Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2012 January 17; 116(3): 2639–2644. doi:10.1021/jp210295e.

Formation of Graphene Oxide Nanocomposites from Carbon Dioxide Using Ammonia Borane

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Abstract

To efficiently recycle CO₂ to economically viable products such as liquid fuels and carbon nanomaterials, the reactivity of CO₂ is required to be fully understood. We have investigated the reaction of CO₂ with ammonia borane (AB), both molecules being able to function as either an acid or a base, to obtain more insights into the amphoteric activity of CO₂. In the present work, we demonstrate that CO₂ can be converted to graphene oxide (GO) using AB at moderate conditions. The conversion consists of two consecutive steps: CO₂ fixation (CO₂ pressure < 3 MPa and temperature < 100 °C) and graphenization (600–750 °C under 0.1 MPa of N₂). The first step generates a solid compound that contains methoxy (OCH₃), formate (HCOO) and aliphatic groups while the second graphenization is the pyrolysis of the solid compound to produce graphene oxide-boron oxide nanocomposites, which have been confirmed by micro-Raman spectroscopy, solid state ¹³C and ¹¹B magic angle spinning-nuclear magnetic resonance (MAS-NMR), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Our observations also show that the mass of solid product in CO₂ fixation process and raw graphene oxide nanocomposites is twice and 1.2 times that of AB initially charged, respectively. The formation of aliphatic groups without using metal-containing compounds at mild conditions is of great interest to the synthesis of various organic products starting from CO₂.

1. Introduction

Carbon dioxide (CO₂), a readily available, low-cost and sustainable carbon source, could be converted to liquid fuels,¹⁻³ useful chemicals,^{4,5} or carbon materials.⁶⁻⁹ Among the chemical transformations of CO₂, attractive options include reducing CO₂ to diamonds and nanotubes, either through direct CO₂ splitting or via reaction with metals subject to pressures higher than 70 MPa.¹⁰⁻¹² Nonetheless, the possibility of CO₂ reduction to other carbon nanomaterials like graphene oxide without using metal-containing compounds and without employing extreme conditions remains unproven. Graphene oxide is not only a suitable and scalable precursor of graphene,¹³⁻¹⁵ but also a flexible platform for biological, chemical, electronic, medical, and optical applications.^{13, 16-18} Here, we report the

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Supporting Information Available: Additional information of CO₂ reaction with AB, characterization of the solid product, thermal decomposition of the solid product, and characterization of the solid residue is available free of charge via the Internet at <http://pubs.acs.org>.

conversion of CO₂ to graphene oxide nanocomposites using ammonia borane (NH₃BH₃), which is a well-known candidate material for hydrogen storage.¹⁹ The conversion involves two consecutive steps: carbon fixation and then graphenization. The carbon fixation is the reaction of CO₂ with NH₃BH₃ under mild temperature and pressure conditions ($T < 100\text{ }^{\circ}\text{C}$ and $P < 3\text{ MPa}$) to produce a solid compound that contains methoxy (OCH₃), formate (COOH) and aliphatic groups, whereas the graphenization is the pyrolysis of this solid compound at high temperatures ($T > 600\text{ }^{\circ}\text{C}$) and atmospheric pressure of nitrogen to generate graphene oxide-boron oxide nanocomposites. This finding demonstrates an unprecedented avenue for the synthesis of graphenic materials from CO₂ that is derived from chemical, fermentation and natural processes.

The formation of C-H and C-C bonds (aliphatic groups) via CO₂ activation is of strong fundamental interest in the context of organic syntheses starting from CO₂. Although CO₂ is a renewable, abundant and eco-friendly carbon source, only a few industrial processes are employing CO₂ as a raw material;⁵ this is because the nature of CO₂, a thermodynamically stable molecule, poses difficulties for being chemically transformed. To utilize CO₂ efficiently and explore its potential fully, the reactivity of CO₂ needs to be thoroughly understood. Carbon dioxide, being amphoteric in nature, can react with acid and base simultaneously; thus, the reaction CO₂ with NH₃BH₃, which is a potential reductant and one simplest Lewis acid-base adduct,¹⁹ offers insights into exploiting the amphoteric reactivity of CO₂ to develop novel routes for reducing CO₂ efficiently and selectively, especially for transforming CO₂ into organic compounds. In the present work, we demonstrate the formation of graphene oxide nanocomposites from the solid product of CO₂ reaction with NH₃BH₃.

2. Experimental

2.1 Materials

Ammonia borane (NH₃BH₃) with a purity of 97 % was obtained from Sigma-Aldrich. Carbon dioxide (CO₂) with a purity of > 99.8 % was purchased from T. W. Smith. Hydrochloric acid (37 wt. % in water) was supplied by Sigma-Aldrich. Methanol with a purity of 99.9 % was acquired from Fisher Scientific. All chemicals were used as received without further purification. Deionized (D. I.) water was produced in our lab with a resistivity of 18 M cm⁻¹.

2.2 Reaction of CO₂ with NH₃BH₃

The reaction was performed using a high-pressure differential scanning calorimeter (Micro-DSC VII, SETARAM). A detailed description of this equipment has been provided in our prior work²⁰. The total volume of the sample cell and pipelines with fittings was 5.26 cm³. Exteriors of the pipelines and fittings were mostly exposed to the normal ambient condition, while only the sample and reference cells were subjected to the heating and cooling cycles. Gauge pressure was monitored using an ITS-5M pressure transducer (ONEhalf20, 0 to 34.47 MPa) with an uncertainty in the pressure measurement of 0.05 MPa. The temperature, heat flow, and pressure of the sample cell were acquired by the SETSOFT interface. After loading 8.8 mg of NH₃BH₃ into the sample cell (made of stainless steel) at normal ambient conditions, the cell was pressurized with CO₂ to a preset value. The sample and reference cells were kept at 25 °C for 5 min, and then heated to 65 °C at 1.00 °C min⁻¹, followed by heating to 100 °C at 0.25 °C min⁻¹. Both were then cooled to 25 °C at 3.00 °C min⁻¹ and subsequently kept at this temperature for 5 min. Once the heating/cooling cycle was completed, the sample cell was depressurized to atmospheric pressure, and then opened to the normal ambient condition. The solid product was collected and stored in a glass vial at normal temperature and pressure.

2.3 Thermolysis of NH_3BH_3

About 5.0 mg of NH_3BH_3 was loaded into the sample cell of the Micro-DSC VII under normal ambient conditions. The sample and reference cells were kept at 25 °C for 5 min, and then heated to 115 °C at 0.50 °C min⁻¹; both were then cooled to 25 °C at 3.00 °C min⁻¹, and maintained at this temperature for 5 min. Once the heating/cooling cycle was completed, the sample cell was depressurized to atmospheric pressure, and then opened to normal ambient conditions. The thermolysis product, referred to as polyaminoborane, was collected and stored in a glass vial at normal ambient conditions.

2.4 Pyrolysis of solid product

The pyrolysis was carried out on a combined thermogravimetry-differential scanning calorimeter (Q600, TA Instruments) under 0.1 MPa N_2 (gauge pressure) with at a flowrate of 100 cm³ STP min⁻¹. After loading the solid product of CO_2 reaction with NH_3BH_3 (between 6 and 10 mg) to the sample cup (made of alumina), the sample and reference cups were heated to 50 °C at 10.0 °C min⁻¹, then held at this temperature for 5 min, following by heating to the target temperature at 5.0 °C min⁻¹. Finally, the cups were radiantly cooled to room temperature. The solid residue was collected and stored in a glass vial under ambient temperature and pressure.

2.5 Treatment of solid residue

All treatment was performed at normal ambient conditions. About 5 mg of solid residue, generated from the pyrolysis of solid product (produced at a CO_2 pressure of 2.96 MPa) at temperatures up to 750 °C in nitrogen, was put into a 10 cm³ glass vial, following by addition of 10 cm³ of 5 M HCl, resulting in a brownish suspension of fine particles. The suspension was placed in a closed vial for three days, following which black particulates precipitated, creating a clear supernatant. The liquid was withdrawn with a 10 cm³ Transferpette (BRAND) pipette, to which 10 cm³ of D.I. water was added, followed by capping the vial. Again, a brownish suspension formed, which after one day precipitated, again resulting in a clear supernatant. The procedure of withdrawing the clear liquid and adding 10 cm³ of D.I. water was repeated two more times, and finally 10 cm³ of methanol was used for washing. After the clear supernatant was withdrawn in the last washing step, the resultant black particles were kept in the open vial for several hours and subsequently dried overnight in an oven at ca. 120 °C.

2.6 Characterization

ATR-FTIR (attenuated total reflection Fourier-transform infrared) spectra were recorded on a Varian 7000 FTIR using MIRacle ATR accessory; the internal reflection element of which is a Ge single reflection plate. FTIR spectra were recorded at a resolution of 2 cm⁻¹ from 850 to 4000 cm⁻¹ using the Varian Resolution Pro. 4.01. Raman spectra were obtained by using an HR800 Horiba Jobin Yvon micro-Raman system equipped with a CCD detector and an Olympus BX41 microscope with a $\times 100$ objective lens. Samples were placed on a cover glass and excited with 632.8 nm HeNe laser radiation. The spectrum was obtained by multiple-spectral bandpasses between 500 and 3500 cm⁻¹ using the Labspec 4.18 software. ¹¹B and ¹³C solid state MAS-NMR (magic angle spinning-nuclear magnetic resonance) spectra were recorded at 150.74 and 192.34 MHz, respectively, on a Varian VNMRs system equipped with BioMAS probe (3.2 mm), operating in a 14.1 T magnet. Samples were spun at 10 kHz for ¹¹B and 9 kHz for ¹³C with the sample temperature maintained at 25 °C (ref. 21). The ¹³C solid state MAS-NMR spectra were referenced to the methylene carbon of adamantane at 38.48 ppm (ref. 22). The chemical shifts of ¹¹B were referenced to 0 ppm based on a calculation using frequency ratios of ¹¹B and ¹³C, as recommended by IUPAC guidelines²³. All data were processed with 100 Hz line

broadening. TEM (transmission electron microscopy) images were recorded on a Zeiss EM 902 transmission electron microscope at an accelerating voltage of 80 kV using the Mega View III-iTEM digital image acquisition system. The line and point resolutions of TEM are 0.34 and 0.5 nm, respectively. AFM (atomic force microscope) images were acquired using Thermomicrope Explorer head equipped with a Veeco 1950-00 ultrasharp tip, and using the contact mode with SPMLab NT 5.01. Optical microscope images were recorded using the above micro-Raman system. Samples for TEM observations were prepared by dispersing about 1 mg of treated solid residue in 20 cm³ D. I. water. They were subject to ultrasonication for 15 min to form a suspension of fine particles. A drop of the resultant suspension was placed onto a copper grid coated with a layer of amorphous carbon; the grid was then dried at normal ambient conditions. Samples for AFM and microscopy measurements were prepared by fast dipping a silicon wafer coated with a 100 nm SiO₂ layer into the above suspension followed by drying the wafer at normal ambient conditions after withdrawing it from the suspension.

3. Results and Discussion

In calorimetric investigations of CO₂ reaction with NH₃BH₃, a single resolved exothermic peak is observed as the temperature is varied from 25 to 100 °C (Figure 1). The exothermic peak is associated with the conversion of CO₂ to a solid compound and the thermal decomposition of NH₃BH₃; the latter process is known to be promoted by CO₂.²⁴ Figure 1 shows enthalpograms obtained for the reaction at CO₂ pressures of 0.845, 1.53, 2.27 and 2.96 MPa. The CO₂ pressure is quoted as the value at 25 °C (Supporting Information, Figure S2). For the first three pressures, the occurrence of carbon fixation is inferred from the enthalpy of the exothermic event ($\Delta H = -63$ to -95 kJ mol⁻¹), which is significantly greater in magnitude than the enthalpy of NH₃BH₃ thermolysis ($\Delta H = -22$ kJ mol⁻¹).²⁵ As Figure 1 shows, the peak temperature (where the heat flow reaches a maximum) decreases monotonically from 83.4 to 76.6 °C as the pressure increases from 0.845 to 2.27 MPa. For the highest pressure (2.96 MPa), the heat flow profile displays a major exothermic event at 74.6 °C and a minor event at 82.6 °C; and we find that the mass of solid product is twice that of the NH₃BH₃ initially present (the final mass of the solid product after the CO₂ fixation is 17.2 ± 0.5 mg from sixteen repeated experiments.). Based on the preceding observations, the first exothermic peak is attributed to carbon fixation accompanying NH₃BH₃ thermolysis; however, the second minor event needs additional study before its origin can be determined.

To obtain more insight into the proposed carbon fixation process, we characterized the solid product of CO₂ reaction with NH₃BH₃ using micro-Raman spectroscopy. As shown in Figure 2, for CO₂ pressures of 0.845 and 1.53 MPa, the spectra display structural features reported previously for the solid product resulted from CO₂ reduction and NH₃BH₃ thermolysis.^{24,26} Bands centered at ca. 1461, 2957 and 3423 cm⁻¹ are assigned to CH₃ rocking, C-H, and *sp*² N-H stretching modes, respectively. For CO₂ pressures of 2.27 and 2.96 MPa, the bands assigned to *sp*³ N-H and *sp*³ B-H stretching modes for the solid product of NH₃BH₃ thermolysis are weak (Figure 2). By contrast, bands attributable to B-O-C bending, C-O, B-O and C=O stretching modes become stronger as the CO₂ pressure is increased. On the basis of enthalpies of exothermic events and Raman spectroscopic data for the solid product, we conclude that carbon fixation and NH₃BH₃ thermolysis both occur with the former process becoming favorable at high CO₂ pressures.

The assignment of Raman bands associated with the solid product of carbon fixation is further supported by the ¹¹B and ¹³C solid state MAS NMR (magic-angle spinning nuclear magnetic resonance) investigations on the sample produced at a CO₂ pressure of 2.96 MPa. In the ¹¹B MAS NMR spectrum (Figure 3a), a sharp peak at 1.5 ppm and a broad peak at 16.2 ppm are observed, corresponding to tetrahedral BO₄ groups (*sp*³ B) and trigonal BO₃

groups (sp^2 B), respectively.²⁷ On the other hand, the ^{13}C MAS NMR spectrum displays three principal peaks at 25.2, 50.9, and 165.7 ppm besides the CO_2 resonances (Figure 3b),²⁴ which are assigned to aliphatic, methoxy (OCH_3) and formate (HCOO) groups, respectively.²⁸ The formation of OCH_3 and HCOO groups has been reported in the solid product of CO_2 reaction with NaBH_4 or LiBH_4 ^{29,30}, but, the aliphatic group was not found in the solid product of these two reactions. Thus, by combining spectroscopic investigations and previous studies on the CO_2 reduction by metal borohydrides, we deduce that the solid product of CO_2 reaction with NH_3BH_3 contains BOCH_3 and BOOH groups.

Pyrolysis of the solid product that results from CO_2 reaction with NH_3BH_3 , decomposing it at temperatures up to 750 °C in nitrogen (Supporting Information, Figures S4 & S5), yields a yellowish-brown solid residue for the samples produced at CO_2 pressures of 0.845 and 1.53 MPa, and a black solid residue for the samples produced at CO_2 pressures of 2.27 and 2.96 MPa (Supporting Information, Figure S7). For the latter two cases, the yields of solid residue at temperatures up to 750 °C are about 65 and 60 %, respectively (Supporting Information, Figure S4); moreover, we found that 600 °C is the lowest temperature for generation of the black solid residue from the solid product resulted CO_2 reaction with NH_3BH_3 at a CO_2 pressure of 2.96 MPa (Supporting Information, Figure S8). Attempts to characterize the yellowish-brown solid residue using the micro-Raman were precluded by high fluorescence intensity; in continuing studies we plan to use a low temperature cold finger to minimize the emission. For the black solid residue, however, the Raman spectra are consistent with that for the graphitic carbon (Figure 4a and Figure S9 in Supporting Information). Specifically, over the spectral range of 500 to 3500 cm^{-1} , two sharp bands centered at ca. 1350 and 1590 cm^{-1} are observed; they are attributable to breathing (D band) and stretching (G band) modes of sp^2 carbon-carbon bonds, respectively.^{31,32}

To further understand the pyrolysis of the solid product (produced at a CO_2 pressure of 2.96 MPa), we acquired the ^{11}B and ^{13}C solid-state MAS NMR of the solid residue. The ^{11}B MAS NMR spectrum exhibits a strong, broad peak at 12.1 ppm and a downfield shoulder (Figure 3a). The peak is attributed to trigonal BO_3 groups (sp^2 B). In addition to the broad peak, another small feature is observed at 1.5 ppm, which is associated with tetrahedral BO_4 groups (sp^3 B); no other B-containing species are detected. In the ^{13}C solid MAS NMR spectrum, only peaks related to $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds (sp^2 C) are observed (Figure 3b). MAS NMR structural characterizations coupled with micro-Raman investigations lead us to hypothesize that the formation of graphitic carbon requires both formate and aliphatic groups, with methoxy groups converting to gaseous species, because the pyrolysis of sodium formatomethoxyborane ($\text{NaBO}(\text{OCH}_3)(\text{OOCH})$) produces methyl borate, methyl formate, boron oxide and sodium salts.³⁰

As noted above, the solid residue from pyrolysis of the solid product (produced at a CO_2 pressure of 2.96 MPa) contains graphitic carbon. To identify the type of carbon, we treated the resultant residue sequentially with 5 M HCl, deionized water and methanol and then characterized the treated residue using micro-Raman, ATR-FTIR (attenuated total reflection Fourier-transform infrared spectroscopy), optical microscopy, TEM (transmission electron microscopy) and AFM (atomic force microscopy). The treatment has little effect on the state of the graphitic carbon (Figure 4a), but appears to dehydrate the boron-containing compounds, because both the in-plane B-O-H bending and O-H stretching modes diminish in intensity (Figure 4b). After the treatment, the Raman spectrum for the solid residue displays a weak broad band centered at ca. 2685 cm^{-1} (Figure 4a); it is assigned to $2D$ band.^{33,34} Optical microscopy images of treated residue reveal the presence of transparent flakes (Figure 5a). Also, the presence of flakes is further supported by the TEM images (Figure 5b, c). The thickness of a typical flake is less than 6 nm, as determined from the AFM images (Figure 5d). On the basis of microscopy studies, NMR and Raman

spectroscopic observations, we deduce that graphene oxide is produced during pyrolysis. Furthermore, we view the treated solid residue as a graphene oxide-boron oxide sandwich-like nanocomposite because boron oxide cannot be totally removed by acid- and water-washing (Figure 4b).

4. Conclusion

In summary, from a conflation of microscopy, magnetic resonance, and Raman spectroscopy measurements, we have demonstrated that CO₂ can be converted to graphene oxide nanocomposites by NH₃BH₃ via two consecutive steps: NH₃BH₃ first reduces CO₂ to form a solid compound at temperatures less than 100 °C and CO₂ pressures below 3 MPa (carbon fixation), and subsequently, the solid product decomposes in an inert atmosphere at temperatures above 600 °C to generate graphene oxide (graphenization). Moreover, our study reveals that graphene oxide obtained from CO₂ reacting with NH₃BH₃ may have different properties from those prepared from solid carbon sources like graphite.¹³ These findings present a new approach for converting CO₂ from industrial and natural sources to a variety of graphenic materials. Moreover, the formation of C-H and C-C bonds through CO₂ activation is of great interest in synthesizing liquid fuels and useful chemical from CO₂. To fully explore the method developed here, our ongoing work includes detailed mechanistic studies of both carbon fixation and graphenization, coupled with expanded structure determinations for the product of carbon fixation and the proposed graphene oxide nanocomposites. Also, efforts are made to produce other organic compounds from the solid product of CO₂ reaction with NH₃BH₃.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors are grateful for the financial supports of NSF and NIH under the Grants numbers of HRD-0833180, MCB-0741914, and 5G12 RR03060.

References

1. Olah GA. *Angew. Chem., Int. Ed.* 2005; 44:2363–2369.
2. Roy SC, Varghese OK, Paulose M, Grimes CA. *ACS Nano*. 2010; 4:1259–1278. [PubMed: 20141175]
3. Jiang Z, Xiao T, Kuznetsov VL, Edwards PP. *Phil. Trans. R. Soc. A*. 2010; 368:3343–3364. [PubMed: 20566515]
4. Arakawa H, Aresta M, Armor JN, Barteau MA, Beckman EJ, Bell AT, Bercaw JE, Creutz C, Dinjus E, Dixon DA, et al. *Chem. Rev.* 2001; 101:953–996. [PubMed: 11709862]
5. Sakakura T, Choi J-C, Yasuda H. *Chem. Rev.* 2007; 107:2365–2387. [PubMed: 17564481]
6. Tamaura Y, Tabata M. *Nature*. 1990; 346:255–256.
7. Kodama T, Tabata M, Tominaga K, Yoshida T, Tamaura Y. *J. Mater. Sci.* 1993; 28:547–552.
8. Ehrensberger E, Palumbo R, Larson C, Steinfeld A. *Ind. Eng. Chem. Res.* 1997; 36:645–648.
9. Tomai T, Katahira K, Kubo H, Shimizu Y, Sasaki T, Koshizaki N, Terashima K. *J. of Supercritical Fluids*. 2007; 41:404–411.
10. Motiei M, Hacohen YR, Calderon-Moreno J, Gedanken A. *J. Am. Chem. Soc.* 2001; 123:8624–8625. [PubMed: 11525682]
11. Lou Z, Chen Q, Wang W, Zhang Y. *Carbon*. 2003; 41:3063–3074.
12. Lou Z, Chen Q, Zhang Y, Wang W, Qian Y. *J. Am. Chem. Soc.* 2003; 125:9302–9303. [PubMed: 12889953]

13. Dreyer DR, Park S, Bielawski CW, Ruoff RS. Chem. Soc. Rev. 2009; 39:228–240. [PubMed: 20023850]
14. Wei ZQ, Wang DB, Kim S, Kim SY, Hu YK, Yakes MK, Laracuenta AR, Dai ZT, Marder SR, Berger C, et al. Science. 2010; 328:1373–1376. [PubMed: 20538944]
15. Allen MJ, Tung VC, Kaner RB. Chem. Rev. 2010; 110:132–145. [PubMed: 19610631]
16. Dikin DA, Stankovich S, Zimney EJ, Piner RD, Dommert GHB, Evmenenko G, Nguyen ST, Ruoff RS. Nature. 2007; 448:457–460. [PubMed: 17653188]
17. Sun X, Liu Z, Welsher K, Robinson J, Goodwin A, Zaric S, Dai H. Nano Res. 2008; 1:203–212. [PubMed: 20216934]
18. Loh KP, Bao Q, Eda G, Chhowalla M. Nature Chem. 2010; 2:1015–1024. [PubMed: 21107364]
19. Staubitz A, Roberston PM, Manners I. Chem. Rev. 2010; 110:4079–4124. [PubMed: 20672860]
20. Zhang JS, Lee JW. J. Chem. Eng. Data. 2009; 54:659–661.
21. Guan X, Stark RE. Solid State Nucl. Magn. Reson. 2010; 38:74–76. [PubMed: 21036557]
22. Morcombe CR, Zilm KW. J. Magn. Reson. 2003; 162:479–486. [PubMed: 12810033]
23. Harris RK, Becker ED, de Menezes S. M. Cabral, Goodfellow R, Granger P. Solid State Nucl. Magn. Reson. 2002; 22:458–483. [PubMed: 12637147]
24. Zhang JS, Zhao Y, Akins DL, Lee JW. J. Phys. Chem. C. 2011; 115:8386–8392.
25. Wolf G, Baumann J, Baitalow F, Hoffmann FP. Thermochim. Acta. 2000; 343:19–25.
26. Frueh S, Kellett R, Mallery C, Molter T, Willis WS, King'onde C, Suib SL. Inorg. Chem. 2011; 50:783–792. [PubMed: 21182274]
27. Du LS, Stebbins JF. J. Phys. Chem. B. 2003; 107:10063–10076.
28. Pretsch, E.; Bühlmann, P.; Badertscher, MC. Structure Determination of Organic Compounds: Tables of Spectral Data. 4th Ed. Springer; 2009.
29. Burr JG, Brown WG, Heller HE. J. Am. Chem. Soc. 1950; 72:2560–2562.
30. Wartik T, Pearson PK. J. Inorg. Nuc. Chem. 1958; 7:404–411.
31. Tuinstra F, Koenig J. J. Chem. Phys. 1970; 53:1126–1130.
32. Ferrari C, Robertson J. Phys. Rev. B. 2000; 20:14095–14107.
33. Ferrari C, Meyer JC, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec P, Jiang D, Novoselov DKS, Roth S, Geim AK. Phys. Rev. Lett. 2006; 97:187401. [PubMed: 17155573]
34. Sun Z, Yan Z, Yao J, Beitler E, Zhu Y, Tour JM. Nature. 2010; 468:549–552. [PubMed: 21068724]

Figure 1. Enthalpograms for CO₂ reaction with NH₃BH₃ at CO₂ pressures of 0.845, 1.53, 2.27 and 2.96 MPa. The pressure specified pertains to the start of heating and the heating rate changed from 1.00 to 0.25 °C min⁻¹ at 65 °C.

Figure 2.

Raman spectra for NH₃NH₃, polyaminoborane and the solid product of CO₂ reaction with NH₃BH₃ at CO₂ pressures of 0.845, 1.53, 2.27 and 2.96 MPa.

Figure 3.

^{11}B and ^{13}C MAS NMR spectra for the solid product of CO_2 reaction with NH_3BH_3 and its correspondent solid residue. The solid product was produced at a CO_2 pressure of 2.96 MPa and pyrolysis of the solid product (at temperatures up to 750 °C) in nitrogen generated a solid residue. a) ^{11}B MAS-NMR. b) ^{13}C MAS-NMR. * indicating spinning side bands.

Figure 4. Raman and ATR-FTIR spectra for the pristine and treated solid residue. a) Raman spectra for the pristine and treated solid residue. b) FTIR spectra for the pristine and treated solid residue.

Figure 5. Characterization of the treated solid residue. a) Microscopic images indicating there are flakes in the solid residue. b and c) Representative TEM micrographs showing curled and stacked flakes. d) A representative AFM image demonstrating that the thickness of one flake is less 6 nm.