methane.

Experimental

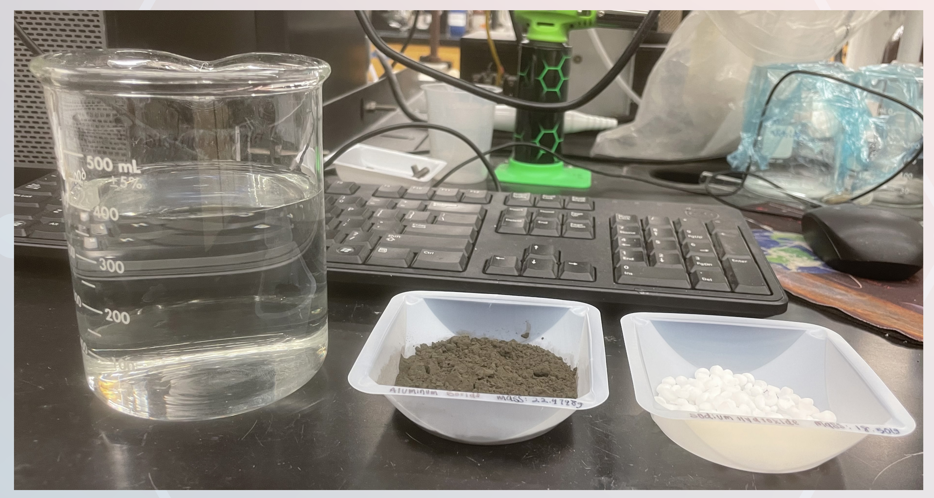

Figure 3- Materials for the Etching of AlB_2 with Sodium Hydroxide

Figure 4 : Ion Exhange Resin and Dry Ion Exhange Resin

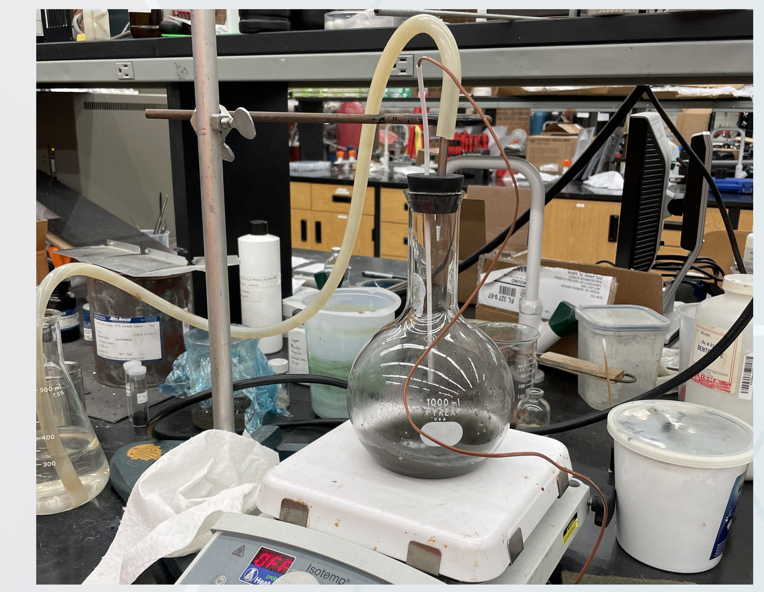

Figure 5: Acetonitrile and Dry Resin Reaction

Sodium Hydroxide Etchant:

Material:

- 22.479g of aluminum boride (AlB_{12})
- 18.501 g of sodium hydroxide (NaOH)
- 400 mL of water

Procedure:

- Stirred over a 19-day period.
- Every two days a sample was filtered through a millipore filtration system

Ion Exchange Resin Etchant:

Materials:

- 2.000g of aluminum boride (AlB2)
- 22.8 g of ion exchange resin
- 400 mL of acetonitrile

Procedure:

- Stirred over for a 24-hour period.
- Sample was filtered through a Millipore filtration system.

Dry Ion Exchange Resin Etchant:

Material:

- 2.000g of aluminum boride (AlB2)
- 22.8 g of dry ion exchange resin
- 400 mL of acetonitrile

Procedure:

- Stir for a 24-hour period.
- Sample was filtered through Millipore filtration system.

X-ray Florences:

- 0.1 g of each sample was suspended in 20 mL of deionized water
- Solutions were briefly sonocated
- Filtered through a Millipore filter.

Figure 6: Vacuum Filtration System

Figure 7: X-Ray Flourences Instrument

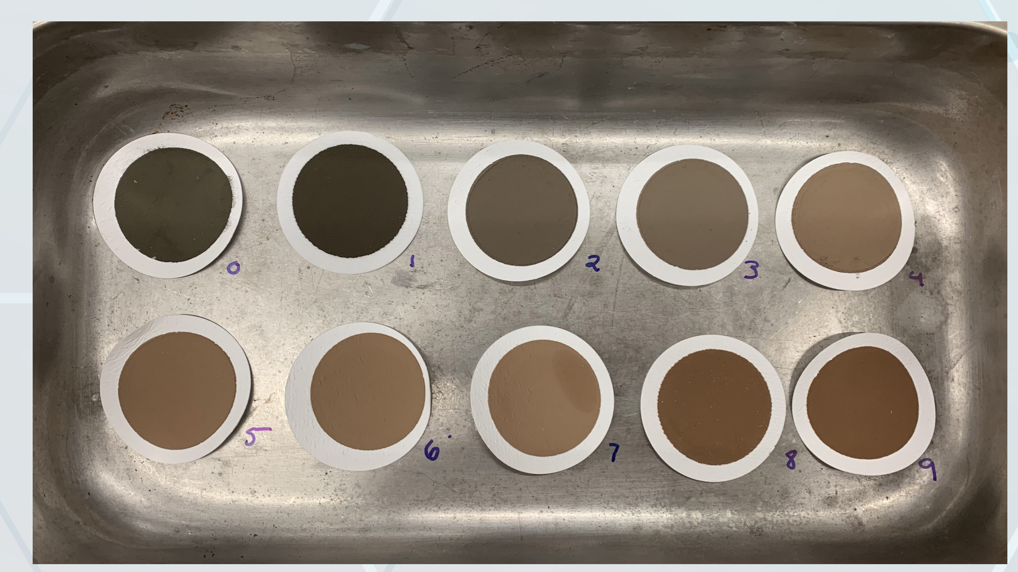

Figure 8: AlB_2 Etched with NaOH throughout a 19-day Period

Results

Table 1: Aluminum Removal of AlB_2

Sample	Aluminum Removed (%)
AlB_2 in NaOH - 1 day	16.69%
AlB_2 in NaOH - 3 day	56.02%
AlB_2 in NaOH - 5 day	65.23.%
AlB_2 in NaOH - 7 day	67.71%
AlB_2 in NaOH - 9 day	69.08%
AlB_2 in NaOH - 11 day	69.62%
AlB_2 in NaOH - 13 day	68.99%
AlB_2 in NaOH - 16 day	70.29%
AlB_2 in NaOH - 19 day	68.54%
AlB_2 in ACN and Ion Exchange Resin- (Sample A)	81.41%
AlB_2 in ACN and Ion Exchange Resin- (Sample B)	79.38%

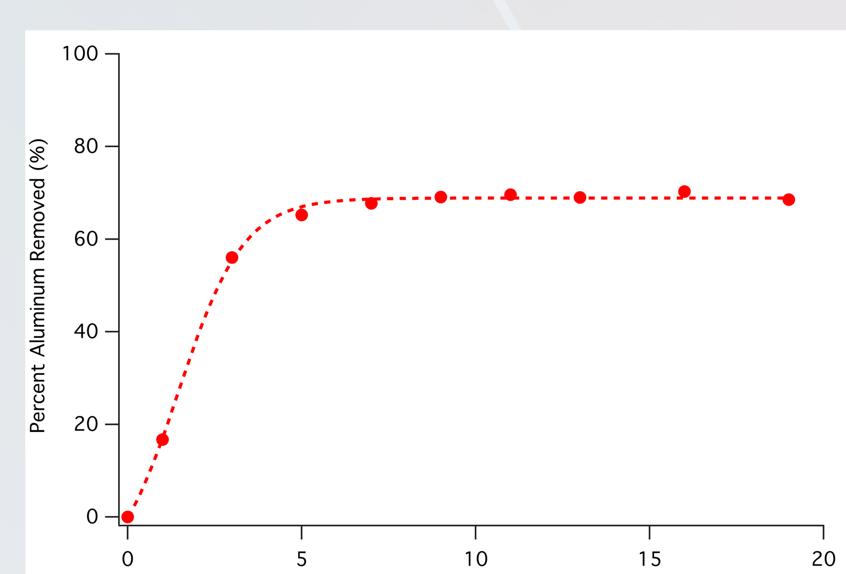

Figure 9- Percentage Aluminum Removal vs Time Etched

Sodium Hydroxide Solution:

- Around the 9th day (sample 5) of stirring, the sample started to reach a plateau around 69% of removal of aluminum.

Acetonitrile and Ion Exchange Resin:

- This solution was able to remove 80% of the aluminum content of the solution

Acetonitrile and Dry Ion Exchange Resin:

- This solution was able to remove 30% of the aluminum content of the solution

Discussion

From x-ray fluorescence data, it was determined that the removal of aluminum was done best with ion exchange resin etching solution. The solution was able to etch out 80% of the aluminum. In future experiments , ion exchange resin will be studied more since it had the highest removal of aluminum content. For the sodium hydroxide etching process, the solution would be decanted, and new sodium hydroxide solution would be added in order to improve the aluminum removal. These experiments also show that the longer the reaction is allowed to occur, the better the removal rate, but the goal is also to find the maximum percentage removed (when there is a plateau). Increasing the removal of aluminum allows for boron structures to remain. Those boron structures are used as a catalyst to create higher order hydrocarbons. This is a topic of interest as it could be a way to sequester and use greenhouse gases.

References

References:

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