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Probing the Transformation of Boron Nitride Catalysts under Oxidative Dehydrogenation Conditions

Alyssa M. Love,^{a,‡} Brijith Thomas,^{c,‡} Sarah E. Specht,^a Michael P. Hanrahan,^{c,d} Juan M. Venegas,^b Samuel P. Burt,^b Joseph T. Grant,^a Melissa C. Cendejas,^a William P. McDermott,^a Aaron J. Rossini,^{c,d}* Ive Hermans^{a,b}*

^aUniversity of Wisconsin - Madison, Department of Chemistry, 1101 University Avenue, Madison WI 53706, USA

^bUniversity of Wisconsin – Madison, Department of Chemical and Biological Engineering, 1415 Engineering Drive, Madison WI 53706, USA

^cUS DOE Ames Laboratory, Ames, Iowa, USA, 50011

^dIowa State University, Department of Chemistry, 2438 Pammel Drive, Ames, IA 50011, USA

ABSTRACT: Hexagonal boron nitride (h-BN) and boron nitride nanotubes (BNNTs) were recently reported as highly selective catalysts for the oxidative dehydrogenation (ODH) of alkanes to olefins in the gas phase. Previous studies revealed a substantial increase in surface oxygen content after exposure to ODH conditions (heating to ca. 500 °C under a flow of alkane and oxygen); however, the complexity of these materials has thus far precluded an in-depth understanding of the oxygenated surface species. In this contribution, we combine advanced NMR spectroscopy experiments with scanning electron microscopy (SEM) and soft X-ray absorption spectroscopy (XAS) to characterize the molecular structure of the oxygen functionalized phase that arises on h-BN and BNNTs following catalytic testing for ODH of propane. The pristine BN materials are readily oxidized and hydrolyzed under ODH reaction conditions to yield a phase consisting of three coordinate boron sites with variable numbers of hydroxyl and bridging oxide groups which is denoted B(OH)_xO_{3-x} (where x = 0-3). Evidence for this robust oxide phase revises previous literature hypotheses of hydroxylated BN edges as the active component on h-BN.

INTRODUCTION

Boron nitride (BN) is a versatile material used in a number of diverse applications because of its mechanical strength, thermal conductivity, and chemical stability.^{1,2} Hexagonal boron nitride (h-BN) is isostructural to graphite, consisting of alternating Band N-atoms that make a hexagonal, honeycomb-like structure. Much like its carbon-based counterpart, h-BN can exist as both two-dimensional sheets that are structurally analogous to graphene, or as boron nitride nanotubes (BNNTs) that are structurally analogous to carbon nanotubes. Additional functional groups can be added to the edges of boron nitride materials to further tune the properties of the material. For example, oxygen functionalization of h-BN (*e.g.*, with –OH or –OR groups) has been used in applications including modification of mechanical and thermal properties in composite materials,^{3,4} drug delivery,⁵ hydrogen storage,^{6,7} and water purification.⁸

Recently, our group, followed by others reported that h-BN and BNNTs are surprisingly selective catalysts for the oxidative dehydrogenation (ODH) of alkanes to olefins.⁹⁻¹⁴ For example, propane ODH at 500 °C over h-BN results in 76.0% selectivity to propylene, 11.5% to ethylene and only 9.4% to CO_x (CO plus CO_2) at 19.1% propane conversion. These selectivities result in an olefin yields that are higher than obtained with state-of-theart supported vanadium oxide catalysts^{15,16} while achieving good productivity (*i.e.*, 2 kg propene per kg of catalyst per hour). These results present a promising route to olefin production from shale gas-derived alkanes, which is potentially far more energy efficient than traditional cracking of oil-derived naphtha.¹⁷

Given the reported chemical inertness of BN, it is of great fundamental and practical significance to understand how its remarkable catalytic activity arises. In an effort to unravel the nature of the catalytically active phase, previous studies characterized BN materials with X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy after ODH catalytic testing.^{9,18} XPS shows a peak shift to higher binding energies in the B 1s region of spent (used) catalysts that indicates increased oxygen coordination to boron. This shift to higher binding energy was not observed in the N 1s region. Additionally, XPS reveals that the atomic composition within the upper surface layer (ca. top 10 nm) of the spent BN catalysts has higher relative quantities of oxygen and boron atoms compared to the fresh materials.^{9,10,18} IR spectra of the spent catalysts contain spectroscopic features that are attributed to BO-H and B-O vibrations at ~3200 and 1190 cm⁻¹, respectively.^{3,19} These spectroscopic features are not detected in fresh h-BN, and are only observed at low intensities in fresh BNNTs.9,10 Given the resistance of h-BN to oxidation in air below 800 °C,4,18,20 early literature reports of h-BN-catalyzed ODH hypothesized that BN oxidation is confined to edge sites that catalyze the ODH reaction.9-13 We also note here that elemental boron and other boron-containing materials — such as NiB, HfB₂, WB, Ti₂B, and B₄C — also exhibit similarly remarkable selectivity to h-BN and BNNTs and show an increase in oxygen content after ODH by the same characterization techniques.¹⁸ The similarities between these materials suggests that the oxidized boron phase plays an important role in the catalytic behavior of BN and other B-containing materials during ODH. In addition, the observation of an induction period to reach maximum alkane conversion during h-BN catalyzed ODH further suggests that the formation of this oxidized phase

on boron containing materials is required for catalytic activity.²¹ Therefore, we report a detailed structural investigation of the oxidized phase on h-BN and BNNTs as an important first step towards understanding the catalytic behavior of these materials. We also emphasize that exposure of BN to ODH conditions conveniently produces oxygen-functionalized BN that might find applications beyond ODH catalysis,³⁻⁸ and that detailed structural characterization of functionalized BN is crucial for their implementation in these applications as well.

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In this study, we apply Magic Angle Spinning (MAS) ¹¹B solid-state NMR spectroscopy,²² scanning electron microscopy (SEM), and X-ray absorption spectroscopy (XAS) to characterize the transformation of h-BN and BNNTs before and after use as catalysts for propane ODH (denoted as fresh and spent, respectively). A general overview of this approach is summarized in Figure S1. First, we obtain quantitative 1D ¹¹B spin echo spectra for each of the h-BN and BNNT samples. Since ¹¹B is a half-integer quadrupolar nucleus (I = 3/2), the different boron sites exhibit complex lineshapes. 2D ¹¹B Multiple-Quantum Magic Angle Spinning (MQMAS) experiments are used to resolve overlapping ¹¹B powder patterns and provide an experimental basis for the choice of peak positions within fits of the quantitative spin echo NMR spectra. Double resonance ¹¹B-¹H \widehat{NMR} experiments such as ${}^{11}B{}^{1}H{}$ Dipolar Heteronuclear Multiple-Quantum Coherence (D-HMQC), ${}^{11}B \rightarrow {}^{1}H$ Insensitive Nuclei Enhanced by Polarization Transfer (INEPT) and ¹¹B{¹H dephased} spin echo spectra are then used to identify ¹¹B spins that are proximate to or distant from ¹H nuclei. These experiments show that a fraction of the boron atoms in the oxidized part of the spent materials are proximate to protons, suggesting the formation of an amorphous mixed oxide/hydroxide phase with $B(OH)_xO_{3-x}$ sites (x = 0-3) in the spent catalyst materials. Additional information about changes in the surface properties of the material were obtained with surface selective dynamic nuclear polarization (DNP) NMR experiments in combination with qualitative observations in surface morphology changes from SEM. Finally, XAS data on the h-BN and BNNT samples provide information about the coordination of B and O atoms that support the observations from the NMR experiments. In the B K-edge X-ray absorption spectra for h-BN and BNNT, we observe a shift from primarily BN3 coordinated species (based on a feature observed at 192 eV) in the fresh materials to a mixture of BN₃ and BO₃ (signal features at 194 eV) species in the spent materials. The extended X-ray absorption fine structure (EXAFS) regions for both B and O (> 195 eV for B; > 537 eV for O) for the spent materials are distinct from bulk B2O3 under XAS measurement conditions and are consistent with the formation of a disordered B(OH)_xO_{3-x} phase.

RESULTS AND DISCUSSION

¹¹B solid-state NMR Spectroscopy. Figure 1 shows the MAS ¹¹B spin echo solid-state NMR spectra of h-BN and BNNTs before and after use as propane ODH catalysts (materials denoted fresh and spent, respectively). We also report the spectra of spent materials treated at 500 °C for 16 h under dry air (denoted as spent dehydrated). The ¹¹B spin echo NMR spectra are quantitative because they were obtained with recycle delavs of at least three times the boron longitudinal relaxation time constant $(T_1(^{11}B))$ of the slowest relaxing boron site within a sample and all sites have a similar quadrupolar coupling constants (C_0). Saturation recovery experiments showed that the h-BN phase has an unexpectedly long $T_1(^{11}B)$ of ca. 175 s (Figure S2), therefore, the ¹¹B spin echo NMR spectra of the h-BN materials in Figures 1a-1c were obtained with a 600 s recycle delay. ¹¹B spin echo spectra obtained with shorter recycle delays of 50 s and 0.1 s emphasize the signals from the oxidized boron phase because this component has a much shorter $T_1(^{11}\text{B})$ of ca.

1.4 s (Figure 1b, inset). The $T_1({}^{11}\text{B})$ of the BN phase in spent BNNTs was ca. 10 s (Figure S2); quantitative ${}^{11}\text{B}$ spin echo of the BNNT materials in Figures 1d-1f were obtained with a 50 s recycle delay.



Figure 1. MAS ¹¹B spin echo solid-state NMR spectra of a) fresh h-BN, b) spent h-BN, c) spent dehydrated h-BN, d) fresh BNNT, e) spent BNNT and f) spent dehydrated BNNT. The dashed traces below the experimental spectra represent analytical simulations of the data, and the overlapping features below represent the individual peaks corresponding to the total analytical fit. The inset in b) compares ¹¹B spin echo pulse NMR spectra obtained with recyle delays of 600 s, 50 s, and 0.1 s. The ¹¹B NMR parameters determined from the analytical simulations—which are not chemically meaningful and are rather meant to approximate a distribution of boron species—are summarized in the main text and Table 1.

Analytical simulations of the MAS ¹¹B spin echo solid-state NMR spectra provide the isotropic chemical shift (δ_{iso}) — analogous to chemical shifts measured in solution NMR experiments - as well as the electric field gradient (EFG) tensor parameters: C_Q and the EFG tensor asymmetry parameter (η_Q).^{23,24} δ_{iso} for each site occurs at a higher frequency than the leftmost edge of each MAS powder pattern because of the quadrupole induced shift.^{23,24} For this reason, δ_{iso} was determined from the analytical simulations of the MAS powder patterns.^{23,24} The breadth of the simulated powder patterns indicates the magnitude of C_0 . The C_0 depends upon the degree of spherical symmetry at the nuclear site, with spherically symmetric nuclear environments leading to small or vanishing values of C_0 .^{23,24} For boron, 4-coordinate tetrahedral sites usually give rise to C_0 values below 1 MHz and narrow NMR signals, while anisotropic 3-coordinate trigonal-planar sites typically result in a C_0 between 2.5 and 3 MHz and relatively broad NMR signals (Table 1; Table S1).25,26

The ¹¹B spin echo NMR spectrum of the fresh h-BN sample shows one major feature that can be simulated with a δ_{iso} of 30.4 ppm, a C_Q of 2.9 MHz and an η_Q of 0.0 (Figure 1a), consistent with previous solid-state NMR studies on h-BN.^{7,11,27,28} The ¹¹B spin echo of the fresh BNNT resembles that of fresh h-BN and was simulated with similar NMR parameters. A 2D ¹¹B MQMAS spectrum of the fresh BNNT confirms that a predominant boron site with a δ_{iso} of 30.4 ppm is present (Figure S3). Therefore, the ¹¹B NMR signal with a δ_{iso} of 30.4 ppm in

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the spin echo NMR spectra of fresh h-BN and fresh BNNT are attributed to boron atoms with trigonal planar symmetry and three coordinating nitrogen atoms (BN₃). The spin echo spectra for both fresh samples contain small amounts (5 % for h-BN and 10 % for BNNT) of an impurity with δ_{iso} values corresponding to three-coordinate oxidized boron species (BO₃) similar to that of boric acid that are likely residual impurities from the commercial synthesis of these materials by nitriding boron oxide with ammonia.²⁹ Although we observe evidence for oxidized impurities in the ¹¹B NMR spectrum for fresh h-BN, these impurities do not appear in the powder X-ray diffraction (PXRD) pattern for fresh h-BN either because they are amorphous in nature or their crystallite size is below the detection limit for this technique (Figure S4).

The ¹¹B spin echo NMR spectra of spent h-BN (Figure 1b) and spent BNNT (Figure 1e) show significant changes from the corresponding fresh samples. In both ¹¹B spin echo NMR spectra we observe the appearance of a new feature at a lower chemical shift from the original BN₃ peak. Based on previous observations of oxidized boron species from XPS and IR^{9,18} as well as the isotropic chemical shifts, we attribute this feature to the formation of oxidized and hydrolyzed boron species on the h-BN and BNNT materials. Given the complexity of the oxidized boron feature in the spectrum for spent h-BN, we utilized 2D ¹¹B MQMAS NMR and double resonance ¹¹B-¹H NMR experiments to resolve and identify the different boron coordination environments in spent h-BN (Figure 2).^{22,24,30,31}

Figure 2a and Figure S3 show the 2D ¹¹B MQMAS spectrum for spent h-BN and spent BNNTs, respectively. The 2D ¹¹B MQMAS spectrum of h-BN shows only signals from the oxidized phase because a recycle delay of 1.0 s was used. The horizontal axis gives a typical 1D ¹¹B MAS NMR spectrum of the material, whereas the vertical axis of the MQMAS spectrum shows a high resolution isotropic ¹¹B dimension free of quadrupolar broadening. The horizontal projections from different points along the indirect isotropic dimension in the 2D MQMAS spectrum illustrate that there is a large distribution of δ_{iso} values ranging from ca. 20 ppm to 13 ppm (right side of Figure 2a). Analytical simulations indicate C_Q is approximately 2.7 MHz and $\eta_Q = 0.0$ for all boron sites within the distribution (Table S1). The MQMAS spectrum of spent h-BN is reminiscent of the MQMAS spectra of boron oxide glasses where the distribution in δ_{iso} for the trigonal planar BO₃ sites arises because the sites within boroxol rings and sites that link the rings have different chemical shifts.³¹ In spent h-BN the large distribution in δ_{iso} likely arises because there is a variety of trigonal planar boron sites with different numbers of oxide and hydroxide ligands (see discussion below).

Using the information obtained from the 2D MQMAS spectra the ¹¹B spin echo NMR spectra could be fit with analytical simulations (Figure 1). In order to simplify the analysis and interpretation of the data the distribution of NMR signals arising from the oxidized/hydrolyzed sites was accounted for by using simulations of five distinct boron sites with $C_0 = 2.7$ MHz and $\eta_Q = 0.0$ but different δ_{iso} that varied by about 2 ppm over the range of ca. 20 ppm to 10 ppm (Table 1 and Table \$1). Simulations of the MAS ¹¹B solid-state NMR spectra obtained at both 14.1 T and 9.4 T showed good agreement with the experimental NMR spectra (> 90% overlap between experimental and simulated data), confirming the validity of the fits (Figure S5). The distinct chemical shifts used in the simulations are not chemically meaningful, rather, they are required to broaden the simulated pattern and obtain a better match to the experimental spectrum intensity. Simulations with distributions in the isotropic chemical shift and EFG tensor parameters would likely yield improved fits that better reflect the structural disorder present in the spent materials.

Fable 1	l. Summarv	y of Experimentally	¹¹ Measured and Literature ¹¹	B Solid-State NMR Parameters
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Material	NMR Experiment	Assigned Site	δ _{iso} (ppm) ^a	С _Q (MHz) ^b	η _Q ^c	Integrated Intensity (%) ^d		
This Work								
fresh h DN	spin echo	BN ₃	30.4	2.9	0.0	95(10)		
Iresn n-BIN		BO ₃	19.3	2.7	0.0	5(2)		
month DN	spin echo	BN ₃	29.8	2.8	0.0	70(3)		
spent n-Biv		$B(OH)_xO_{3-x}$	19.2 to 13.0	2.7	0.0	30(3)		
spent dehydrated	spin echo	BN ₃	30.4	2.8	0.0	70(9)		
h-BN		$B(OH)_xO_{3-x}$	19.5 to 13.0	2.7	0.0	30(8)		
fresh DNNT	spin echo	BN ₃	30.4	2.9	0.0	90(9)		
IICSII DININ I		BO ₃	19.3	2.7	0.0	10(1)		
spent BNNT	spin echo	BN ₃	30.4	2.8	0.0	20(1)		
spent BINN I		$B(OH)_xO_{3-x}$	19.2 to 11.5	2.7	0.0	80(4)		
spont dehydrated	spin echo	BN ₃	30.4	2.9	0.0	20(1)		
spent denyulated		$B(OH)_xO_{3-x}$	19.0 to 11.5	2.7	0.0	80(3)		
Literature								
h-BN	-	BN ₃	30.4	2.9	0.0	Jeschke et al.28		
B(OH) ₃	-	B(OH) ₃	18.8	2.55	0.0	Müller et al. ³²		
horey	-	B(OH) ₃	19.0	2.56	0.10	Turner et al.44		
UUTAX		BO_4	2.1	0.49	0.62	Turner et al.44		
B ₂ O ₃	-	BO ₃	14.6	2.69	0.05	Kroeker et al.25		
cubic-BN	-	BN ₄	1.6	0.05	0.0	Jeschke <i>et al</i> . ²⁸		

 ${}^{a}\delta_{iso}$ (ppm) – isotropic chemical shift. ${}^{b}C_{Q}$ (MHz) – quadrupolar coupling constant. ${}^{c}\eta_{Q}$ – electric field gradient tensor asymmetry parameter. d Uncertainties (shown in parentheses) in the integrated intensities were evaluated from the residual intensity between the experimental spectra and fits for the nitride and oxide regions (Figure S19)

¹¹B-¹H double-resonance experiments and trends in δ_{iso} were used to detect distinct boron coordination environments within the oxidized/hydrolyzed boron phase and to assist with structural assignments within this phase (Figures 2b-2c). The ¹¹B{¹H} D-HMQC spectrum shows the ¹¹B spectrum of proximate, dipolar-coupled ¹¹B and ¹H spins, while a ¹¹B{¹H dephased} experiment with 0.5 ms of dipolar-dephasing shows the NMR signals from ¹¹B spins that are *distant* from ¹H spins (Figure 2b; analogous experiments performed for BNNTs are provided in Figure S6). In addition, the 2D $^{11}B\rightarrow^{1}H$ dipolar refocused INEPT (D-RINEPT) spectrum shows both the ¹¹B and ¹H NMR spectra of dipolar-coupled ¹¹B and ¹H spins (Figure 2c). The ¹¹B NMR spectrum obtained with D-HMQC (and D-RINEPT) shows a more positive δ_{iso} compared to the ¹¹B{¹H dephased} NMR spectrum, however, both ¹¹B patterns fit within the broad NMR signal of the oxidized phase obtained with a spin echo pulse sequence (Figure 2b). Boric acid $(B(OH)_3)$ consists of trigonal planar boron sites coordinated by three hydroxide ligands and has previously been reported to have ¹¹B NMR parameters of $\delta_{iso} = 18.8$ ppm, $C_Q = 2.5$ MHz and $\eta_Q = 0.0.^{32} B_2 O_3$ consists of trigonal planar BO₃ sites with bridging oxide ligands and has reported ¹¹B NMR parameters

 $\delta_{iso} = 14.6$ ppm, $C_0 = 2.7$ MHz and $\eta_0 = 0.05$ (Table 1), although, 3-coordinate oxygen coordinated boron sites can take on a range of δ_{iso} values from 14.6 to 22.5 ppm depending on whether the oxide ligands are terminal or bridging.^{22,25} Therefore, based upon the 11B-1H double-resonance experiments and previously reported δ_{iso} , the ¹¹B NMR signals with the most positive δ_{iso} are assigned to sites with three hydroxyl groups, intermediate shifts likely have a mixture of oxide and hydroxide ligands, and sites with lower chemical shift are coordinated by three bridging oxide bonds. Note that the ¹H chemical shift observed in the 2D ${}^{11}B \rightarrow {}^{1}H$ D-RINEPT for spent h-BN has a maximum intensity at ca. 5 ppm, while pure boric acid has a ¹H chemical shift of ca. 8 ppm (Figure S7). The ¹¹B and ¹H NMR spectra of spent h-BN therefore suggest that the boron environments within the oxidized/hydrolyzed phase are distinct from those of pure boric acid or boron oxide. Based upon all solidstate NMR experiments, the broad range of NMR signals in the oxide chemical shift region are assigned to a phase denoted $B(OH)_xO_{3-x}$ where x = 0-3 to indicate that there are 3-coordinate boron sites with different numbers of bridging

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Figure 2. a) 2D ¹¹B MQMAS spectrum of spent h-BN. Several rows extracted from the 2D NMR spectrum and their corresponding analytical simulations are shown to the right. b) Comparison of ¹¹B SSNMR spectra of spent h-BN obtained with a spin echo pulse sequence (black trace), ¹¹B {¹H} D-HMQC pulse sequence (top red trace), and a ¹¹B {¹H dephased} NMR spectrum (lower red trace) of spent h-BN. c) 2D ¹¹B→¹H D-RINEPT spectrum. All spectra were obtained with a 1.0 s recycle delay.

oxide and hydroxide ligands. The B(OH)_xO_{3-x} phase must result from varying degrees of oxidation/hydrolysis of the BN materials under the ODHP reaction conditions.

The ¹¹B spin echo spectra presented in Figure 1 are quantitative; therefore, the extent of oxidation in these materials can be determined by comparing the percent area of the BN₃ feature in the fresh and spent h-BN and BNNT samples. Based on this analysis, approximately 30 % of the boron nitride phase in fresh h-BN is converted to $B(OH)_xO_{3-x}$ species in the spent material. Remarkably, 80% of the boron nitride phase in fresh BNNTs is converted to $B(OH)_xO_{3-x}$ species in the spent material (Table 1). The NMR peak fits are in good agreement with the boron XAS which shows a higher degree of oxidation/hydrolysis in spent BNNT as compared to spent h-BN (vide infra). The higher extent of oxidation in BNNT likely occurs because BNNT has a much higher surface area than h-BN, and therefore a larger fraction of boron atoms are surface exposed in BNNT and available for reaction. This hypothesis is also consistent with the fact that BNNT are a much more active catalyst for ODH than h-BN (vide infra).

¹¹B solid-state NMR experiments were also performed on spent BNNT and spent h-BN samples that were treated at 500 °C for 16 hours under dry air to observe any changes in the oxidized boron phase upon removal of water (Figures 1c, 1f). The dehydrated samples were handled in a glove box and the NMR rotors were spun with dry nitrogen gas to prevent re-adsorption

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of moisture during spectral acquisition. The ¹¹B spin echo NMR spectra of the B(OH)_xO_{3-x} phase in dehydrated spent h-BN and dehydrated spent BNNTs are very similar to those observed from the corresponding untreated samples, however, there is a slight increase in intensity of sites with a lower δ_{iso} (Figure S9 and S10). Lower δ_{iso} are likely associated with BO₃ sites, suggesting dehydroxylation of some boron sites in the B(OH)_xO_{3-x} phase upon dehydration at high temperatures. This observation was also corroborated with Raman spectroscopy (Figure S8). However, 2D ¹¹B{¹H} D-HMQC spectra of both dehydrated spent h-BN and dehydrated spent BNNTs show that many of the boron spins are still proximate to ¹H nuclei even after dehydration (Figures S9 and S10). The ¹¹B-¹H double resonance NMR experiments suggest that hydroxyl groups are likely present under ODH conditions and are potentially relevant to the catalytic performance of the material.

DNP-Enhanced ¹¹**B solid-state NMR spectroscopy and Scanning Electron Microscopy.** Dynamic nuclear polarization (DNP)-enhanced ¹¹B solid-state NMR experiments were also performed to specifically probe the surface of the h-BN and BNNT samples (Figure 3). All fresh and spent h-BN and BNNTs were prepared for DNP experiments by impregnating the powdered solids with a 15-20 mM solution of the biradical polarizing agent TEKPol in 1,1,2,2-tetrachloroethane (TCE).^{33,34} The measured *direct* and *indirect* boron DNP enhancements provide insight into the textural properties and macroscopic arrangement of the different phases in the fresh and spent materials. SEM images of the fresh and spent catalysts are provided in Figure 4 and used in combination with the DNP experiments to help understand how changes in the morphological properties of the catalysts are related to the observed DNP enhancements.

During a DNP experiment, electron spins from the TEKPol biradical are polarized with microwaves and the magnetization from these electrons is transferred to ¹¹B nuclei in the sample either via a *direct* (*i.e.*, electron \rightarrow ¹¹B) or an *indirect* (*i.e.*, electron \rightarrow ¹¹H \rightarrow ¹¹B) pathway that depends on the choice of NMR experiment (Figure S11). The *direct* excitation ¹¹B spin echo NMR experiments probe all of the boron sites in the material, although the direct boron DNP enhancement (ε_B) should strongly depend upon the proximity of the boron nuclei to the polarizing agent (high ε_B for small particles/surface signals) and the ¹¹B T_1 (high ε_B for longer T_1). Indirect DNP-enhanced ¹H \rightarrow ¹¹B CPMAS solid-state NMR spectra were also recorded and are briefly discussed in the Supporting Information (Figure S12).



Figure 3. DNP-enhanced ¹¹B spin echo NMR spectra of a) fresh h-BN, b) spent h-BN, c) fresh BNNT and d) spent BNNT.

Figure 3 shows the ¹¹B solid-state NMR spectra collected with a 263 GHz/400 MHz DNP solid-state NMR spectrometer. The NMR parameters extracted from simulations of the DNPenhanced ¹¹B NMR spectra are reported in Table S2. Figure S13 shows the ¹¹B solid-state NMR spectra obtained with and without microwaves and illustrates how DNP enhancements (ε_B and ε_B_{CP} for direct and indirect DNP enhancements, respectively) were determined for different signals. The maximum theoretical ¹¹B direct DNP enhancement (ε_B) is given by the ratio of electron to ¹¹B gyromagnetic ratios (γ_e/γ_B ; ca. 1050 for ¹¹B); however, typical enhancements—including most of the enhancements reported in Figures 3a-3d—usually range from 10 to 200.³⁵ DNP-enhanced ¹H spin echo solid-state NMR experiments for fresh and spent h-BN and measured proton DNP enhancements (ϵ_H) and are provided in Figure S14.

A very high ε_B of ca. 120 was measured for the boron nitride signal of fresh h-BN (Figure 3a). This high ε_B is somewhat surprising because h-BN consists of hexagonal sheets that are ca. 1 μ m in diameter with a thickness of ca. 50 – 100 nm (SEM, Figure 4a). Therefore, most of the ¹¹B spins in h-BN should not have a substantial dipolar coupling to unpaired electrons of the radical polarizing agent and direct DNP enhancements is expected to be small. However, $T_1(^{11}B)$ is exceptionally long (ca. 175 s) in h-BN, and a long nuclear T_1 will favor high DNP enhancements. A second signal was visible at lower frequency and is assigned to a small amount of oxidized boron impuritiespotentially residual from the commercial synthesis of the material—present on the surface of fresh h-BN material. This signal has a small relative integrated intensity (ca. 20%) and a slightly higher $\varepsilon_{\rm B}$ of ca. 140, which suggests that the oxidized impurities exist as small particles or are found on the surface of the h-BN. A moderately high ε_B of 18 was measured for the DNPenhanced ¹¹B spin echo for fresh BNNT (Figure 3c). A substantial DNP enhancement is expected because the BNNTs are small in diameter (ca. 3 nm, Figure 4c) and the radical polarizing agents can potentially approach within a few nanometers of all ¹¹B spins. Clearly, while the magnitude of DNP enhancements can give valuable information about the textural and morphological properties of a sample, the DNP mechanisms can be very complex (as seen in the case of fresh h-BN) and therefore these apparent enhancements are non-quantitative.

Figures 3b and 3d show the DNP-enhanced ¹¹B spin echo spectra for spent h-BN and BNNTs, respectively. The DNPenhanced ¹¹B spin echo NMR spectra of spent h-BN and spent BNNT samples show signals corresponding to BN3 coordinated nuclei and additional intense signals from the B(OH)xO3-x phase. The ε_B for the BN₃ nuclei in spent h-BN decreased to 5 from an original ε_B of 120 in the fresh material, despite the fact that there was no change in $T_1(^{11}\text{B})$ for the h-BN signals. The ε_{B} for BN₃ nuclei in the spent BNNTs decreased to 12 from an original $\varepsilon_{\rm B}$ of 18 in the fresh BNNTs. The reductions in $\varepsilon_{\rm B}$ observed for the nitride signals in the spent materials could arise if the B(OH)_xO_{3-x} phases form at the surface and block access of the radical to the nitride phases. In each of the spent materials, ε_B is ca. 2 for the B(OH)_xO_{3-x} phase. This suggests that the B(OH)_xO_{3-x} phase consists of large particles where majority of boron spins are distant from the radical polarizing agents, although the short $T_1(^{11}\text{B})$ of ca. 1 s will also contribute to reduced ε_B . Indeed, the SEM image of spent h-BN shows clear degradation of the original platelet-like nanostructures (Figure 4b). SEM of the spent BNNT shows that the nanotube structures of the fresh

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Figure 4. SEM of a) fresh h-BN, b) spent h-BN, c) fresh BNNT (higher magnification shown to the right) and d) spent BNNT (higher magnification shown on right).

material have been mostly transformed into an amorphous surface phase devoid of distinct nanostructure (Figure 4d). Additional transmission electron microscopy (TEM) images illustrating the transformation of BNNTs under ODH conditions are provided in the Supporting Information (Figures S15). The large reduction in ε_B for the spent h-BN is likely due to sintering and is consistent with an observed loss in BET surface area from $8\pm1 \text{ m}^2 \cdot \text{g}^{-1}$ to $2\pm2 \text{ m}^2 \cdot \text{g}^{-1}$ (isotherms provided in Figure S16). The indirect DNP enhancements measured with ${}^{1}\text{H} \rightarrow {}^{11}\text{B}$ CPMAS experiments confirm these qualitative descriptions of particle size/morphology reached with SEM and direct DNP (Figure S12, S17).

X-ray Absorption Spectroscopy. Figure 5a shows the boron K-edge XAS spectra of fresh and spent h-BN and BNNTs. In the X-ray absorption near edge structure (XANES) region for both the fresh and spent h-BN and BNNTs (< 195 eV), we observe a strong feature at 192 eV which is attributed to a BN₃ coordination environment.³⁶ The feature at 194 eV present in the fresh BNNT and both spent materials corresponds to a BO₃ coordination environment.³⁶ A small BO₃ feature in the fresh BNNT is indicative of residual impurities from the material synthesis that is consistent with our observations from the ¹¹B spin echo NMR spectrum of fresh BNNT (Figure 1d). The increase in intensity of the BO₃ feature in the spent materials confirms oxidation occurs under ODH conditions. The intensity of the BO₃ feature relative to the BN₃ feature is significantly greater in the spent BNNT than in the spent h-BN, consistent with the signal intensities observed in the ¹¹B solid-state NMR spectra (Figure 1). This difference in relative BO₃ and BN₃ NMR and XAS signal intensities might be explained by the higher rate of propane consumption with BNNT ($1.3 \times 10^{-3} \text{ mol } C_3 H_6 \cdot m^{-2} \cdot hr^{-1}$, normalized by surface area) compared to the rate for h-BN (4.0 $x10^{-4}$ mol C₃H₆·m⁻²·hr⁻¹, normalized by surface area), which suggests a greater number of reactive sites on this material.⁹ In addition, although the feature at 194 eV also appears in the reference B₂O₃ material, features in the EXAFS region (> 195 eV) of BNNT and h-BN remain unchanged after exposure to ODHP

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conditions and are considerably different from that of the reference compounds. The difference in fine structure suggests that the long-range order of the boron atom on the fresh and spent BN surfaces does not match that of B_2O_3 . This agrees with our conclusions from ¹¹B MAS NMR experiments, which indicate the formation of a mixture of BO_3 species that are distinct from bulk B_2O_3 on the surface of BN catalysts after ODHP.

The oxygen K-edge XAS spectra of h-BN and BNNT (Figure 5b) provide additional support to the conclusion that the B(OH)_xO_{3-x} phase on both spent h-BN and BNNT catalysts are structurally distinct from bulk B₂O₃. The O K-edge XAS spectra of fresh and spent h-BN (Figure 5b) show a major signal at ~532 eV. This signal is attributed to a B-O bond, and is distinct from the B-O bond of B₂O₃, which shows a signal at 536 eV.^{37,38} A smaller signal is also observed in fresh h-BN at 530.6 eV that has been previously attributed to N=O bonding (in O 1s XPS spectra that give comparable information to the XANES region in XAS) and disappears in the spent catalyst.³⁸ Identical B-O features at ~532 eV are observed in fresh and spent BNNT (Figure 5b). The spectrum of fresh BNNT shows an additional signal at 528 eV. This signal is too low in energy to correspond to water or an -OH species39 and is not expected to be a contribution from a metal impurity, as prior elemental analyses showed no evidence for metal impurities.9 Therefore, we attribute this signal to a strained and relatively unstable oxygen species at the surface of fresh BNNT. After exposure to ODH conditions, unstable surface oxygen species are no longer present. We hypothesize that this is due to exfoliation or 'unzipping' of the BNNT material, leading to the disappearance of the signal at 528 eV in spent BNNTs.19



Figure 5. a) Boron K-edge and b) Oxygen K-edge X-ray absorption spectra of fresh h-BN, spent h-BN, fresh BNNT, spent BNNT, and B_2O_3 .

CONCLUSIONS

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In conclusion, solid-state characterization techniques including 11B solid-state NMR, SEM, and XAS were used to identify and characterize an amorphous B(OH)xO3-x phase that forms on the surface of h-BN and BNNTs following exposure to ODH conditions. Quantitative ¹¹B spin echo experiments provide information about the changes in ¹¹B coordination environment between fresh and spent samples, and 2D 11B MQMAS experiments provide an experimental basis for the deconvolution of these spectra. ¹H-¹¹B double resonance experiments verify the presence of a distribution of boron sites with different degrees of hydroxylation within the B(OH)_xO_{3-x} phase. DNP NMR and SEM experiments on the fresh and spent h-BN and BNNTs reveal an increase in particle size (and decrease in surface area) following catalytic testing. Complementary XAS studies on the fresh and spent materials verify our observations of an increase in BO₃-coordinated species atoms after ODH. This work shows that the oxidation of h-BN and BNNT catalysts is far more extensive than was previously hypothesized in the literature.

These studies represent an important step towards understanding the transformation of boron nitride catalysts during ODH reactions, as well as towards the elucidation of an active site for these materials. In addition, these results will enable the construction of appropriate computational models to study possible active sites on the catalyst surface. It is also important to reconcile observations from these *ex situ* studies with further *in situ* spectroscopic studies to understand the dynamic transformation of this phase under catalytic conditions. Furthermore, oxidation of boron nitride at lower temperature treatments (500 °C in an air and alkane mixture as opposed to > 800 °C in air) could have implications for the oxygen functionalization of BN for other applications.

EXPERIMENTAL SECTION

Sample preparation. Fresh h-BN and BNNTs were obtained from Sigma-Aldrich and BNNT, LLC, respectively, and were used without any further treatment. To make the spent samples, 50-100 mg h-BN or BNNTs was added to a quartz reactor tube (9 mm diameter). The reactor tube was heated to 500 °C under a flow of O_2 and N_2 (20% and 80%, respectively; total flow rate 40 mL·min⁻¹) and held at 500 °C for 1 h. The gas feed was then switched to a flow of O_2 , C_3H_8 , and N_2 (15 %, 30%, and 55%,

respectively), while maintaining a total flow rate of 40 mL·min⁻¹. The samples were heated under these conditions for a total of 24 h. The spent dehydrated h-BN and BNNT samples were prepared by transferring the spent materials to another quartz reactor tube fitted with vacuum valves at the inlet and outlet. The samples were then heated to 500 °C in a flow (approx. 20 mL·min⁻¹) of air for 16 h. The samples were then sealed under vacuum and handled in a glovebox prior to NMR analysis.

Solid-State NMR spectroscopy. Conventional room temperature solid-state NMR experiments were conducted on Bruker 9.4 T wide-bore (v_0 (¹H) = 400 MHz) or Bruker 14.1 T wide-bore (v_0 (¹H) = 600 MHz) NMR spectrometers. The 9.4 T spectrometer was equipped with a Bruker Avance III HD console and the 14.1 T spectrometer was equipped with a Bruker Avance II console. Bruker 2.5 mm broad band HXY MAS probes were employed on both systems and the MAS frequency was 25 kHz in all cases. The 1H NMR chemical shifts were referenced to tetramethylsilane in CDCl₃ by using adamantane as a secondary chemical shift standard ($\delta_{iso}(^{1}H) = 1.82$ ppm). For DNP experiments the ¹H chemical shift of the frozen tetrachlorethane solvent was used as the secondary shift standard ($\delta_{iso}(^{1}\text{H})$) = 6.2 ppm). ¹¹B chemical shifts were indirectly referenced to the established chemical shift standards using the previously published relative NMR frequencies.⁴⁰ The 0.0 ppm ¹¹B frequency was then calculated by multiplying the ¹H 0.0 ppm frequency by a factor 0.32083974. The dehydrated samples were packed into rotors in an inert nitrogen atmosphere glove box, and MAS experiments were performed with nitrogen gas to prevent rehydration. Specific experimental details for the NMR pulse experiments reported in this manuscript are provided in the Supporting Information and pulse sequence illustrations are provided in Figure S18.

Dynamic Nuclear Polarization NMR Spectroscopy. Prior to DNP analysis, samples were ground with a mortar and pestle and the powdered sample was then impregnated with $15-20 \,\mu\text{L}$ of the DNP polarizing agent solution. TEKPol was used as the polarizing agent, and was prepared as a $15-20 \,\text{mM}$ solution in tetrachloroethane.³⁴ After the samples were impregnated, they were packed into a sapphire 3.2 mm DNP rotor, with a Teflon screw insert and a zirconia drive cap.

DNP-enhanced solid-state NMR experiments were performed on a Bruker 9.4 T 400 MHz/263 GHz DNP solid-state NMR spectrometer equipped with a Bruker Avance III console.⁴¹ A Bruker 3.2 mm double resonance DNP probe, was used for acquisition of all DNP spectra. The sample temperature for DNP experiments was approximately 110 K and a MAS frequency of 10 kHz was employed. The microwave power for optimal DNP enhancements was directly optimized on the samples of interest. ¹H pulse lengths and RF fields were calibrated on each sample directly. ¹H chemical shifts were referenced with respect to tetramethylsilane. All cross-polarization magicangle spinning (CPMAS) experiments were employed with a variable amplitude ¹H contact pulse which was linearly ramped from 90% to 100% RF field (S12F). The variable amplitude ¹H contact pulse helps to broaden the Hartmann-Hahn match condition.⁴² SPINAL-64 ¹H heteronuclear decoupling was applied during signal acquisition with a ¹H RF field of ca. 100 kHz.⁴³

All experiments on the same nucleus have been processed with the same window function parameters for a quantitative comparison of the signal to noise ratio (SNR). ¹¹B NMR spectra of catalysts were processed with 100 Hz exponential line broadening. Simulations of all MAS ¹¹B solid-state NMR spectra

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were performed in the solid line shape analysis (SOLA) module v2.2.4 included in the Bruker Topspin v4.0.1 software.

Scanning Electron Microscopy. Fresh and spent h-BN and BNNT materials were characterized by SEM (LEO Supra55 VP) using an accelerating voltage of 2 keV.

X-Ray Absorption Spectroscopy. X-ray absorption experiments were carried out at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL). Beamline 6.3.2 was used for all experiments. Powdered samples were loaded onto carbon tape on an electrically-grounded sample stage for analysis. All spectra were taken in Total Electron Yield (TEY) mode under 10⁻⁷ torr. Spectra in this paper are shown after subtracting the dark spectrum to account for systematic error and electronic noise in the detector. Spectra were normalized to a maximum intensity of 1. Specific parameters for boron and oxygen K-edge measurements are listed in Tables S3 and Table S4.

ASSOCIATED CONTENT

Supporting Information. Additional solid-state ¹¹B NMR and DNP NMR experiments for h-BN and BNNTS, Raman spectra of fresh and spent h-BN and BNNTs, SEM & TEM Images for BNNTs, PXRD patterns for fresh h-BN, BET isotherms for fresh and spent h-BN, illustration of solid-state NMR pulse sequences, additional experimental descriptions for solid-state NMR, Raman spectroscopy, and TEM experiments, table summarizing additional ¹¹B solid-state NMR analytical simulation parameters, table summarizing measured DNP enhanced ¹¹B NMR parameters, tables summarizing XAS acquisition parameters (PDF).

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AUTHOR INFORMATION

Corresponding Author

*Prof. Aaron Rossini (arossini@iastate.edu); Prof. Ive Hermans (hermans@chem.wisc.edu)

Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. / ‡Authors A. M. Love and B. Thomas contributed equally to this work.

Notes

The authors declare no competing financial interest.

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