Synthesis of Borazine and Its Polymer-Derived Boron Nitride

Kyo-Tae Moon, Dong-Soo Min, and Dong-Pyo Kim

Dept. of Fine Chemical Engineering & Chemistry, Chungnam National University, Tajon 305-764, Korea
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Abstract: The study of borazine has been limited due to the cost of raw materials and the reaction apparatus in addition to the low yield less than 30%. Pure borazine has been synthesized by using inexpensive raw materials (NaBH₄ and (NH₄)₂SO₄) and simple glass reaction apparatus with much improved yield over 50%. The synthesized borazine and its polymerized product are characterized by IR, ¹H-NMR and TGA/DSC, then compared to commercial products. It was, finally, confirmed that the borazine polymer was converted to a pure boron nitride (h-BN) on heating to 1500°C with 75% ceramic yield.

1. Introduction

Inorganic polymers have been used for the preparation of ceramic fibers, coatings and matrices in ceramic fiber/ceramic matrix composites. Polymeric precursors allow the fabricating processes at lower temperatures than the processes of ceramic powders. The major processing problems associated with polymeric precursors are their low ceramic yields and phase purity. These obstacles must be overcome to fully exploit the benefits of polymer pyrolysis over the conventional processing techniques [1].

Recently we reported the first successful preparation of carbon fiber BN matrix composite(C/BN) using low viscous borazine polymer synthesized from the purchased monomer [2]. These composites displayed outstanding mechanical properties and excellent resistance to oxidation up to 850°C, meaning is unclear. In addition, it was found that further polymerization at 5°C for 2 weeks led to mesophase formation such as a pitch mesophase [3]. It is interesting to note that chemistry of polyborazine as a BN precursor is quite similar to that of polyaromatic compounds as a graphite precursor.

Since the discovery of borazine by Alfred Stock in 1926 it as a by-product from thermal decomposition of boron hydride-ammoniates, it has been commercially synthesized by heating diborane and ammonia as solid-gas phase reaction in a stainless steel reactor. Borazine has also been prepared by reacting sodium borohydride with ammonium chloride in a laboratory scale [4]. However those methods has serious disadvantages such as the uses of expensive raw materials, complicated synthetic equipments and purification system. Borazine can, however, be purchased at a resonsably low price of $25/g in a limited quantity.

In this context, availability of less expensive borazine may provide various potential applications such as BN coating, fiber and other specialties. It has been demonstrated that SiC from polysilanes and Si₃N₄ from polysilazanes as well as versatile oxide ceramics from sol-gel polymers have provided new structural and electronic materials.

In this report, we present the simple synthetic route of borazine by the reaction of NaBH₄ and (NH₄)₂SO₄ in a simple glass apparatus at improved yield over 50%. And it is proved that the synthesized borazine has comparable quality to commercial borazine, and its polymerized product converts into stable BN on heating to 1500°C.

2. Experimental

2.1. Materials

NaBH₄ (Aldrich; 98%) and (NH₄)₂SO₄ (Aldrich; 99%) were purchased as the boron(B) and nitrogen(N) sources and used without further purification. High boiling tetraglyme as a solvent was freshly distilled
prior to reaction. Borazine has the following physical properties: refractive index (RI): 1.3921, low melting point: -56.2°C and low boiling point: 55°C.

2.2. Experimental Procedure

NaBH₄ solution was prepared by dissolving 0.81 mol of NaBH₄ in 350ml of tetraglyme in a 1L round bottomed flask, and then the mixture was agitated for 12-15 h under N₂ atmosphere. 0.62 mol of (NH₄)₂SO₄ placed in a 3-neck 2L round bottomed flask equipped with a reflux condenser and a vacuum adaptor was dried for 3 hours under 2.5 torr vacuum at 120°C. The exit of condenser was connected to a standard vacuum line equipped with a twin liquid nitrogen trap. When the temperature reached at 70°C, NaBH₄ solution was added to the flask containing dry (NH₄)₂SO₄ by cannular transfer.

The solution was slowly added to prevent the catastrophic buildup of H₂ gas due to vigorous reaction. The reaction mixture was gradually warmed to 120°C in 1 h and kept for 2-3 h under different vacuum pressures. The product was continuously collected in the cold-trap. The trapped borazine was further purified by the vacuum fractionation through a series of three traps: -45°C (liquid nitrogen + chlorobenzene) for tetraglyme solidification, -94°C (liquid nitrogen + acetone) for purified borazine solidification, and the last -196°C (liquid nitrogen) for excluded borazine.

In a typical polymerization reaction, 10g of the synthesized borazine was heated with stirring under nitrogen atmosphere at 70°C in a 3-ounce pressure reaction vessel(Ace Glass Co.). The reaction was continued for 40 h with periodic H₂ degassing until the formation of white solid polymer. The solid polyborazine was heated to 1500°C in a tube-furnace under Ar atmosphere to convert into stable BN powder. Fig. 1 shows the overall procedure for the synthesis of borazine monomer and BN ceramic as a flow chart.

2.3. Analytical Method

Purified borazine was compared with commercial borazine by infrared spectroscopy(BIO WIN RAD) and ¹H nuclear magnetic spectroscopy (Varian Unity 400 (400MHz)). For the dehydrocoupled borazine oligomer, thermogravimetric analysis(TGA; TA Instrument 2950) and differential scanning calorimetry(DSC; 2910) were done at a heating rate of 10°C/min to 500°C and 1000°C under N₂ atmosphere, respectively. After heat-treatment of borazine oligomer up to 1500°C under Ar atmosphere, powder X-ray diffraction(RIGAKU) was conducted and compared with theoretical h-BN listed in the JCPDS file.

3. Results and Discussion

It is well known that borazine(B₃N₃H₆), a colorless liquid, is the best starting compound for BN as a pitch for graphite. Borazine has a planar six membered ring structure with alternating boron and nitrogen atoms each with a hydrogen atom attached. Borazine is iso-electronic with benzene so it called "inorganic benzene". However, it is readily decomposed into NH₃ and B₂O₃ upon exposure to moisture, and therefore it should be handled carefully under dry atmosphere[5].

Table 1 shows the synthetic yields of borazine at various reaction conditions. It is most likely that the reaction involves the initial generation of ammonia-borane and subsequent pyrolysis to form borazine.

\[
6\text{NaBH}_4 + 3(\text{NH}_4)_2\text{SO}_4 \rightarrow n\text{NH}_3 \cdot \text{BH}_3 \rightarrow 2\text{B}_3\text{N}_3\text{H}_6 + 3\text{Na}_2\text{SO}_4 + 18\text{H}_2
\]

The reaction is based on two old works[6,7]. One is that borazine was produced from pyrolysis of ammonia-borane(H₃N·BH₃) in diglyme in 70% yield. And it has previously shown that ammonia-borane is readily generated by the reaction of LiBH₄ with (NH₄)₂SO₄ in ether at room temperature. Therefore, ammonia-borane appears be formed by the reaction of BH₄ and NH₃. Subsequent thermal decomposition of ammonia-borane will produce borazine at 120°C.
Tetraglyme was chosen as a solvent to reduce the possible evaporation in vacuum procedure.

Borazine was obtained in a scale of 10g and 15g per run with significantly improved yield of 45-55% range. This value is higher than the previously reported yield, 20-30% of commercial method\cite{4}. And it was observed that reaction temperature higher than 120°C reduced the yield. It is likely that low volatile borazine polymer or oligomer might form at the temperature higher than 120°C. We also observed that the yields of borazine increased with the increase of addition time.

Fig. 2 shows Infrared spectra of the synthesized borazine and its polymerized product(polyborazine) as well as commercial ones. Both synthesized and commercial borazine show the indential absorption bands of N-H, B-H and B-N stretching at 3440cm⁻¹, 2505cm⁻¹ and 1430cm⁻¹, respectively. As polymerization proceeds by dehydrogenative self-condensation, the intensities of N-H and B-H absorption decrease due to the removal of hydrogen by the condensation between the rings. And sharp B-N absorption at 1430cm⁻¹ also changes to a broad absorption. This result was caused by dehydrocoupling reaction that B-H and N-H bonds were transformed into various B-N bond environments surrounded by borazine rings\cite{8}.

In the \textsuperscript{1}H NMR spectrum shown in Fig. 3, B-H proton was observed at \(\delta\) 4-5 as a quartet and N-H proton at 5.4-6 as a triplet\cite{9}. IR and NMR data, show that the prepared. Borazine has a reasonable purity of even though trace amounts of tetraglyme exists in the final product.

Fig. 3. \textsuperscript{1}H-NMR spectrum of synthesized borazine.

Fig. 4 shows the DSC and TGA patterns for thermal properties of polyborazine obtained from two different types of borazine sources. Both types of polymers represent that the broad endothermic peaks at 90-120 °C may indicate the evaporation of low molecular weight volatiles\cite{2}. The TGA of commercial borazine shows a smaller weight loss up to the corresponding temperature than synthesized product. It may be caused by slightly different degree of polymerization in both borazine polymers. The exotherm in the temperature range of 160-200°C is believed to be a

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**Table 1. Synthetic Yield of Borazine at Various Reaction Conditions**

<table>
<thead>
<tr>
<th>Reaction Temperature (°C)</th>
<th>Dropping Time (min)</th>
<th>Reaction Time (min)</th>
<th>Borazine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>70</td>
<td>150</td>
<td>37</td>
</tr>
<tr>
<td>120</td>
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<td>210</td>
<td>55</td>
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<tr>
<td>135</td>
<td>120</td>
<td>210</td>
<td>35</td>
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Fig. 2. IR spectra of borazines and polyborazine; a) commercial borazine and b) its polyborazine, c) synthesized borazine and d) its polyborazine.
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Crosslinking reaction. Exotherm of further condensation and rearrangement is observed above 400°C. Pyrolysis over 400°C involves 5% weight loss which is transformed polymeric phase to amorphous ceramic. It can be remarked that the thermal properties of synthesized and commercial borazine are in a similar manner. It should be pointed out that the ceramic yield of up to 85% of BN from borazine polymer is very high compared to those of other polymeric precursors used to prepare SiC and carbon[10].

Fig. 5 shows powder X-ray diffraction patterns for heat-treated samples at 1500°C under N₂ atmosphere. The transformed BN displays the diffractions corresponding to the (002) and (100) lines with an interlayer spacing of 3.45 Å (theoretical value 3.33 Å). It is known that the (002) peak shifts to a higher diffraction angle with narrower width, indicating a smaller interlayer spacing and larger crystallites, as the specimens is heated to higher temperatures. It should be noted from earlier work that one must heat glassy BN to 2500°C to reduce the interlayer spacing down to 3.5 Å, and that BN with larger interlayer spacings is sensitive to moisture[2]. Therefore, the obtained from the polymeric precursor may have high moisture stability which is extremely important for extensive applications. The samples annealed at 1500°C display a turbostratic BN structure with a diffuse (100), (101) doublet or the less intense (004) peak compared to those of the commercial hexagonal BN[9]. And it shows low crystallinity which presumably caused by the presence of trace amounts of tetracyclene. It is reported that organic impurities act as a carbon source which prevent the crystallization of BN ceramics from amorphous phase[11].

Additionally, the transformed BN starts to oxidize at 850°C while carbon begins to oxidize only at 400°C in air. It means that the trace amounts of carbon has an negligible effect on oxidative stability of the BN. The BN was not completely burned away even after isothermal oxidation at 1000°C.

4. Conclusions

We developed the simple and efficient route to synthesize borazine by using inexpensive reactants with normal laboratory equipments. New synthetic method produced highly pure borazine in 45%-55% yield, which is twice higher than commercial method (20-30% yield). It is proved that the obtained polyborazine plays a role as a excellent precursor to BN with high ceramic yield of 75%. It can be readily scaled-up with designed reactor to meet industrial applications such as thin films via CVD process or any other specialties.

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References