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An investigation on the synthesis of borazine

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ABSTRACT

Borazine is a promising precursor for boron nitride. A detailed investigation on the reaction of sodium borohydride and ammonium sulfate from 40 °C to 120 °C for synthesis of borazine was performed. The reaction was monitored by means of ^{11}B nuclear magnetic resonance (^{11}B NMR) and Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), mass spectroscopy (MS). The reaction produces mainly ammonia borane (AB), but not borazine at temperatures below 60 °C. Increases of temperature promote yield of borazine, which reaches the maximum around 110 °C. Whereas further increased temperature causes severe polymerization of borazine, and hence holds back yields of borazine.

1. Introduction

Boron nitride has a lot of important applications as high temperature structural and functional materials, due to its unique properties such as high thermal stability, excellent chemical, thermal-shock, corrosion and oxidation resistances, low dielectric constant and loss, high electrical resistivity and thermal conductivity [1]. However, it is not feasible to be prepared in forms of fibers, coatings, and complicatedly shaped bodies by conventional high temperature sintering process. Precursor derived ceramic routes provide an approach to this issue [2–4]. Borazine ($B_3H_3N_3H_3$) is reported to be a promising precursor for boron nitride [5–8].

Borazine was originally prepared in 1926 by pyrolysis of the diammoniate of diborane. Subsequently it was observed as product in several other reactions [9]. However, all those reactions involved the use of diborane and gave borazine in small quantity. Later a procedure suitable for laboratory preparation of borazine was reported, which involved the initial preparation of trichloroborazine (TCB) and its subsequent reduction by metal borohydrides [10]. Yet, this approach has some drawbacks such as difficult purification and handling of diborane. In 1979 a method for synthesizing borazine by thermal decomposition of ammonia borane in glymes was described [11]. However, ammonia borane is expensive and can be purchased only in small quantity. Thomas Wideman et al. reported a procedure for the laboratory preparation of borazine by the reaction of $(NH_4)_2SO_4$ and $(NaBH_4)$ in tetraglyme at 120–140 °C in 1995 [12]. This approach was a one-step procedure, starting from inexpensive materials and using standard laboratory equipments. However, they didn't study the effects of conditions on the reaction.

Investigation on the reaction of $(NH_4)_2SO_4$ and $(NaBH_4)$ will help understanding of the formation of borazine, and hence improve yields of borazine. However, there are no reported papers to date about study on the reaction of $(NH_4)_2SO_4$ and $(NaBH_4)$ for synthesis of borazine. Herein, it makes sense to study the reaction under various temperatures.

2. Experimental procedure

2.1. Raw materials

Sodium borohydride, ammonium sulfate and triglyme, all of which were reagent grade, were purchased from commercial resource. Sodium borohydride was used as received. Ammonium sulfate was dried under vacuum at 120 °C for 12 h and grinded to pass 200 mesh sieve before use. Triglyme was vacuum distilled from molten sodium shortly before use.

2.2. Preparation of borazine

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. It is noteworthy that a significant amount of hydrogen was generated during the reaction, which could be a hidden danger of fire hazard. It is strongly recommended to exhaust the reaction gases directly to a well-ventilated hood.

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Grinded ammonium sulfate (150 g, 1.14 mol) and sodium borohydride (60 g, 1.59 mol) were added to a 5 L four-neck round-bottom flask. The flask was fitted with a thermometer, a reflux condenser, a rubber stopper and an additional funnel, which was filled with 500 mL triglyme. The rubber stopper was used to sample the reaction mixture by a syringe for ^{11}B NMR and FTIR analysis during the reaction. The exit of the condenser was connected through a liquid-nitrogen trap series to vacuum pump. The system was vacuumed and flushed with nitrogen gas several times. The solvent triglyme was added to the flask, and the contents were stirred by a magnetic stir bar. The reaction system was warmed to specified temperatures in 30 min and held at those temperatures until the cease of gases release. After the completion of reaction, the reaction mixture was distilled several times for complete separation of borazine, under high vacuum using a vacuum-jacked Vigreux column. Borazine and other volatile condensable compounds were collected in the liquid-nitrogen traps. The liquid-nitrogen trap was connected to a −45 (for condensation of tetraglyme), −78 (for condensation of borazine), and −196 °C (for condensation of other more volatile compounds such as diborane) trap-series for fractionation under vacuum. There was a nonvolatile white solid left in the original liquid-trap after vacuum distillation. Purified borazine was condensed in the −78 °C trap.

2.3. Characterization

The ^{11}B NMR Spectra were obtained at 128 MHz using a Bruker Avance 400 spectrometer, referenced to $BF_3{\cdot}Et_2O$ (0 ppm) as external standard. The FTIR spectra were recorded by a Thermo Nicolet Avatar 360 FTIR spectrometer. X-ray diffraction measurements were carried out at a wavelength of 1.5418 Å (Cu Kα) with a Bruker ADVANCED D8 diffractometer. MS measurements were performed using a Agilent 5975 MS spectrometer.

3. Results and discussion

3.1. Reactions at temperatures below 60 °C

The yields of borazine at various temperature were summarized in Table 1, which showed that the temperature has a significant influence on the yields of borazine. No borazine was collected at temperatures below 60 °C. Fig. 1 shows the ^{11}B NMR spectra of the reaction mixture at 40 °C and 60 °C, respectively after completion of the reaction. Both of the spectra show a strong signal (δ = −25.2 ppm, quartet, J_{BH} = 94 Hz) of ammonia borane [13]. There appears no signal of borazine in the spectrum of the reaction at 40 °C, and only a weak resonance of borazine (δ = 28.5 ppm) for that at 60 °C [14]. The spectrum of the reaction at 60 °C also shows a weak signal around −11 ppm, which is possible due to cyclotriborazane $[BH_2NH_2]_3$ [15]. The reaction mixture was filtered after completion of the reaction at 40 °C, and the insoluble residue was washed with triglyme. A white powder was obtained as the residue after distillation of the filtrate. The white powder was confirmed as ammonia borane by XRD analysis (Fig. 2), which is also consistent with the ^{11}B NMR spectroscopic results [16].

Herein it is concluded that the reaction of $NaBH_4$ and $(NH_4)_2SO_4$ at 40 °C formed mainly ammonia borane rather than borazine. This is in agreement with the previous reports on preparation of ammonia borane by reacting $NaBH_4$ and $(NH_4)_2SO_4$ in tetrahydrofuran or dioxane at room temperature [17].

Table 1
Yields of borazine at various temperatures.

Reaction temperature (°C)	40	60	80	100	110	120
Yield (%)	–	–	14	27	34	18

"–" Means no borazine was isolated.

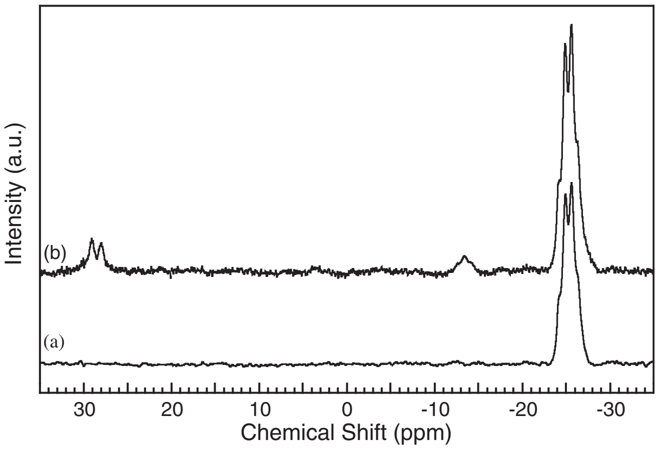

Fig. 1. ^{11}B NMR spectra of the reaction mixture (a) at 40 °C, and (b) at 60 °C. It indicates that the reaction formed mainly ammonia borane at relatively low temperature.

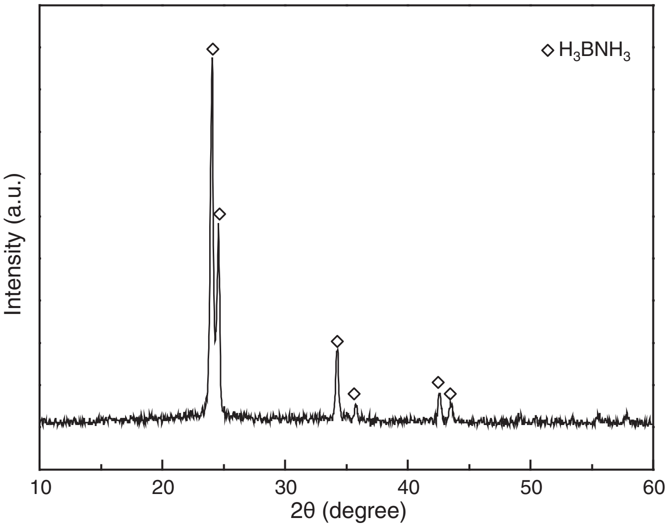

Fig. 2. XRD pattern of a white powder obtained as the residue by evaporation of the filtrate of the reaction mixture at 40 °C. It shows that the reaction at 40 °C produced ammonia borane.

3.2. Reactions at temperatures between 80 and 110 °C

When the reaction of $NaBH_4$ and $(NH_4)_2SO_4$ was performed above 80 °C, borazine was apparently observed in the ^{11}B NMR spectra. Yields of borazine increases with the increase of temperature, and reaches maximum at 110 °C. The process of the reaction at 110 °C was carefully monitored by means of ^{11}B NMR spectroscopy (Fig. 3).

The quintet at −45.2 ppm (J = 82 Hz) suggests the presence of $NaBH_4$. As the reaction proceeded, the peaks of $NaBH_4$ decreased, and finally disappeared, indicating complete consuming of $NaBH_4$. A strong doublet at 28.2 ppm (J_{BH} = 136 Hz) of borazine was observed. Besides, there appeared some other weak resonances at −28.9 ppm, −24.8 ppm, −13.5 ppm resulting from μ-aminodiborane ($(\mu\text{-}NH_2)B_2H_5$), ammonia borane and cyclotriborazane ($[H_2B\text{–}NH_2]_3$), respectively. Previous research also reported the appearance of cyclotriborazane as an intermediate in the thermal decom-

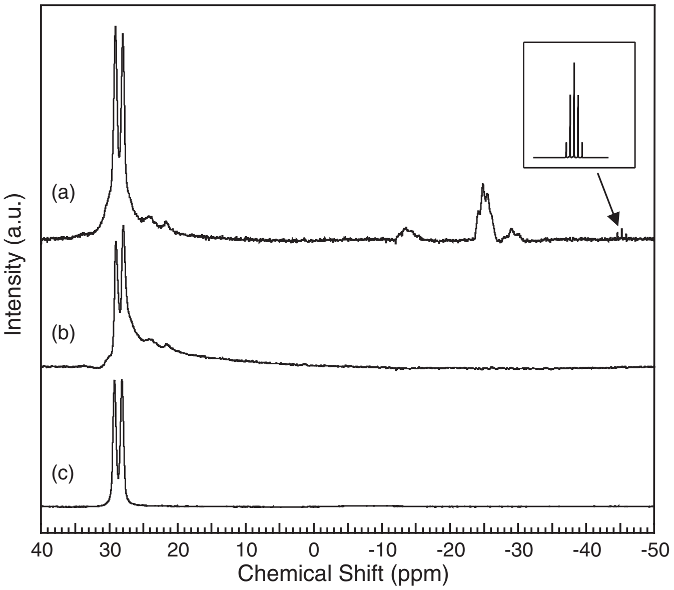

Fig. 3. ^{11}B NMR spectra of the reaction mixture at 110 °C. (a) After 3 h, (b) after 8 h, and (c) purified borazine. The spectra show strong signals of borazine (δ = 28.2 ppm, doublet, J_{BH} = 136 Hz), as well as weak signals of ammonia borane (H_3BNH_3, −24.8 ppm), cyclotriborazane ($[BH_2NH_2]_3$, −13.5 ppm), μ-aminodiborane ($(\mu\text{-}NH_2)B_2H_5$, −28.9 ppm) and $NaBH_4$ (−45.2 ppm).

position of ammonia borane in ether solvents [18]. In addition, it was reported that the thermal decomposition of cyclotriborazane in glymes caused dehydrogenation leading to the formation of borazine as the main product [14].

Hence, the reaction of $NaBH_4$ and $(NH_4)_2SO_4$ mostly proceeds as follows: the reaction firstly forms ammonia borane, which subsequently undergoes thermal dehydrogenation to form cyclotriborazane. Cyclotriborazane further dehydrogenates to form borazine. However alternative reaction sequences are not ruled out.

MS analysis was carried out for the compounds collected in the liquid-trap when the liquid trap was warmed to room temperature (Fig. 4). It shows the occurrence of diborane and borazine [19]. The occurrence of diborane indicated by MS and μ-aminodiborane indicated by ^{11}B NMR suggests that the reaction at 110 °C is a complex system.

Moreover, a nonvolatile white powder was collected in the liquid-nitrogen trap after evaporation of borazine and some other volatile products. XRD analysis of the nonvolatile white powder showed it was amorphous. Elemental analysis showed it has a formula of $[BH_2NH_2]_x$. It was reported that the thermal decomposition of ammonia borane produced a reactive intermediate monomeric aminoborane $H_2B–NH_2$, which was only stable and detected at temperatures below −196 °C and converted to polymeric aminoborane $[BH_2NH_2]_x$ on warming to room temperature [19,20]. Hence the nonvolatile white powder in the liquid-nitrogen trap was possibly formed from monomeric aminoborane $H_2B–NH_2$, which was produced and condensed into the liquid-nitrogen traps at −196 °C. However, since monomeric aminoborane $H_2B–NH_2$ is probably formed in small quantity and is highly reactive, it is not observed in ^{11}B NMR and MS analysis.

^{11}B NMR analysis also shows the signal of borazine is broadened compared to that for purified borazine, indicating that some polymerization of borazine occurred. However, the polymerization occurred only in a slight degree suggested from the shapes of the ^{11}B NMR peaks [14]. H_2 (2.95 equivalent) per mole of $NaBH_4$ was released overall during the reaction, which further confirmed the low degree of polymerization of borazine.

3.3. Reactions at temperatures up to 120 °C

Yields of borazine decreased sharply when the temperature of the reaction was elevated to as high as 120 °C (Table 1). The reaction mixture became more and more viscous as the reaction proceeded, so that the stirring became very difficult. This was the result of polymerization of borazine. Increased viscosity of the reaction mixture also restrained the effective contact between $(NH_4)_2SO_4$ powder and the $NaBH_4$ solution. Accordingly, the reaction rate was reduced, which further promoted the polymerization of borazine in turn. Fig. 5 shows the ^{11}B NMR spectrum of the reaction mixture at 120 °C. after completion of the reaction There is a very broad featureless resonance around 30 ppm, which confirms the polymerization of the borazine [21]. The reaction mixture was filtered after reaction. The filtrate was distilled under vacuum at room temperature, which gave a transparent viscous glue as the residue. Elemental analysis of the transparent viscous glue gave a

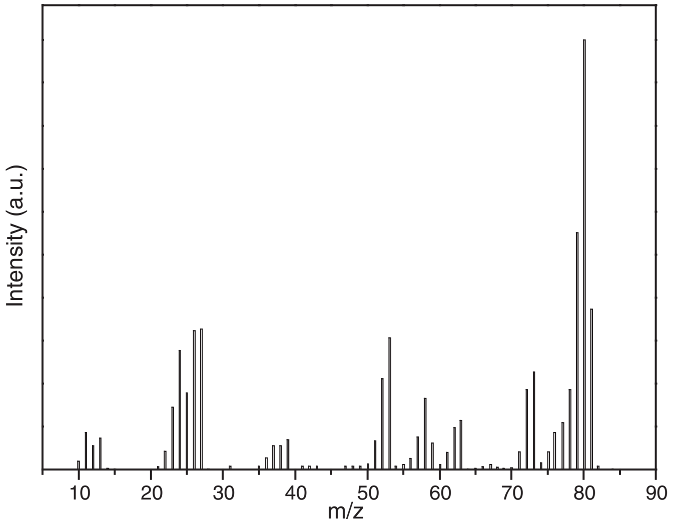

Fig. 4. Mass spectrum of the compounds collected in the liquid-nitrogen trap. It shows the occurrence of diborane and borazine.

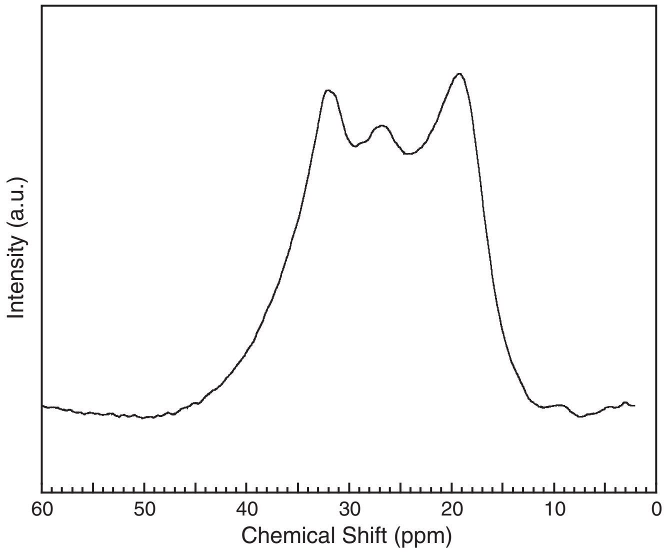

Fig. 5. ^{11}B NMR spectrum of the reaction mixture at 120 °C. It indicates that severe polymerization of borazine occurred at temperature as high as 120 °C.

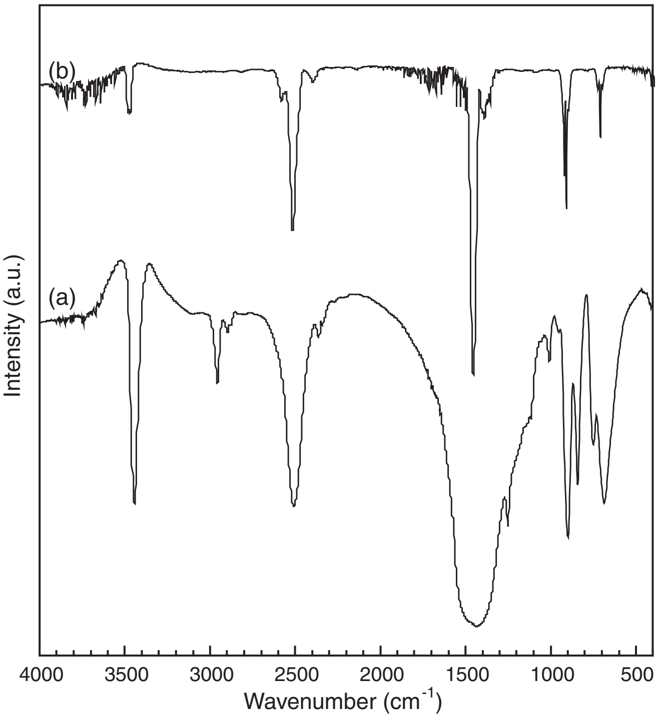

Fig. 6. FTIR spectra of (a) the transparent viscous glue isolated from the reaction mixture at 120 °C, and (b) purified borazine. The characteristic broad band between 1400–1600 cm^{-1} indicates that borazine underwent polymerization partially at temperature as high as 120 °C.

formula of $[B_{3.0}N_{2.9}H_{4.2}]_x$. FTIR spectrum of the transparent viscous glue was shown in Fig. 6, together with that of purified borazine. The absorption peaks at 3490 cm^{-1} and 915 cm^{-1} are attributed to the stretching and bending of N–H, respectively. The absorption peaks at 2525 cm^{-1} and 718 cm^{-1} are attributed the stretching and bending of B–H, respectively. The absorption peaks at 1464 cm^{-1} are attributed to the deformation of $[B–N]_3$ ring. The absorption peak around 1400 cm^{-1} of the transparent viscous glue is apparently broader than that of purified borazine, which is due to the polymerization of borazine. It is reasonable to consider the transparent viscous glue to be polyborazylene $[B_{3.0}N_{2.9}H_{4.2}]_x$ formed from polymerization of borazine [22].

4. Conclusions

In summary, the reaction of $NaBH_4$ and $(NH_4)_2SO_4$ in triglyme developed very differently depending on the temperature. The reaction produced mainly ammonia borane (AB), but not borazine at temperatures below 60 °C. Yields of borazine increased with the increase of temperature, and reached the maximum (34%) around 110 °C. However, further increase of temperature (up to 120 °C) caused severe polymerization of borazine, and hence decreased the yield of borazine. Hydrogen, ammonia borane and cyclotriborazane were found as the main intermediates, together with trace amounts of μ-aminodiborane and diborane.

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