gadiite is a good adsorbent for heavy metals without the need for any chemical treatment.

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A Route to Boron Nitride Via Simply Prepared Borazine Precursor

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Borazine ($B_3N_3H_6$) as an inorganic analogue of benzene was synthesized by reaction of cheap raw materials ($NaBH_4$ and $(NH_4)_2SO_4$), and by using simple glass reaction apparatus in a scale up to 20 g per run with highly improved yield over 50%. It appears that synthesis of borazine is competing with formation of poly (aminoborane) as an inorganic analogue of polyethylene. The synthesized borazine and its polymerized product were characterized by comparison with products obtained from a commercial one. Bulk pyrolysis of the borazine polymer to 1500 °C produced a pure boron nitride (BN) with 75% ceramic yield, which displayed good oxidation resistance under dry air.

Introduction

Inorganic polymeric precursors have been used for the preparation of ceramic fibers, coatings and matrices in ceramic fiber/ceramic matrix composites. It has been reported that liquid inorganic polymers could be used to utilize the processibility of polymers as well as excellence of ceramics, and to readily control the microstructure and composition of ceramic products. Polymer-derived SiC and Si_3N_4 ceramics are beginning to be commercialized in market as fibers while a variety of sol-gel processes are widely used in electronic and structural industries.[1]

However there has been little attention to extensive applications and/or related researches on preparation of BN from polymeric precursors, although BN shows the similar structure and properties, compared to graphite, but higher oxidation resistance and lower dielectrics.[1] It has been mainly caused by the limited availability of starting monomer, borazine, that has proven to be an almost ideal chemical precursor.

Recently we demonstrated the first successful preparation of carbon fiber/BN matrix composite(C/BN) by using low viscous borazine polymer prepared from borazine monomer purchased with a price of $25/g.[2] These composites displayed outstanding mechanical properties and excellent resistance to oxidation up to 850 °C, presently leading to develop airbrake materials. In addition, it was found that low temperature treatment of the polyborazine led to mesophase formation as similar to 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.

It is believed that the efficient synthetic route for borazine must open its related basic studies as well as the potential applications such as coating, fiber and other specialties. Therefore, various attempts are expected to develope the convenient and less cost-consuming procedures for the synthesis of borazine. Since borazine was discovered by

Alfred Stock in 1926 who isolated it as a by-product from thermal decomposition of $B_2H_6 \cdot 2NH_3$ at 200 °C, borazine has been commercially synthesized by an old process in a stainless steel reactor, or by a solid state reaction between alkali metal borohydrides and NH_4Cl in laboratory scale.[4] However, these procedures are limited by the disadvantages of low yields, high cost starting compounds and complicated apparatus.

In this point of view, the following works came to our attention to establish the efficient synthetic route of borazine. First, it was reported that HCl from decomposition of NH_4Cl partially degraded the produced borazine to trichloroborazine, and thus caused reduced yields and purification problem.[5] This work suggested that NH_4Cl might be replaced by other ammonium salts excluding chlorine. Secondly it was published that borazine could be produced from pyrolysis of expensive ammonia-borane(H_3N BH_3) in diglyme with quite a reasonable yield of 70%.[6] On the other hand, ammonia-borane was readily generated upon reaction of $LiBH_4$ with $(NH_4)_2SO_4$ in ether at room temperature.[5a] As reviewed above, it brought that one might anticipate the reaction of $NaBH_4$ and $(NH_4)_2SO_4$ in low volatile solvent such as glymes.

In this report, we established the synthetic conditions of borazine as a monomeric precursor of BN by reaction of $NaBH_4$ and $(NH_4)_2SO_4$ in simple glass apparatus with superior yield of 20 g/run over 50%. And it was proved the synthesized borazine is comparable quality to commercial borazine, then we investigated the conversion of the polyborazine to BN on heating up to 1500 °C under inert atmosphere. The oxidation resistance of synthesized BN was compared with the pitch based carbon fiber up to 1000 °C under dry air atmosphere.

Experimental Section

Materials. $NaBH_4$ (Aldrich; 98%) and $(NH_4)_2SO_4$ (Aldrich; 99%) were used for boron (B) and nitrogen (N) sources without further purification. Tetraglyme as a solvent (boiling point; 278 °C) was freshly used right after distillation with a liquid sodium. Borazine has low melting point (− 56.2 °C) and low boiling point (55 °C).

Experimental procedure. $NaBH_4$ solution was prepared by dissolving 1 mol of $NaBH_4$ in 350 mL of distilled tetraglyme in 1 L one-neck flask with a rubber septum cap, and then the mixture was agitated at room temperature for 12-15 hours under N_2 atmosphere. 0.80 mol of $(NH_4)_2SO_4$ was ground with a coffee mill for several seconds in a N_2-filled glove bag to increase the surface area. The powder was poured into 2 L 3-neck round bottom flask which was fitted with a reflux condenser and a vacuum adaptor, followed by drying for 3 hours under 2-5 torr vacuum at 120 °C. The exit of the condenser was connected to a standard vacuum line equipped with a twin liquid nitrogen trap.

When the temperature went down to 70 °C, the $NaBH_4$/tetraglyme solution was slowly added using a cannula to the flask containing dry $(NH_4)_2SO_4$. The dropping rate of the solution was slow enough to prevent the catastrophic buildup of H_2 gas from too vigorous reaction. Reaction mixture was gradually warmed to 120-135 °C for 1 hour and ran for 2-4 hours under different vacuum pressures to find

out the best synthetic conditions, based on previous Sneddon's paper.[6] The product would be continuously collected in a 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, 10 g of the synthesized borazine was heated with stirring at 70 °C in a 3-ounce pressure reaction vessel(Ace Glass Co.). The reaction was continued for ~40 h with periodic H_2 degassing until white solid polymer was formed. The solid polyborazine was heat-treated to 1500 °C in a tube-furnace under Ar atmosphere to convert into stable BN powder.

Analytical method. Purified borazine was compared with commercial borazine by infrared spectroscopy(BIO WIN RAD) and characterized by ^1H nuclear magnetic spectroscopy(Varian Unity 400(400 MHz)). For the dehydrocoupled polyborazine, thermogravimetric analysis(TGA; TA Instrument 2950) and differential scanning calorimetry (DSC; 2910) were carried out at a heating rate of 10 °C/min to 1000 °C and 500 °C under N_2 atmosphere, respectively. Molecular weight distribution was measured by GPC(gel permeation chromatography, Waters). Powder X-ray diffraction of the BN ceramic was performed using Rigaku Cu $K\alpha$ system. Thermal stability of BN was measured by heat scanning of TGA under dry air to 1000 °C at a heating rate of 10 °C/min.

Results and Discussion

Borazine ($B_3N_3H_6$), a colorless liquid, is a planar six membered ring with alternating boron and nitrogen atoms each with a hydrogen atom attached. Borazine is isoelectronic with benzenes, so it is called "inorganic benzene". However, it readily decomposes in moisture into NH_3 and B_2O_3 so that it should be carefully handled under dry atmosphere.[7]

In order to efficiently produce the borazine, a variety of the reactions under different reactant ratios, various reaction temperatures and vacuum pressures have been investigated using tetraglyme as a solvent for $NaBH_4$. The best results were obtained in a molar ratio of 1.2-1.4 $NaBH_4/(NH_4)_2SO_4$ at 120 °C. Finely ground $(NH_4)_2SO_4$ increased yield due to the improved dispersion and contact area with $NaBH_4$. Table 1 summarizes the synthetic yields of borazine under

**Table 1.** Synthetic yield of borazine under various reaction conditions

Reaction temperature (°C)	Dropping time (min)	Reaction period (min)	Byproduct (%)	Borazine (%)	Vacuum (mm Hg)
120	15	215	4	29	2-5
120	110	170	5	47-41	"
120	120	90	5	53	"
120	135	210	5	55	"
120	70	150	1	32	100-200
120	140	215	2	48	200-300
135	120	210	5	35	2-5

various reaction conditions. In the procedure, borazine was obtained in a scale of 15-20 g per run with significantly improved yields of 45-55% range at 120 °C. This value is nearly twice higher than 20-30% yield of previous synthetic routes.[4] It is observed that the yields of borazine are increased with longer dropping time of NaBH₄ solution, because the gradual formation of the borazine may reduce polymerizable contacts among the produced molecules.

When the reaction was performed under 300 torr by back-filled nitrogen, less amount of products was obtained only with below 40% yield. It seems that the synthesized borazine might stay longer at 120 °C to be polymerized into low volatile polymer or oligomer. It also appears that lower yield of the reaction at 135 °C results from the faster polymerization of the borazine. It is worthy to note that borazine was polymerized at 70 °C in a controlled manner.

In addition, we reproducibly found a white non-volatile solid with about 5% yield in a twin liquid trap even after vacuum fractionation. It has previously reported that monomeric aminoborane was formed by vapor phase pyrolysis of ammonia borane(H₃N·BH₃), and then presumably polymerized on warming up to room temperature to give an "inert white solid".[x] It is believed to be polymeric aminoborane, (NH₂BH₂)ₓ, as an inorganic analogue of polyethylene. A detailed characterization of its preparation and properties is under investigation and will be reported in a separate paper.

Eventually, it is most likely that the reaction must involve an initial generation of ammonia-borane, followed by its pyrolysis to form borazine and by dehydropolymerization to poly(aminoborane) which are competing with each other.[9]

$$6NaBH_4 + 3(NH_4)_2SO_4 \rightarrow nH_3N \cdot BH_3 \rightarrow$$
$$2(B_3N_3H_6, (H_2NBH_2)_x) + 3Na_2SO_4 + 18H_2$$
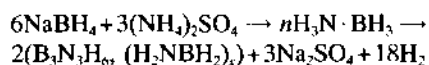
We deliberately carried out the reaction of borazine with itself to produce a viscous or solid polymers. FT-IR provides a convenient tool for examining the changes in structure on conversion of the borazine to BN. Figure 1 shows IR spectra of the synthesized borazine, its polymerized product, polyborazine and 400 °C heat-treated BN for 3 hours. Borazine shows the characteristic N-H, B-H and B-N stretching at 3440 cm⁻¹, 2505 cm⁻¹ and 1430 cm⁻¹, respectively. As polymerization proceeds, N-H and B-H absorption decrease in intensity because hydrogens are removed by condensation between the rings. And sharp B-N absorption at 1430 cm⁻¹ also changes to a broad absorption. It is convenient to describe these reactions in terms of condensation of six-membered benzene-like rings through two types of intermediates corresponding to biphenyl and naphthalene.[10]

On further heating at higher temperatures, the polyborazine crosslinked to form an insoluble white solid. During this process, the N-H and B-H peaks gradually disappeared and the B-N peak continued to broaden until it was nearly identical to that observed in fully crystalline BN.[10] The ¹H NMR spectrum of borazine showed a quartet of B-H at 4-5 ppm and a triplet of N-H at 5.4-6 ppm with little trace of tetraglyme, which were consistent with literature data.[11]

Table 2 shows the GPC results of the polyborazine at different reaction periods. As the reaction goes on, number av-
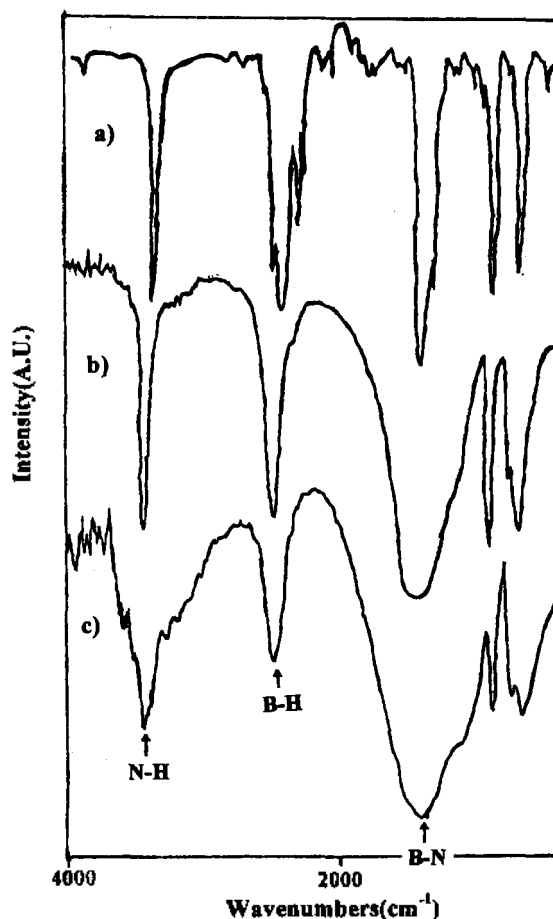
Figure 1. IR spectra of a) the synthesized borazine, b) polyborazine reacted at 70 °C for 40 hours, then c) heat-treated at 400 °C for 3 hrs.

erage molecular weight is increased to 1256 g/mol for reaction time of 30 hours with an increase of the polydispersity. And it also determined that the molecular weight distribution is comparable to oligomeric polymer which is in the range 400-3000 g/mol including a small amount of borazine monomer even after reaction is completed to solid product.

Thermal properties of the polyborazine is shown in Figure 2 for the conversion of the polymerized borazine to BN product. In analysis of DSC and TGA patterns, the polyborazine represents that the various endothermic peaks at 90-120 °C may indicate the evaporation of low molecular weight volatiles.[2] And it is corresponding to a rapid weight loss of 15%. The exotherm in the temperature range 150-270 °C is believed to be a crosslinking reaction involving a weight loss of 10%. Subsequent exotherm of further condensation and rearrangement occurr above 400 °C only with

Table 2. GPC result of polyborazine synthesized at 70 °C for various reaction times

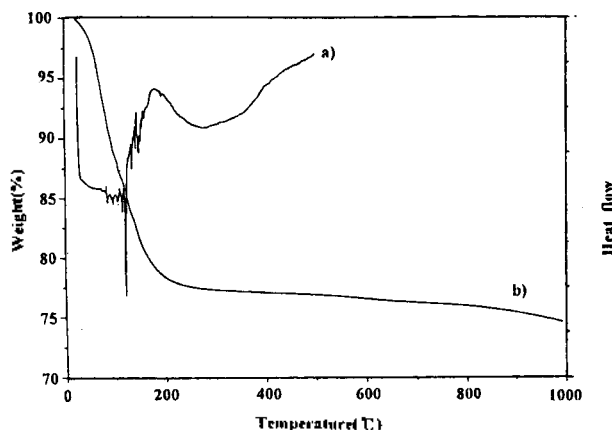| Reaction time (hours)	Mn (g/mol)	Mw (g/mol)	PDI
10	773	822	1.06
20	1064	1276	1.20
30	1256	1654	1.30

Figure 2. (a) DSC and (b) TGA patterns of the polyborazine.
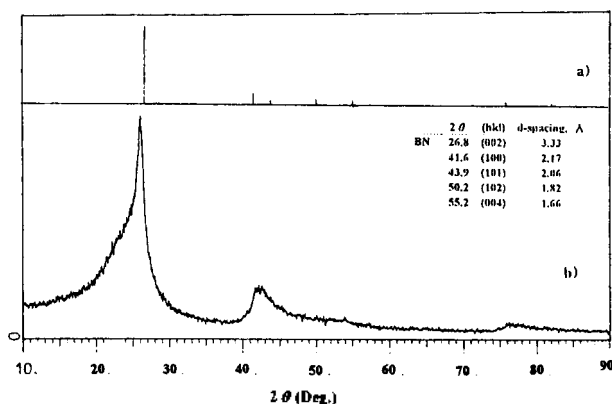
Figure 3. XRD patterns of (a) BN JCPDS standard and (b) BN prepared from polyborazine at 1500 °C.
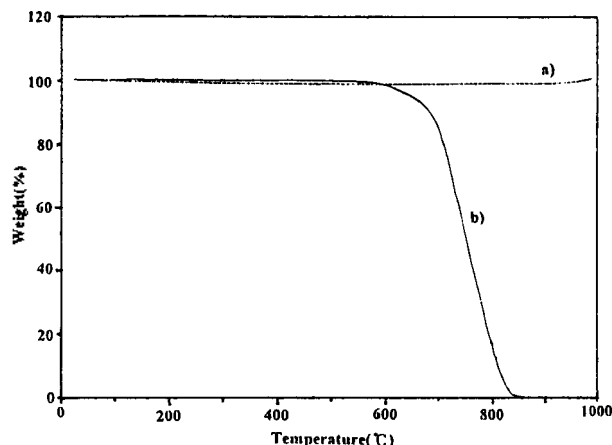

Figure 4. Oxidation behaviour of (a) BN ceramics derived from polyborazine at 1500 °C and b) pitch based carbon fiber.

doublet or the less intense (004) peak compared to those of the commercial hexagonal BN.

In Figure 4, the oxidation resistance of the prepared BN with d-spacing of 3.40 Å is compared with the pitch based carbon fiber in dry air to 1000 °C. The stability of the prepared BN is maintained up to 800 °C, followed by a slight weight gain at higher temperatures due to the oxidation of BN to B_2O_3. However, the carbon fiber begins to oxidize over 600 °C and rapidly burned out at higher temperatures. It is shown that the prepared BN has better oxidation resistance than carbon fiber which is now commercially available. Additionally, it is well known that the stabilized BN starts to be oxidized at 850 °C while the oxidation of the amorphous carbon begins only at 425 °C. It means that the trace carbon is negligible to the oxidative stability of the BN.[14]

Conclusion

We established economical conditions to synthesize borazine by using cheap reactants with normal laboratory equipments. New synthetic method of borazine gave us a high yield, 45-55%, which is twice higher than commercial method (20-30% yield). It has been proved that the obtained borazine followed by dehydrogenative polymerization plays a role as an excellent precursor to BN with a high ceramic yield of 75%. The prepared BN has better oxidation resistance than the commercial carbon fiber at high temperatures. Finally, it is suggested to be readily scale-up by batch or continuous processes to facilitate industrial applications such as structural BN as well as thin films via CVD processes.

a little weight loss, which is transformed polymeric phase to amorphous BN. Presumably, different rate of weight loss in crosslinking and pyrolytic stages may indicate different dehydrogenative mechanism. On the other hand, ceramic yield of 75% is slightly lower than 85% of the polyborazine obtained from a commercial borazine, presumably due to lower degree of polymerization.[10] However, it should be pointed out that the ceramic yield of BN from borazine polymer is very high compared to those of other polymeric precursors used to prepare SiC and carbon.[12] Thus it suggests that the preceramic polymer may convert to dense BN without large volume shrinkage.

Figure 3 shows powder X-ray diffraction patterns for heat-treated at 1500 °C under N_2 atmosphere. Generally when heated to higher temperatures, the characteristic (002) peak shifts to higher diffraction angle with a narrower width, indicating a smaller interlayer spacing and larger crystallites. Finally the polymer are transformed into crystalline BN from amorphous with a interlay spacing of 3.40 Å (theoretical value 3.33 Å) on heating to 1500 °C for one hour. And (002) diffraction pattern displays an asymmetrical shape due to the presence of amorphous region. It is probably caused by the presence of trace carbon converted from trapped tetraglyme. It is reported that carbon impurities might prevent the crystallization of ceramics from amorphous phase.[13] The samples annealed at 1500 °C display a turbostratic BN structure with a diffuse (100), (101)

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Reaction of Phosphite with Acetal Derivatives: Syntheses of 1-Alkoxymethylphosphonates and 1-Alkylthiomethylphosphonates

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1-Alkoxymethylphosphonates 4 and 1-alkylthiomethylphosphonates 5 can be prepared by the reaction of acetal derivatives and diethyl trimethylsilyl phosphite in the presence of Lewis acid under mild conditions. The dependency of the chemoselectivities with Lewis acid on the reaction of O,S-acetals with phosphites is described.

Introduction

Phosphonates are valuable intermediates for the formation of carbon-carbon double bonds because their use provides control of alkene regio- and stereoselectivity.[1] The α-substituted phosphonates are useful reagents in organic synthesis since they react easily with carbonyl compounds to form corresponding alkenes via the Horner-Wadsworth-Emmons (HWE) condensation.[1,2] 1-Alkoxymethylphosphonates and 1-alkyl(or aryl)mercaptomethylphosphonates are important intermediates for the conversion under HWE condition into α,β-unsaturated ethers and α,β-unsaturated sulfides, respectively, which afford the ketones by the subsequent hydrolysis. A number of synthetic approaches for the preparation of 1-alkoxymethylphosphonates and 1-alkyl (or aryl)mercaptomethylphosphonates have been developed, ranging from the direct Arbuzov reaction of trialkyl phosphites with α-haloalkyl ethers (or sulfides)[3] to the more sophisticated methods via [3,2] sigmatropic shift of S-allyl sulfides.[4] They have limitations in terms of the reaction conditions employed. The preparation of 1-alkoxy-1-arylmethylphosphonates have been reported by the reaction of benzaldehyde diethyl acetals with triethyl phosphite.[5] 1-Alkylthiomethylphosphonates have been obtained by the addition of dialkyl disulfide or elemental sulfur to alkylphosphonate carbanions,[6] alkylation of 1-mercaptoalkylphos-

phonates,[2c] and Friedel-Crafts reaction of chloro(alkylthio) methylphosphonate.[7]

In the course of our studies of α-substituted phosphonates,[8] we have developed the synthetic method for the preparation of 1-alkoxy (or 1-alkylmercapto)methylphosphonates from the reaction of diethyl trimethylsilyl phosphite with acetal derivatives.[9] Herein we report the reaction of phosphites with acetal derivatives in more details, providing information on its scopes and limitations.

Results and Discussion

Synthesis of 1-Alkoxymethylphosphonates 4 and 1-Alkylmercaptomethyl-phosphonates 5. Diethyl trimethylsilyl phosphite 3b has been widely used for various transformations and syntheses of both phosphorus and non-phosphorus containing compounds.[10] The presence of a silyl ester linkage rather than an alkyl ester in the phosphite increases the nucleophilicity of the phosphorus center and thus its reactivity in the Arbuzov type reactions.[11] Diethyl trimethylsilyl phosphite 3b reacted with acetals 1 in the presence of Lewis acid to yield the 1-alkoxyalkylphosphonates 4 in good yields (Table 1). Treatment of acetals 1 with the Lewis acid presumably leads to formation of intermediate benzyl oxonium ions.[12] In a subsequent nucleophilic reaction diethyl trimethylsilyl phosphite 3b reacts with this ions to yield products 4.