

Structure Determination of Boron-Based Oxidative Dehydrogenation Heterogeneous Catalysts with Ultra-High Field 35.2 T ^{11}B Solid-State NMR Spectroscopy

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Abstract

Boron-based heterogeneous catalysts, such as hexagonal boron nitride (*h*-BN) as well as supported boron oxides, are highly selective catalysts for the oxidative dehydrogenation (ODH) of light alkanes to olefins. Previous catalytic measurements and molecular characterization of boron-based catalysts by ^{11}B solid-state NMR spectroscopy and other techniques suggests that oxidized/hydrolyzed boron clusters are the catalytically active sites for ODH. However, ^{11}B solid-state NMR spectroscopy often suffers from limited resolution because boron-11 is an $I = 3/2$ half-integer quadrupolar nucleus. Here, ultra-high magnetic field ($B_0 = 35.2$ T) is used to enhance the resolution of ^{11}B solid-state NMR spectra and unambiguously determine the local structure and connectivity of boron species in *h*-BN nanotubes used as a ODH catalyst (spent *h*-BNNT), boron substituted MCM-22 zeolite [B-MWW] and silica supported boron oxide [B/SiO₂] before and after use as an ODH catalyst. One-dimensional direct excitation ^{11}B NMR spectra recorded at $B_0 = 35.2$ T are near isotropic in nature, allowing for the easy identification of all boron species. Two-dimensional ^1H - ^{11}B heteronuclear correlation NMR spectra aid in the identification of boron species with B-OH functionality. Most importantly, 2D ^{11}B dipolar double-quantum single-quantum homonuclear correlation NMR experiments were used to unambiguously probe boron-boron connectivity within all heterogeneous catalysts. These experiments are practically infeasible at lower, more conventional magnetic fields due to a lack of resolution and reduced NMR sensitivity. The detailed molecular structures determined for the amorphous oxidized/hydrolyzed boron layers on these heterogeneous catalysts will aid in the future development of next generation ODH catalysts.

Keywords: Solid-State NMR, Ultra-High Magnetic Field Strengths, ODH catalysis, Boron-based Catalysts, Quadrupolar Nuclei

Introduction

Light olefins are critical chemical feedstocks. Recently, boron-based heterogeneous catalysts have been shown to have remarkable selectivity for the oxidative dehydrogenation (ODH) of light alkanes to light olefins.¹⁻⁸ In 2016, hexagonal boron nitride (*h*-BN) was shown to outperform the previous state-of-the-art silica-supported vanadium oxide catalysts (V/SiO₂) for the ODH of propane to propylene (*e.g.*, *h*-BN: 79 % selectivity at 14 % conversion, V/SiO₂: 61 % selectivity at 9 % conversion).¹ Since this discovery, subsequent studies have sought to identify the active sites and design new boron-based ODH active heterogeneous catalysts. For example, Grant *et al.* tested a variety of boron containing materials for ODH catalysis and observed that only materials which became oxidized under ODH conditions were active catalysts.⁹

Previously, we used a combination of scanning electron microscopy (SEM), ¹¹B solid-state NMR (SSNMR) spectroscopy and soft X-ray absorption spectroscopy to show that a oxidized/hydrolyzed boron layer [denoted B₂O_x(OH)_{6-2x} (*x* = 0–3)] forms on the surface of bulk *h*-BN and *h*-BN nanotubes (*h*-BNNT) under ODH reaction conditions (500 °C, flow of C₃H₈, O₂ and N₂).¹⁰ Notably, bulk *h*-BN and *h*-BNNT does not show any signs of ODH deactivation after 24 hours on stream,¹ despite formation of significant amounts of surface oxidized/hydrolyzed boron species after just a few hours of ODH (Figure 1). The formation of surface oxidized/hydrolyzed boron species under reaction conditions may be relatively surprising because *h*-BN is known to be an inert material with high oxidative resistance.¹¹⁻¹⁴ Consistent with this observation, Zhou *et al.* previously reported the critical necessity of an induction period under reaction conditions to reach maximum ethane conversion for the ODH of ethane to ethylene, suggesting some degree of boron oxide functionality increases *h*-BN catalytic performance (Figure 1).^{7, 15} Recently, we have used ¹H, ¹¹B, ¹⁴N, and ¹⁵N SSNMR spectroscopies and plane-wave DFT calculations to show that the edges of bulk and exfoliated *h*-BN nanosheets are terminated with amine (N-H) and boron oxide/hydroxide functional groups, such as BN₂OH and BNO(OH)/BNO₂.¹⁶ The functional groups residing on the edges of *h*-BN likely play a key role in the formation of a surface/edge oxidized/hydrolyzed boron layer under ODH conditions.

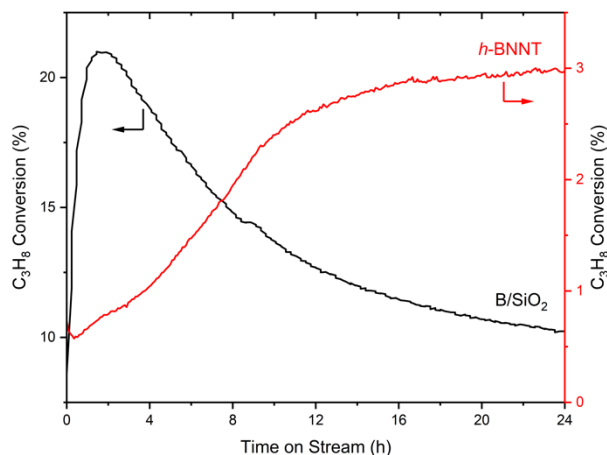


Figure 1. Propane conversion as a function of time on stream (TOS) for (red) *h*-BNNT and (black) B/SiO₂. The shape of the *h*-BNNT induction period curve shows a steady increase, indicating surface oxidation that generates active sites. The shape of the B/SiO₂ curve shows a large increase at short TOS followed by a loss of conversion at longer TOS, indicating surface restructuring, followed by the loss of active species.

Further exploration of ODH active boron species have been conducted through the synthesis and catalytic testing of supported boron oxide heterogenous catalysts.^{7-8, 17-18} Specifically, incipient wetness impregnation of triisopropyl borate [B(O^{*i*}Pr)₃] onto silica yields a silica supported low weight percent (~ 1 wt. % B) boron oxide heterogenous catalyst (B/SiO₂) that performs comparable to that of *h*-BN, with only slightly lower propylene selectivity.⁷ However, B/SiO₂ does display a *ca.* 50 % decrease in propane conversion over a 24 hour period before stabilizing (Figure 1); during this induction period, *ca.* 50 % of boron also leaches from the catalyst.⁷ Via ¹H and ¹¹B SSNMR, Raman, and infrared (IR) spectroscopies, it was suggested that clusters of oxidized/hydrolyzed boron on the surface of silica corresponded to the active sites, supporting the hypothesis that oxidized/hydrolyzed boron in *h*-BN is catalytically active.⁷ However, precise identification of the boron molecular structure and boron-boron connectivity within the oxidized/hydrolyzed boron clusters is lacking. Interestingly, an MCM-22 zeolite isomorphously substituted with boron (*ca.* 1 wt. % B, referred to as B-MWW) was found to be catalytically inactive.¹⁷ The lack of catalytic activity for this material was ascribed to the fact that most of the boron exists as isolated three-coordinate boron oxide fully incorporated into the zeolite framework [B(OSi)₃]. The results of this study and others therefore suggests that multiple boron atoms must be clustered, forming a B-O-B network, to provide an active site for ODH catalysis. Furthermore, a recent study investigating the ODH reaction mechanism by comparing quantum

chemical calculations with catalytic activity measurements illustrated that the formation of a oxidized/hydrolyzed boron cluster is required to promote ODH.¹⁹

In summary, taking into consideration all of these prior studies of boron-based ODH catalysts, there is a consensus that oxidized/hydrolyzed surfaces of *h*-BN host the catalytically active sites. However, the molecular structure composing the interface between the *h*-BN framework and the proposed catalytically active oxidized/hydrolyzed boron layer is not clearly known, ultimately hindering further examination of this highly important catalyst.

High-resolution magic-angle spinning (MAS) SSNMR spectroscopy is a very powerful technique to probe molecular structure of active sites within heterogeneous catalysts.²⁰⁻²⁹ As mentioned above, MAS ¹¹B SSNMR spectroscopy has been previously used to investigate *h*-BN, *h*-BNNT, B/SiO₂ and B-MWW before and after ODH. Boron-11 (¹¹B) is a spin $I = 3/2$ half-integer quadrupolar nucleus that exhibits a relatively high Larmor frequency (~ 3.1 times lower than ¹H) and high natural isotopic abundance ($\sim 80\%$). ¹¹B electric field gradient (EFG) tensors – quadrupolar coupling constant (C_Q) and asymmetry parameter (η) – and isotropic chemical shifts (δ_{iso}) provide information about the local chemical environment (bonded atoms and symmetry) surrounding the boron nucleus.³⁰⁻³² One major difficulty associated with ¹¹B SSNMR spectroscopy studies is that the resulting NMR signals are broadened by the second-order quadrupolar interaction (QI).^{30, 33-34} The broadening of central-transition (CT) NMR signals by the second-order QI is proportional to the square of C_Q . C_Q is related to the symmetry at the nucleus, with trigonal planar boron sites having C_Q between 2.5 and 3 MHz, while for tetrahedral sites C_Q is generally less than 1 MHz.^{32, 35} Fortunately, broadening of the CT NMR signals by the second-order QI is inversely proportional to magnetic field strength (B_0). Therefore, increasing B_0 decreases the second-order QI and results in narrower ¹¹B NMR signals. The interested reader is referred to a number of excellent reviews on solid-state NMR spectroscopy of half-integer quadrupolar nuclei.^{30-31, 34} For the previously mentioned boron-based heterogeneous catalysts (*h*-BN, *h*-BNNT, B/SiO₂ and B-MWW), there is significant ¹¹B NMR signal overlap between almost all boron species at $B_0 = 9.4 - 14.1$ T.^{7-8, 10, 17} This extensive ¹¹B NMR signal overlap hinders the ability to unambiguously probe boron structural connectivity through 2D homonuclear correlation NMR experiments. Recent advances in magnet design has led to the development of a 36 T Series-Connected Hybrid (SCH) magnet available for high resolution SSNMR spectroscopy at 35.2 T ($\nu_0(^1H) = 1500$ MHz).³⁶ The advantages of the 35.2 T SCH magnet for studying half-integer

quadrupolar nuclei such as ^{17}O , ^{27}Al , ^{43}Ca and ^{67}Zn has recently been demonstrated for a variety of solid materials.³⁷⁻⁴⁵

In this contribution, 35.2 T ^{11}B SSNMR spectroscopy is used to determine the boron molecular structure and connectivity in boron-based heterogeneous catalysts (*h*-BNNT, B/SiO₂ and B-MWW). One-dimensional (1D) direct excitation ^{11}B solid-state NMR spectra recorded with a B_0 of 35.2 T are near isotropic in nature, allowing for the straightforward identification of all boron species in the catalysts. 2D $^{11}\text{B}\{^1\text{H}\}$ dipolar heteronuclear multiple-quantum correlation (D-HMQC) NMR spectra aid in the identification of boron species with B-OH functionality. Most importantly, the 35.2 T SCH magnet offers enough sensitivity to record 2D ^{11}B double-quantum-single-quantum (DQ-SQ) homonuclear correlation NMR spectra and line narrowing in both spectral dimensions provides resolution to enable the unambiguous determination of molecular structure in all boron-based heterogeneous catalysts.

Experimental

Materials

The preparation and catalytic testing for each material discussed here have been previously described. Fresh *h*-BNNT were obtained from BNNT, LLC and used without further treatment. B/SiO₂ was prepared via incipient wetness impregnation of amorphous SiO₂ (Aerosil 300 from Evonik, specific surface area of 300 m²·g⁻¹) with a solution of triisopropyl borate (B(O^{*i*}Pr)₃, Sigma Aldrich) in dry isopropanol, as detailed in our previous work.⁷ The impregnated material was calcined to 550 °C at 1 °C·min⁻¹ and held at 550 °C for 3 h. The hydrothermal synthesis of B-MWW is described in our previous report.¹⁷ B-MWW was calcined to 580 °C at 2 °C·min⁻¹ and held at 580 °C for 6 h.

To prepare the spent samples, 50–100 mg of each material was added to a quartz reactor tube (8 mm i.d.) and supported on a bed of quartz wool. For *h*-BNNT and B/SiO₂, the reactor tube was heated to 500 °C under a flow of O₂ and N₂ (20% and 80%, respectively; total flow rate 40 mL·min⁻¹) and held at 500 °C for 1 h to allow the temperature to stabilize. After temperature stabilization, the gas feed was then switched to a flow of O₂, C₃H₈, and N₂ (15%, 30%, and 55%, respectively), while maintaining a total flow rate of 40 mL·min⁻¹. The *h*-BNNT sample was treated under these conditions for 2 h time on stream (TOS) and the B/SiO₂ sample for 24 h TOS. B-MWW and fresh and spent B/SiO₂ were dehydrated at 500 °C for 12 h under a flow of air to mimic

reaction conditions. The dehydrated samples were flame-sealed in ampules and handled in an inert nitrogen atmosphere glovebox. The B-MWW and B/SiO₂ materials were packed into the NMR rotors inside a N₂ filled glovebox. The spent *h*-BNNT material was handled in air.

Catalytic Measurements

To generate the induction period plot, 25 mg *h*-BNNT (Millipore Sigma) and 25 mg B/SiO₂ were added to a quartz reactor tube (8 mm i.d.) in separate experiments and supported on a bed of quartz wool. The reactor tube was heated to 500 °C under a flow of O₂ and N₂ (20% and 80%, respectively; total flow rate 40 mL·min⁻¹) and held at 500 °C for 1 h to allow the temperature to stabilize. After temperature stabilization, the gas feed was then switched to a flow of O₂, C₃H₈, and N₂ (15%, 30%, and 55%, respectively), while maintaining a total flow rate of 40 mL·min⁻¹. Both materials were treated for 24 hours on stream.

Solid-State NMR Spectroscopy at Iowa State University

$B_0 = 9.4\text{ T}$. A direct excitation ¹¹B spin echo NMR spectrum of spent *h*-BNNT was recorded on a 9.4 T ($\nu_0(^1\text{H}) = 400\text{ MHz}$) Bruker wide-bore magnet spectrometer equipped with a Bruker Avance III HD console and 2.5 mm HXY MAS probe configured in double resonance mode. The ¹¹B spin echo NMR spectrum was recorded with a 25 kHz MAS frequency, a 50 s recycle delay ($\sim 10 \times T_1$), 16 transients, 2 rotor cycles of evolution per half echo (80 μs) and 100 kHz radio frequency (RF) field of SPINAL-64 ¹H heteronuclear dipolar decoupling throughout the entire experiment.⁴⁶ The ¹¹B $\pi/2$ and π pulse lengths were 15 and 30 μs in duration, corresponding to a 8.3 kHz RF field and a 16.67 kHz CT nutation frequency. The ¹¹B NMR spectrum was indirectly referenced through ¹H chemical shifts referenced to neat tetramethylsilane with adamantane as a secondary chemical shift reference ($\delta(^1\text{H}) = 1.82\text{ ppm}$) and the IUPAC recommended relatively ¹¹B NMR frequency (BF₃·Et₂O).⁴⁷

$B_0 = 14.1\text{ T}$. A direct excitation ¹¹B spin echo NMR spectrum of spent *h*-BNNT was recorded on a 14.1 T ($\nu_0(^1\text{H}) = 600\text{ MHz}$) Bruker wide-bore magnet spectrometer equipped with a Bruker Avance II console and 2.5 mm HXY MAS probe configured in triple resonance mode. The ¹¹B spin echo NMR spectrum was recorded with a 25 kHz MAS frequency, a 50 s recycle delay ($\sim 10 \times T_1$), 16 transients, 1 rotor cycle of evolution per half echo (40 μs) and 100 kHz RF field of SPINAL-64 ¹H heteronuclear dipolar decoupling throughout the entire experiment.⁴⁶ The ¹¹B

$\pi/2$ and π pulse lengths were 15 and 30 μs in duration, corresponding to a 8.3 kHz RF field and a 16.67 kHz CT nutation frequency. The ^{11}B NMR spectrum was indirectly referenced through ^1H chemical shifts referenced to neat tetramethylsilane with adamantane as a secondary chemical shift reference ($\delta(^1\text{H}) = 1.82$ ppm) and the IUPAC recommended relatively ^{11}B NMR frequency ($\text{BF}_3 \cdot \text{Et}_2\text{O}$).⁴⁷

Solid-State NMR Spectroscopy at the NHMFL

$B_0 = 19.6$ T. A direct excitation ^{11}B spin echo NMR spectrum of spent *h*-BNNT was recorded on a 19.6 T ($\nu_0(^1\text{H}) = 833$ MHz) magnet spectrometer equipped with a Bruker Avance NEO console and 3.2 mm Low-E HX MAS probe. The NMR spectrum was recorded with a 14 kHz MAS frequency, a 100 s recycle delay, 8 transients, 10 rotor cycles of evolution per half echo (0.7 ms) and 50 kHz RF field of SPINAL-64 ^1H heteronuclear dipolar decoupling throughout the entire experiment.⁴⁶ The ^{11}B $\pi/2$ and π pulse lengths were 5 and 10 μs in duration, corresponding to a 25 kHz RF field and a 50 kHz CT nutation frequency. The ^{11}B NMR spectrum was referenced by calibrating the 4-coordinate ^{11}B NMR signal to 1.46 ppm, as determined from the ^{11}B NMR spectrum recorded at $B_0 = 14.1$ T. The 4-coordinate NMR signal could be used to reference the ^{11}B NMR spectrum recorded at $B_0 = 19.6$ T because the quadrupolar induced shift is negligible for the 4-coordinate ^{11}B NMR signal when $B_0 > 9.4$ T.

$B_0 = 35.2$ T. The Series Connected Hybrid (SCH) magnet was built and is operated at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL.³⁶ SSNMR experiments were performed on the SCH magnet operating at $B_0 = 35.2$ T ($\nu_0(^1\text{H}) = 1500$ MHz), equipped with a Bruker Avance NEO console and 3.2 mm Low-E HX probe designed and built at the NHMFL. All NMR spectra were recorded with an 18 kHz MAS frequency and the rotors were spun with N_2 gas. The magnet field strength of the hybrid powered SCH magnet is regulated with an integrated control system of a magnetic flux sensor and ^7Li NMR signal from an external lock sample placed 9 mm below the NMR sample.³⁶ ^1H chemical shifts reported in the 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra were referenced by calibrating the chemical shift of one of the resolved ^1H NMR signals to that previously determined at lower magnetic field strengths ($B_0 = 9.4$ T or 14.1 T).^{7, 10, 17} All ^1H NMR spectra recorded at the lower magnetic field strengths were referenced to neat tetramethylsilane with adamantane as a secondary chemical shift reference ($\delta(^1\text{H}) = 1.82$ ppm). ^{11}B chemical shifts were initially referenced indirectly using ^2H shifts of D_2O at room temperature ($\delta(^2\text{H}) = 4.7$ ppm) and the IUPAC relative ^{11}B NMR frequency (of $\text{BF}_3 \cdot \text{Et}_2\text{O}$).⁴⁷ To ensure the ^{11}B NMR frequencies

reported here are accurate, previously reported NMR spectra acquired at lower magnetic field strengths ($B_0 = 9.4$ T or 14.1 T) were used to correct the slight referencing inaccuracies.^{7, 10, 17} The ^{11}B spectra of spent *h*-BNNT were referenced by calibrating the 4-coordinate ^{11}B NMR signal to 1.46 ppm, as determined from the ^{11}B NMR spectrum recorded at $B_0 = 14.1$ T. The 4-coordinate NMR signal could be used to reference the ^{11}B NMR spectrum recorded at $B_0 = 35.2$ T because the quadrupolar induced shift is negligible for the 4-coordinate ^{11}B NMR signal when $B_0 > 9.4$ T. The ^{11}B NMR spectra of B-MWW were indirectly referenced by recording a ^1H NMR spectrum of B-MWW at $B_0 = 35.2$ T and calibrating the resolved Si-OH ^1H NMR signal to 2.45 ppm, as determined from the 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra reported here and previously reported ^1H NMR spectra recorded at $B_0 = 9.4$ T.¹⁷ The previously reported IUPAC recommended relative ^{11}B NMR frequency ($\text{BF}_3\cdot\text{Et}_2\text{O}$) was used to determine the ^{11}B NMR spectrometer frequency from the referenced ^1H NMR spectrometer frequency determined from the ^1H NMR spectrum of B-MWW recorded at $B_0 = 35.2$ T.⁴⁷ B/SiO₂ ^{11}B NMR spectra were indirectly referenced using the ^1H NMR spectrometer frequency determined from the $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra of B/SiO₂ recorded at $B_0 = 35.2$ T. The ^{11}B NMR spectrometer frequency was then determined via the previously reported IUPAC recommended relative ^{11}B NMR frequency ($\text{BF}_3\cdot\text{Et}_2\text{O}$).⁴⁷ An analytical simulation of the $^{11}\text{B}\{^1\text{H}\}$ D-HMQC NMR spectrum of fresh B/SiO₂ recorded at $B_0 = 35.2$ T shows that the $\delta_{\text{iso}}(^{11}\text{B})$ are within *ca.* 0.4 ppm of that previously determined at $B_0 = 9.4$ T.⁷ All NMR spectra of the same sample were recorded on the same day without changing the magnetic field strength (i.e. ramping up or down). Therefore, all subsequent ^{11}B NMR spectra could be referenced from the initially referenced ^{11}B NMR spectrum mentioned above (if the spectra were recorded within *ca.* 30 mins to ensure not much field drift occurred) or by calibrating a well resolved ^{11}B NMR signal observed in the initially referenced ^{11}B NMR spectrum. It should be noted that there is *ca.* 1 ppm reproducibility with repeated sample changes for the chemical shift referencing and the homogeneity is *ca.* 1 ppm over 1 cm^3 . In addition, there can be significant magnetic field drift of up to *ca.* 0.5 ppm during an NMR experiment which may broaden the NMR signals. Therefore, taking into consideration the potential for magnetic field drift and the indirect referencing methods mentioned above, we note that there may potentially be up to *ca.* 1 ppm uncertainty in the reported ^{11}B NMR frequencies. However, this uncertainty does not affect the analysis presented in this contribution.

All experimental NMR parameters (recycle delay, number of scans, transmitter offset, t_1 TD points, t_1 dwell (Δt_1), t_1 acquisition time, dipolar recoupling duration, and total experimental acquisition time) are given in Table S1 of the Supporting Information (SI). Direct excitation ^{11}B spin echo NMR spectra were performed with 1 rotor cycle of evolution (55.6 μs) per half echo and ^{11}B $\pi/2$ and π pulse lengths of 3 μs and 6 μs , corresponding to a 41.6 kHz RF field and a 83.3 kHz CT nutation frequency. Direct excitation ^{11}B pulse acquire NMR spectra were performed with a 1 μs 30° excitation pulse (41.6 kHz RF field, 83.3 kHz CT nutation frequency). $^{11}\text{B}\{^1\text{H}\}$ dipolar heteronuclear multiple-quantum correlation (D-HMQC) experiments were recorded with the symmetry-based $SR4_1^2$ heteronuclear dipolar recoupling sequence applied to the ^1H spins.⁴⁸⁻⁵¹ ^{11}B $\pi/2$ and π pulse lengths were 12 μs and 24 μs in duration, corresponding to an *ca.* 10.4 kHz RF field (20.8 kHz CT nutation frequency), and the ^1H $\pi/2$ pulse length was 5.4 μs in duration, corresponding to an *ca.* 46.3 kHz RF field. ^{11}B dipolar double-quantum-single-quantum (DQ-SQ) homonuclear correlation experiments were recorded by directly exciting DQ coherence, evolving the chemical shift under t_1 , and then converting the DQ coherence to SQ coherence for detection.⁵²⁻

⁵⁴ A central-transition selective π pulse was applied during the t_1 evolution to further ensure only CT DQ coherence was selected during phase cycling (i.e. coherence between two spins) and any DQ coherence involving the satellite transitions (ST) were rejected.⁵² The $BR2_2^1$ homonuclear dipolar recoupling sequence was used to generate DQ coherence directly from Z-magnetization, as previously described by Wang *et al.*⁵⁴ Each π pulse in the $BR2_2^1$ recoupling block was 1 rotor cycle in duration (55.6 μs at 18 kHz MAS). 50 kHz RF field of ^1H heteronuclear decoupling was performed throughout the entire DQ-SQ experiment using the SPINAL-64 decoupling sequence.⁴⁶ As mentioned in Table S1, two-dimensional (2D) ^{11}B DQ-SQ NMR spectra of *h*-BNNT were recorded with a t_1 dwell of half a rotor cycle (~ 27.8 μs), corresponding to an indirect spectral window of twice the spinning frequency, needed to cover the entire DQ frequency range. The dipolar Hamiltonian under the $BR2_2^1$ recoupling depends on the rotor rotation angle. A half rotor period shift results in a sign reversal of the NMR signal.⁵⁵ In order to correct the sign reversal of the NMR signal, the 2D NMR experiments were recorded with the States 2D acquisition mode and processed with the States-TPPI 2D acquisition mode. A WURST pulse with a frequency sweep equal to the MAS frequency was applied at either 300 kHz or 250 kHz off-resonance before the start of all $^{11}\text{B}\{^1\text{H}\}$ D-HMQC and ^{11}B DQ-SQ NMR experiments, respectively, to enhance the CT

polarization from STs for sensitivity enhancement.⁵⁶⁻⁵⁸ A schematic illustration of the $^{11}\text{B}\{^1\text{H}\}$ D-HMQC and ^{11}B DQ-SQ pulse sequences is given in Figure S1. Analytical simulations of the experimental spectra were performed using the ssNake NMR software.⁵⁹

Results and Discussion

Spent h-BNNT – Probing the Interface between BN and Boron Oxide. We first demonstrate the utility of ultra-high field, $B_0 = 35.2$ T, ^{11}B SSNMR spectroscopy for structural characterization of boron-based heterogeneous catalysts by studying a spent *h*-BNNT ODH catalyst. The spent sample was obtained by flowing propane, O_2 , and N_2 (6:3:11 $\text{C}_3\text{H}_8:\text{O}_2:\text{N}_2$, total flow rate 40 mL min^{-1}) over ~ 100 mg of *h*-BNNT at 500 °C for two hours. 1D direct excitation ^{11}B spin echo SSNMR spectra of the spent *h*-BNNT were recorded at magnetic fields of 9.4 T ($\nu_0(^1\text{H}) = 400$ MHz), 14.1 T ($\nu_0(^1\text{H}) = 600$ MHz), 19.6 T ($\nu_0(^1\text{H}) = 833$ MHz) and 35.2 T ($\nu_0(^1\text{H}) = 1500$ MHz) (Figure 2). Due to the decrease in broadening by the second-order QI and the increase in chemical shift dispersion, the resolution of the ^{11}B SSNMR spectra will increase with the square of the applied magnetic field (assuming other inhomogeneous broadening is negligible). However, structural disorder and magnetic field drift will slightly decrease the resolution gain. Comparison of 1D ^{11}B NMR spectra obtained at different magnetic fields shows that the broadening by the second-order QI is dominant at lower fields and illustrates the dramatic increase in resolution upon increasing the field to 35.2 T. At $B_0 = 9.4$ T, all ^{11}B NMR signals overlap, making it challenging to fully analyze the 1D ^{11}B NMR spectrum. Even at $B_0 = 19.6$ T there is still considerable signal overlap in the higher frequency ^{11}B NMR resonances. At these lower fields, time-consuming 2D ^{11}B triple-quantum multiple-quantum MAS (3Q-MQMAS) NMR experiments are required to resolve the ^{11}B NMR signals.⁶⁰⁻⁶¹ However, by increasing the B_0 to 35.2 T, all ^{11}B NMR signals are resolved because the second-order QI becomes small for ^{11}B NMR signals with $C_Q < 3$ MHz at $B_0 = 35.2$ T (~ 1 ppm for $C_Q = 3$ MHz), resulting in nearly isotropic CT lineshapes (Figure S2, see Supporting Information for more discussion). The remaining line width can be mostly attributed to chemical shift distribution resulting from structural disorder and magnetic field inhomogeneity fluctuations, estimated to cause less than 1 ppm of broadening.³⁶ The 1D MAS ^{11}B spin echo spectrum of spent *h*-BNNT recorded at $B_0 = 35.2$ T was recorded with a recycle delay $\geq 5 \times T_1$ to give quantitative peak areas (Table 1, Figure S4).

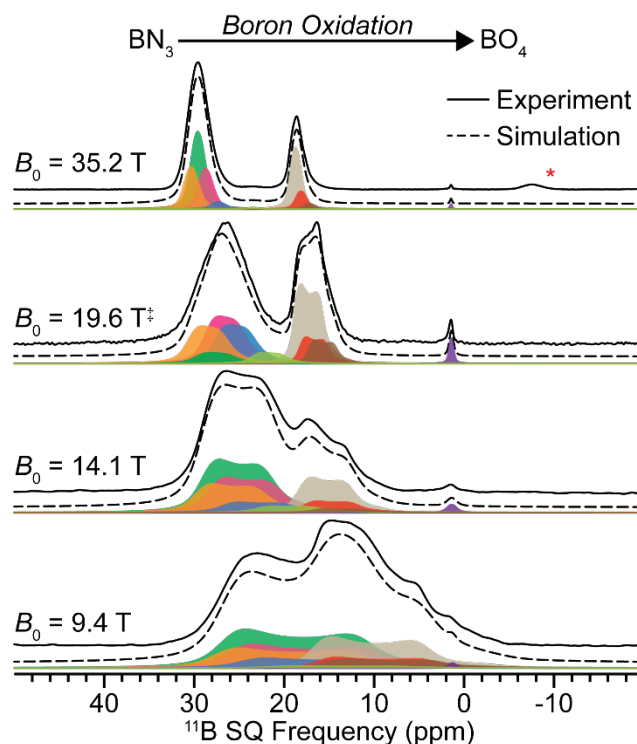


Figure 2. 1D direct excitation ^{11}B spin echo spectra of spent *h*-BNNT recorded at (top to bottom) 35.2 T ($\nu_0(^1\text{H}) = 1500$ MHz), 19.6 T ($\nu_0(^1\text{H}) = 833$ MHz), 14.1 T ($\nu_0(^1\text{H}) = 600$ MHz) and 9.4 T ($\nu_0(^1\text{H}) = 400$ MHz). The solid lines represent the experimental spectra while the dashed lines are analytical simulations of the CT quadrupolar powder patterns. Note that the relative peak intensities are different (and not quantitative) in the ^{11}B spectrum recorded at $B_0 = 19.6$ T because a *ca.* 1.5 ms total echo period was used in the spin echo sequence (see Figure S5 Supporting Information for more discussion).

The 1D ^{11}B spin echo spectrum shows two main groups of signals centered at *ca.* 29 ppm and *ca.* 18 ppm. The trigonal planar BN_3 sites of *h*-BNNT are known to have $\delta_{\text{iso}}(^{11}\text{B})$ of *ca.* 30 ppm. The $\delta_{\text{iso}}(^{11}\text{B})$ decreases as nitrogen atoms in trigonal planar BN_3 units are replaced with bridging oxygen atoms or hydroxyl groups, while the C_Q remains relatively constant ($\sim 2.5 - 3.0$ MHz).^{10, 16, 32, 35} Therefore, we can assign the ^{11}B NMR signals to BN_3 (31.2 – 30.5 ppm), $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ ($x = 0 - 1$; 29.6 – 28.2 ppm), $\text{BNO}_x(\text{OH})_{2-x}$ ($x = 0 - 2$; 24.2 ppm), $\text{BO}_x(\text{OH})_{3-x}$ ($x = 0 - 3$; 19.4 – 17.8 ppm) and $\text{BO}_x(\text{OH})_{4-x}$ ($x = 0 - 4$; 1.5 ppm). Note that, unless stated otherwise, the formulas given in the preceding and following sentences refer to number of atoms bonded to boron, rather than the chemical formula of the phase. The relative populations of all boron species were determined through both analytically simulating the experimental NMR spectrum and integrating all ^{11}B NMR signals (Table 1). The analytical simulation was required to differentiate the populations between BN_3 and $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ since the peaks are still partially overlapped at $B_0 = 35.2$ T. Based upon

the peak areas, the BN_3 units corresponds to *ca.* 50 % of all boron species present in the spent *h*-BNNT catalyst after two hours of ODH catalysis. The other 50 % of all boron species are either fully or partially oxidized, with *ca.* 28 % being fully oxidized ($\sim 27.5\%$ $\text{BO}_x(\text{OH})_{3-x}$ and $\sim 0.5\%$ $\text{BO}_x(\text{OH})_{4-x}$) and *ca.* 22 % being partially oxidized ($\sim 20\%$ $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ and $\sim 0.5 - 2\%$ $\text{BNO}_x(\text{OH})_{2-x}$). It should be noted that analytical simulations of ^{11}B NMR spectra recorded at lower magnetic fields (9.4 – 19.6 T) lead to less accurate determinations of boron populations due to significant NMR signal overlap, further illustrating the power of using ultra-high field NMR for quadrupolar nuclei. Below, ^1H - ^{11}B heteronuclear and ^{11}B homonuclear 2D correlation NMR experiments are used to confirm these assignments and probe the molecular structure and connectivity between all boron species present. Unless stated otherwise, all following NMR experiments were performed at $B_0 = 35.2$ T with a MAS frequency of 18 kHz.

Table 1. NMR Fitting Parameters^a and Relative Populations for the 1D ^{11}B Spin Echo Spectrum of Spent *h*-BNNT Recorded at $B_0 = 35.2$ T.

Boron Species ^b	$\delta_{\text{iso}}(^{11}\text{B})$ (ppm)	C_Q (MHz)	Population Determined from Analytical Simulation (%)	Population Determined from Integration (%)
BN_3	31.2 – 30.5	2.85	51.2	69.8 ^c
BN_2O	29.6 – 28.2	2.85	20.3	
BNO_2	24.2	2.7	0.6	1.9
BO_3	19.4 – 17.8	2.5	27.5	27.6
BO_4	1.5	1.2	0.4	0.7

^aAll peaks were fit with $\eta = 0$. ^bOnly heteroatoms covalently bonded to boron are listed.

^cIntegration includes BN_3 and BN_2O due to spectral overlap.

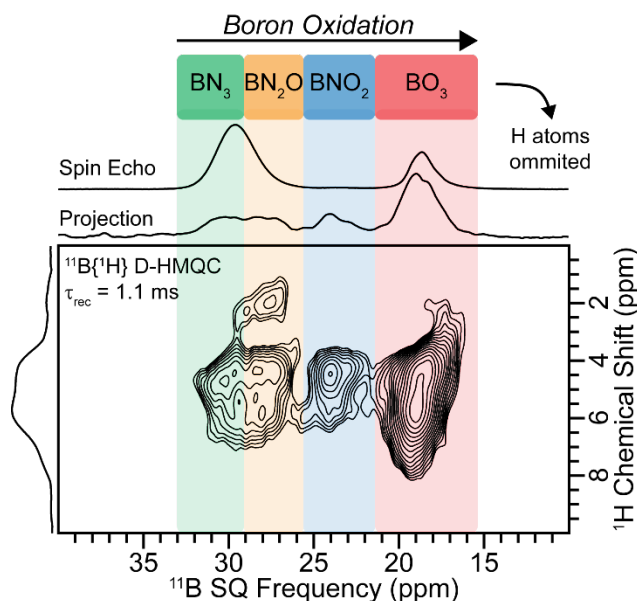


Figure 3. 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC NMR spectrum of spent *h*-BNNT recorded at 35.2 T ($\nu_0(^1\text{H}) = 1500$ MHz) with 18 kHz MAS and 1.1 ms of total $SR4_1^2$ heteronuclear dipolar recoupling applied to the ^1H spins. The highlighted colors indicate which heteroatoms are bonded to the trigonal planar boron units. The complete formula of each unit is as follows: BN_3 , $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ ($x = 0 - 1$), $\text{BNO}_x(\text{OH})_{2-x}$ ($x = 0 - 2$), $\text{BO}_x(\text{OH})_{3-x}$ ($x = 0 - 3$).

While the $\delta_{\text{iso}}(^{11}\text{B})$ is sensitive to the degree of oxidation (i.e. BN_2O vs. BNO_2), it is not as sensitive to whether the oxygen species correspond to bridging oxygen atoms or hydroxyl groups (i.e. BN_2OB vs. BN_2OH). ^1H - ^{11}B dipolar-based heteronuclear correlation SSNMR experiments can probe the local proximity of hydrogen atoms to boron atoms and aid in differentiating boron species with hydroxyl groups and bridging oxygen atoms because the dipolar coupling between two spins is inversely proportional to the cube of their internuclear distance ($D_{ij} \propto r_{ij}^{-3}$). 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra of spent *h*-BNNT were recorded with either 1.1 ms or 1.6 ms of total $SR4_1^2$ heteronuclear dipolar recoupling applied to the ^1H spins (Figure 3 and S6, respectively).⁴⁸⁻⁵⁰ Longer recoupling times enable weaker dipolar couplings and correlations arising from further internuclear distances to be probed. Both 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra display two intense ^1H NMR signals at ~ 4.2 and ~ 5.7 ppm and a lower intensity shoulder at ~ 7.1 ppm. The 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectrum recorded with 1.1 ms of total $SR4_1^2$ heteronuclear dipolar recoupling displays an additional ^1H NMR signal at ~ 2 ppm. The observed ^1H NMR signals display strong heteronuclear correlations to all ^{11}B NMR signals that were observed in the direct excitation 1D

spin echo spectrum, although the relative intensity of the ^{11}B NMR signals is clearly different in the HMQC spectrum. As expected, the ^{11}B NMR signals from BN_3 units are greatly attenuated in the D-HMQC spectrum because most will be distant from nearby ^1H spins. The D-HMQC signals for BN_3 likely arise from NH groups found on the zigzag or armchair edges, or alternatively, they could arise from BN_3 units that are adjacent to hydroxide terminated units (e.g., BN_2OH , BNOOH , etc.).¹⁶

Comparison of $^{11}\text{B}\{^1\text{H}\}$ D-HMQC signal build-up rates for the different boron species shows that the HMQC NMR signal for $\text{BO}_x(\text{OH})_{3-x}$ is significantly reduced in the 2D spectra due to a short ^{11}B refocused transverse relaxation constant (T_2') under ^1H heteronuclear dipolar recoupling (Figure S7). The other boron species only see a slight reduction in signal intensity as they possess a much longer ^{11}B T_2' (Figure S7). However, comparison of the $^{11}\text{B}\{^1\text{H}\}$ D-HMQC build-up curves shows that the fully oxidized boron species $[\text{BO}_x(\text{OH})_{3-x}]$ generated at least an 80% more intense $^{11}\text{B}\{^1\text{H}\}$ HMQC NMR signal than that of all other boron species. The relative populations of the boron species determined above and their respective signal intensities observed in the $^{11}\text{B}\{^1\text{H}\}$ D-HMQC build-up curves suggest that the fully oxidized boron species $[\text{BO}_x(\text{OH})_{3-x}]$ contain a much higher population of hydroxyl groups than that of the partially oxidized boron species $[\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ or $\text{BNO}_x(\text{OH})_{2-x}]$. For the partially oxidized boron species, a higher relative percent of $\text{BNO}_x(\text{OH})_{2-x}$ contains hydroxyl groups than that of $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ as their $^{11}\text{B}\{^1\text{H}\}$ D-HMQC signal intensities are similar, despite their *ca.* 1:20 ratio in population given by the quantitative ^{11}B spin echo spectrum. As is shown below, most $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ species contain a bridging oxygen atom (BN_2O) which connects the BN framework to the fully oxidized/hydrolyzed boron phase.

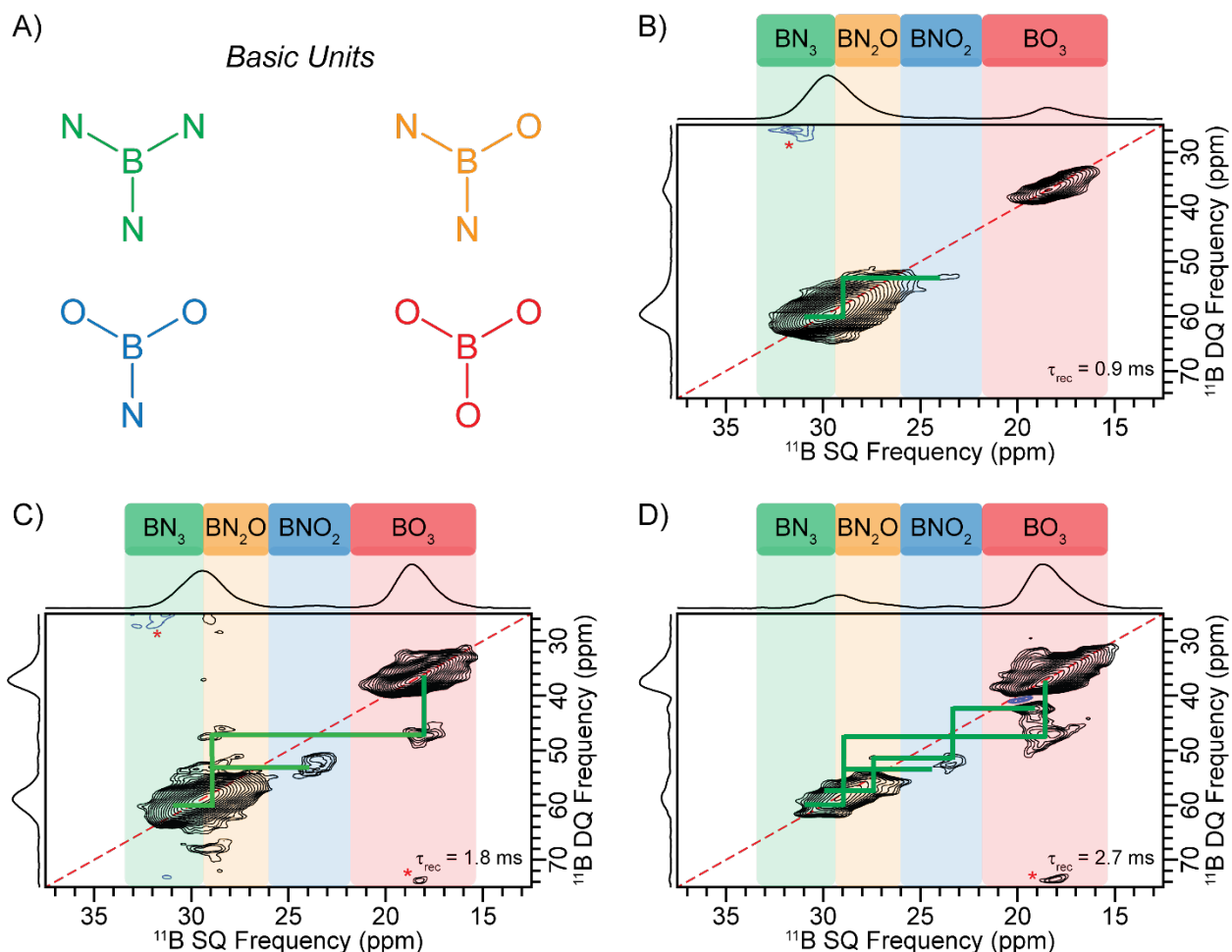


Figure 4. (A) Basic boron-centered units present in spent *h*-BNNT (H atoms are omitted for simplicity). (B-D) 2D ^{11}B dipolar DQ-SQ NMR spectra of spent *h*-BNNT recorded at 35.2 T ($\nu_0(^1\text{H}) = 1500$ MHz) with 18 kHz MAS and either (B) 0.9 ms, (C) 1.8 ms or (D) 2.7 ms of total $BR2\frac{1}{2}$ homonuclear dipolar recoupling. The highlighted colors correspond to which heteroatoms are bonded to trigonal planar boron, as shown in (A). The solid green line illustrates the correlations observed between different boron species. The dashed red line indicates auto-correlations. The red asterisk (*) indicates spinning sidebands.

2D ^{11}B dipolar DQ-SQ homonuclear correlation SSNMR experiments were performed on the spent *h*-BNNT catalysts to probe the connectivity between the BN framework and the oxidized/hydrolyzed boron phase. 2D homonuclear DQ correlation solid-state SSNMR experiments are powerful techniques to determine connectivity and structure in solids. For example, Deng and co-workers demonstrated the value of high field ($B_0 = 18.8$ T) ^{11}B DQ-SQ NMR for structural characterization of (B, Ag)-codoped TiO_2 catalysts.⁶² 2D dipolar DQ-SQ homonuclear correlation NMR experiments have been previously applied to a number of half-integer quadrupolar nuclei, such as ^7Li , ^{11}B , ^{17}O , ^{23}Na and ^{27}Al .^{44, 52-54, 62-71} Dipolar DQ-SQ NMR

experiments show correlations between homonuclear spins that are dipole coupled (spin pairs separated by less than approximately 4-5 Å). In a 2D dipolar DQ-SQ experiment, an NMR signal (DQ coherence) is observed in the indirect dimension at a frequency offset equal to the sum of the frequency offsets of the two correlated spins. Auto-correlations arise when the coupled spins have the same frequency and fall along the dashed diagonal line on the 2D plots where the indirect dimension offset is equal to twice the direct dimension frequency. Performing the DQ-SQ homonuclear correlation experiments at $B_0 = 35$ T provides line narrowing by reducing the second-order QI along both the DQ and SQ dimensions, providing sufficient resolution to distinguish correlations between nearly all possible pairs of correlated ^{11}B spins.

Three 2D ^{11}B dipolar DQ-SQ homonuclear correlation NMR spectra of spent *h*-BNNT were recorded with either 0.9 ms, 1.8 ms or 2.7 ms of total $BR2\frac{1}{2}$ homonuclear dipolar recoupling (Figure 4).^{52, 54} Longer recoupling times will probe ^{11}B - ^{11}B spins separated by larger distances. As expected, the 2D ^{11}B DQ-SQ NMR spectrum recorded with 0.9 ms of homonuclear dipolar recoupling displays intense autocorrelations for the signals assigned to BN_3 , $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ and $\text{BO}_x(\text{OH})_{3-x}$. The strong BN_3 and $\text{B}(\text{O})_x(\text{OH})_{3-x}$ autocorrelations suggest that these sites predominantly reside in large networks of similar species, consistent with having a BN framework and an oxidized/hydrolyzed boron phase. In addition, this spectrum also shows weak, off-diagonal signals arising from correlations between BN_3 - $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ and $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ or $\text{BNO}_x(\text{OH})_{2-x}$ sites. The BN_3 - $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ off-diagonal correlations likely arise from surface/edge $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ units covalently bonded to the BN framework.¹⁶

As the duration of homonuclear dipolar recoupling was increased from 0.9 ms to 1.8 ms, the DQ-SQ NMR spectrum shows new $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ - $\text{BO}_x(\text{OH})_{3-x}$ off-diagonal correlations in addition to the previously mentioned autocorrelations (Figure 4C). The $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ - $\text{BO}_x(\text{OH})_{3-x}$ off-diagonal correlations confirm the $\text{BO}_x(\text{OH})_{3-x}$ oxidized/hydrolyzed boron species are in close spatial proximity to the BN framework. The $\text{BO}_x(\text{OH})_{3-x}$ oxidized/hydrolyzed boron species are likely connected to the BN framework via a bridging oxygen atom to $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ species (BN_2O species, Figure 5). As the homonuclear dipolar recoupling duration was further increased to 2.7 ms, new $\text{BNO}_x(\text{OH})_{2-x}$ - $\text{BO}_x(\text{OH})_{3-x}$ off-diagonal correlations are observed (Figure 4D). The $\text{BNO}_x(\text{OH})_{2-x}$ - $\text{BO}_x(\text{OH})_{3-x}$ off-diagonal correlations likely arise from longer-range B-O-B connectivity (Figure 5). It should be noted that not all cross peaks are symmetric across the

diagonal, likely due to differences in T_2' under homonuclear dipolar recoupling for the different boron species.

In summary, the ultra-high field ^{11}B dipolar DQ-SQ homonuclear correlations experiments, in combination with ^1H - ^{11}B dipolar heteronuclear correlation experiments, enabled us to probe boron structural connectivity and propose a structural model for spent *h*-BNNT (Figure 5). The DQ-SQ NMR spectra suggest that the boron nitride and oxidized/hydrolyzed boron phases exist as clusters, however, the off-diagonal correlations observed at longer mixing times confirm the connectivity of these two phases, suggesting that the oxidized/hydrolyzed boron phase grows on the nitride layer. $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ units are the dominant species that connect the BN framework to the $\text{BO}_x(\text{OH})_{3-x}$ oxidized/hydrolyzed boron phase. Therefore, most of these interfacial boron species likely have a molecular formula of BN_2O , where a bridging oxygen atom is covalently bonded to the $\text{BO}_x(\text{OH})_{3-x}$ oxidized/hydrolyzed boron species and the two nitrogen atoms are covalently bonded to the BN framework. This is in agreement with the $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra which suggested that the majority of $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ species were mainly hydroxyl free and most hydroxyl groups are associated with the oxidized/hydrolyzed boron phase. However, there are likely some $\text{BN}_2(\text{OH})$ species that do not connect the BN framework to the surface oxidized/hydrolyzed boron layer as the relative ratio of $\text{BN}_2\text{O}_x(\text{OH})_{1-x}$ to $\text{BO}_x(\text{OH})_{3-x}$ is *ca.* 0.75:1 and the ^{11}B DQ-SQ autocorrelations observed for $\text{BO}_x(\text{OH})_{3-x}$ revealed strong B-O-B connectivity arising from large networks of surface oxidized/hydrolyzed boron species. We note that the $\text{BO}_x(\text{OH})_{3-x}$ surface oxidized/hydrolyzed boron phase likely consists of both linear chain-type metaborates and boroxol ring species, as shown in Figure 5. Multiple groups have previously shown (experimentally and computationally) that boron oxide species in boron-based glasses exhibit $\delta_{\text{iso}}(^{11}\text{B})$ typically between ~ 14 -15 ppm and ~ 16 -18 ppm for linear chain-type metaborates and boroxol rings, respectively.^{35, 61, 72-75} Furthermore, the presence of boroxol ring species was confirmed by Raman spectroscopy (vibration at 808 cm^{-1} , a boroxol ring signature in boron-based glasses, Figure S8).^{73, 76} It should be noted that SEM images showed the morphology of BN changes from nanotubular to an amorphous solid under ODH reaction conditions.¹⁰ This morphology change likely occurs via oxidative “unzipping” of the nanotubes which is supported by the work of Nautiyal *et al.* who previously showed that *h*-BNNT unzip to platelets when exposed to air at elevated temperatures (500-1000 °C).⁷⁷

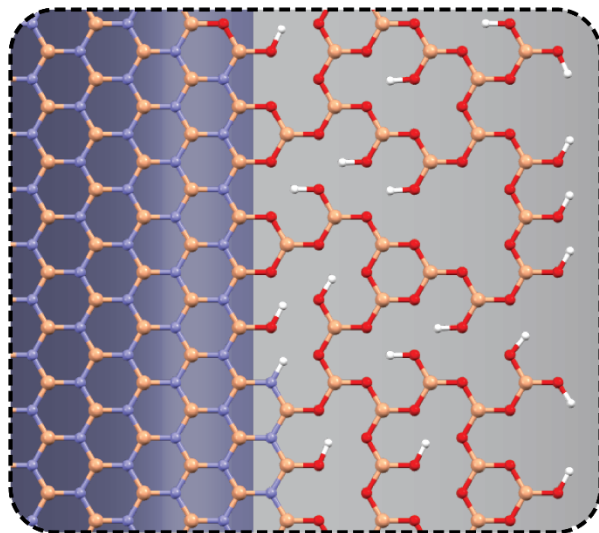


Figure 5. Hypothesized molecular structure of the interface between the BN and the oxidized/hydrolyzed boron [$\text{BO}_x(\text{OH}_{3-x})$] species as determined from the 2D ^{11}B homonuclear correlation SSNMR spectra. The shown structure has been drawn for illustration purposes and did not result from quantum chemical calculations.

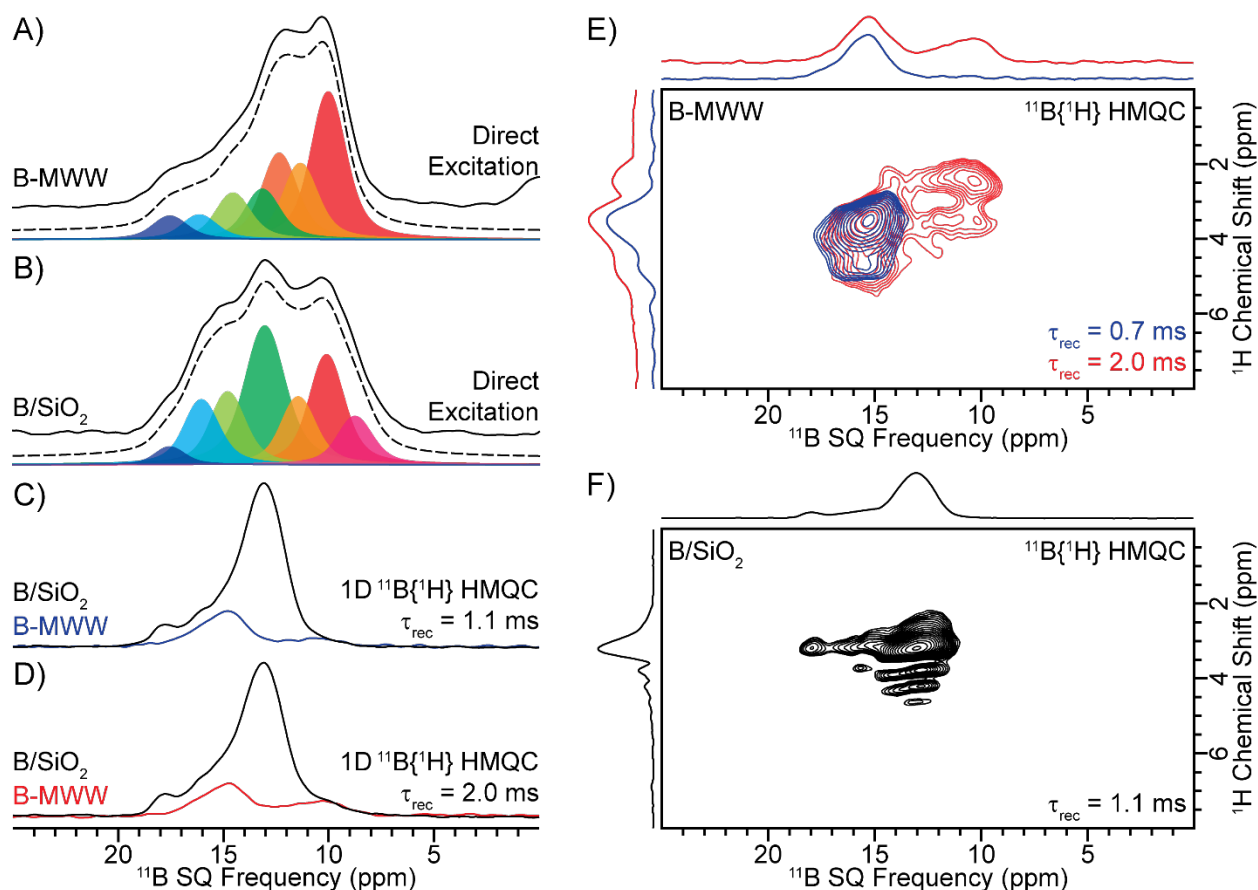


Figure 6. 1D ^{11}B direct excitation small tip angle (30°) spectra of (A) B-MWW and (B) fresh B/SiO₂. The ^{11}B NMR spectrum of B-MWW is zoomed in to only show the 3-coordinate boron ($\sim 91\%$). A full spectrum showing small amounts of 4-coordinate boron ($\sim 9\%$) is shown in Figure S9. (C, D) 1D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra B-MWW and B/SiO₂ recorded with (C) 1.1 ms or (D) 2.0 ms of total $SR4_1^2$ heteronuclear dipolar recoupling applied to the ^1H spins. The ^{11}B NMR spectra of B-MWW are either (C) blue or (D) red while the ^{11}B spectra of B/SiO₂ are black. (E) 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra of B-MWW acquired with either (blue) 0.7 ms or (red) 2.0 ms of total $SR4_1^2$ heteronuclear dipolar recoupling applied to ^1H . (F) 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectrum of B/SiO₂ acquired with 1.1 ms total $SR4_1^2$ heteronuclear dipolar recoupling applied to ^1H . All spectra were recorded at $B_0 = 35.2\text{ T}$ ($\nu_0(^1\text{H}) = 1500\text{ MHz}$) with an 18 kHz MAS frequency.

B-MWW & B/SiO₂ – Probing Boron Speciation in Low-Boron Content Heterogenous Catalysts. We next illustrate the utility of ultra-high field ^{11}B SSNMR spectroscopy by probing molecular structure in low boron weight percent ($\sim 1\text{ wt. \%}$) heterogenous catalysts, specifically B-MWW and B/SiO₂.^{7-8, 17} As we have previously demonstrated, B-MWW shows negligible activity as a catalyst for the ODH of propane, while B/SiO₂ shows comparable activity and worse selectivity as compared to *h*-BN. Therefore, it is important to determine the differences in boron

structure and speciation that cause seemingly similar catalysts consisting of boron dispersed on silica to have such different activity.

Quantitative 1D direct excitation ^{11}B SSNMR (30° tip-angle pulse) spectra of B-MWW and B/SiO₂ before catalysis were recorded at $B_0 = 35.2$ T with 18 kHz MAS (Figure 6A and 6B, respectively). Both ^{11}B NMR spectra were fit to analytical simulations of CT quadrupolar powder patterns containing multiple boron sites (Table S2). It should be noted that the analytical simulations are not necessarily unique and the ^{11}B NMR spectra could likely be fit to less peaks with increased gaussian broadening. Seven peaks were used to analytically simulate the ^{11}B NMR spectra to represent significant chemical shift distribution resulting from structural disorder, as previously observed in a 2D ^{11}B 3Q-MQMAS spectrum of B-MWW.¹⁷ Previously, the lower frequency ^{11}B NMR signals (~ 11 -12 ppm) in B-MWW were attributed to B(OSi)₃ and the higher frequency ^{11}B NMR signals (~ 15 ppm) to B(OSi)₂(OH), both of which were incorporated into the zeolite framework.^{17, 78} For B/SiO₂, the lower frequency ^{11}B NMR signals (~ 12 ppm) were attributed to isolated BO₃ units and the higher frequency ^{11}B NMR signals (~ 16 ppm) to isolated BO₂(OH), linear chain-type metaborates and boroxol rings.⁷ As shown below, the use of ultra-high magnetic field strengths (35.2 T) provide the resolution and sensitivity required to more precisely determine molecular structure in these low boron loading catalysts (~ 1 wt. %).

2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra were again used to probe the proximity of hydrogen atoms to boron atoms and aid in the deconvolution of the observed 1D direct excitation ^{11}B NMR spectra. The 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra of B-MWW were recorded with 0.7 and 2.0 ms of total $SR4_1^2$ heteronuclear dipolar recoupling applied to the ^1H spins (Figure 6E). When a short duration of heteronuclear dipolar recoupling was applied (0.7 ms), only the higher frequency ^{11}B NMR signals ($\delta_{\text{iso}} = 15$ -18 ppm, blue traces) are observed and show correlation to ^1H NMR signals between 3.5 ppm and 4.7 ppm, corresponding to sites with B-OH functionality. The assignment of these ^{11}B NMR signals to B-OH species was further confirmed by monitoring the build-up of $^{11}\text{B}\{^1\text{H}\}$ D-HMQC NMR signal as a function of the total duration of heteronuclear dipolar recoupling (Figure S10A).¹⁷ When the total duration of heteronuclear dipolar recoupling is increased to 2.0 ms, the lower frequency ^{11}B NMR signals appear ($\delta_{\text{iso}} \sim 11$ -12 ppm, red traces) and show correlations to ^1H NMR signals between 2.4 ppm and 3.5 ppm. The ^1H NMR signal at 2.4 ppm was previously assigned to silanol groups (Si-OH) adjacent to isolated B(OSi)₃ (~ 3.5 Å, Figure S10B) that result from displacing 4-coordinate silicon with 3-coordinate boron in the MWW framework.¹⁷

A 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC NMR spectrum of fresh B/SiO₂ was recorded with 1.1 ms of total $SR4_1^2$ heteronuclear dipolar recoupling (Figure 6F). The 2D D-HMQC spectrum reveals strong correlations to an ^{11}B NMR signal at $\delta_{\text{iso}}(^{11}\text{B})$ of *ca.* 13.5 ppm and a ^1H NMR signal at 3.2 ppm, in addition to weaker correlations between higher frequency ^{11}B NMR signals ($\delta_{\text{iso}} = 15\text{-}18$ ppm) and the ^1H NMR signal at 3.2 ppm. The ^{11}B NMR signal with $\delta_{\text{iso}}(^{11}\text{B}) = 13.5$ ppm can be assigned to B(OSi)₂(OH) species because of the high intensity of this correlation in the HMQC spectrum and the $\delta_{\text{iso}}(^{11}\text{B})$ is *ca.* 2-3 ppm greater than that of isolated B(OSi)₃.^{32, 78-82} We note that there are higher frequency ^1H NMR signals observed in the 2D D-HMQC spectrum which likely results from B-OH species with some degree of hydrogen bonding, consistent with our previous observations.⁷ Note that these higher frequency ^1H NMR signals are slightly obscured because of truncation of the most intense ^1H NMR signal (3.2 ppm).

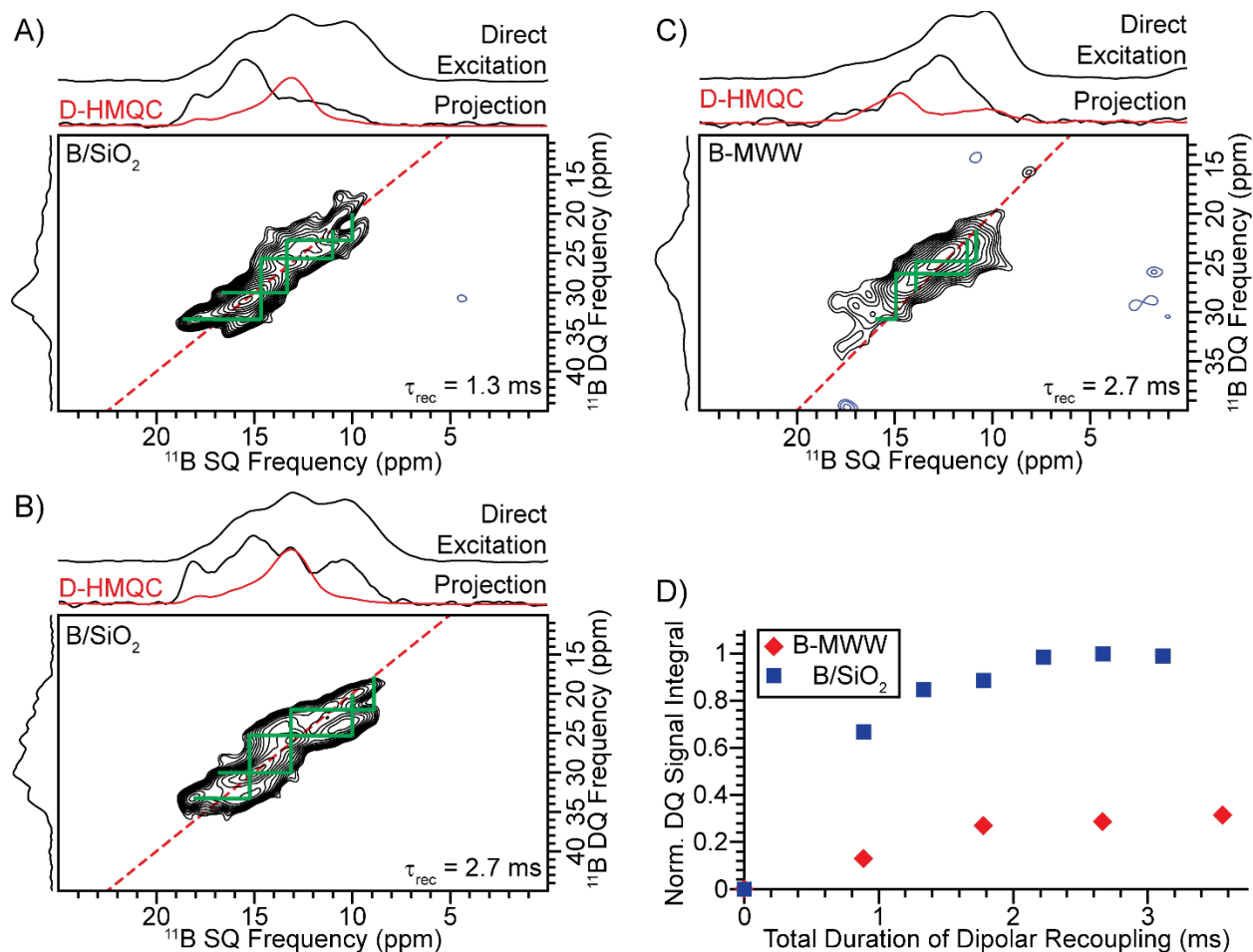


Figure 7. 2D ^{11}B dipolar DQ-SQ NMR spectra of (A, B) fresh B/SiO₂ and (C) B-MWW recorded at 35.2 T ($\nu_0(^1\text{H}) = 1500$ MHz) with 18 kHz MAS and either (A) 1.3 ms or (B, C) 2.7 ms of total $BR2_2^1$ homonuclear dipolar recoupling. 1D (black) direct excitation ^{11}B and (red) $^{11}\text{B}\{^1\text{H}\}$ D-HMQC NMR spectra ($\tau_{\text{rec}} = 2.0$ ms, from Figure 6D) are overlaid above the 2D SQ projections. The solid green line illustrates the correlations observed between different boron species (see Figure S11 for F2 slices). The dashed red line indicates the diagonal (autocorrelations). (D) A plot of the normalized 1D ^{11}B DQ-SQ total signal integration as a functional of the total duration of $BR2_2^1$ homonuclear dipolar recoupling for (blue) B/SiO₂ and (red) B-MWW.

The $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra of B-MWW and B/SiO₂ probed the relative proximities of hydrogen atoms to boron atoms and aided in discriminating B-O-X (X being B or Si) from B-OH. Next, we use 2D ^{11}B dipolar DQ-SQ homonuclear correlation NMR experiments to probe boron-boron local proximities and determine boron connectivity within both materials. Two 2D ^{11}B dipolar DQ-SQ NMR spectra of fresh B/SiO₂ were recorded with either 1.3 ms or 2.7 ms of total $BR2_2^1$ homonuclear dipolar recoupling (Figure 7A and 7B, respectively). The 2D ^{11}B dipolar DQ-

SQ NMR spectrum recorded with 1.3 ms of total homonuclear dipolar recoupling (Figure 7A) displays strong auto and off-diagonal correlations between the higher frequency ^{11}B NMR resonances ($\delta_{\text{iso}} \sim 15\text{-}18$ ppm), revealing B-O-B functionality. There are also medium intensity off-diagonal correlations between ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 10\text{-}12$ ppm and $\delta_{\text{iso}}(^{11}\text{B}) \sim 13\text{-}15$ ppm, in addition to weaker autocorrelations between ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 10\text{-}14$ ppm. As the total duration of homonuclear dipolar recoupling was increased to 2.7 ms (Figure 7B), the off-diagonal correlations between ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 10\text{-}12$ ppm and $\delta_{\text{iso}}(^{11}\text{B}) \sim 13\text{-}15$ ppm and the autocorrelations between ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 10\text{-}14$ ppm increased in intensity, likely suggesting long-range boron-boron connectivity; that is, B-O-Si-O-B rather than B-O-B.

The 2D ^{11}B dipolar DQ-SQ homonuclear correlation NMR spectrum of B-MWW shows strong autocorrelations for ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 13\text{-}14$ ppm and weaker off-diagonal correlations between ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 12\text{-}14$ ppm and $\delta_{\text{iso}}(^{11}\text{B}) \sim 15\text{-}17$ ppm (Figure 7C). Unlike in B/SiO₂, no appreciable ^{11}B DQ-SQ NMR signal was observed for the lowest frequency site ($\delta_{\text{iso}} \sim 11$ ppm), consistent with our previous assignment of this site to isolated framework B(OSi)₃. Interestingly, the boron sites with the highest observed ^{11}B DQ-SQ NMR signal intensity ($\delta_{\text{iso}} \sim 13\text{-}14$ ppm) did not show any appreciable NMR signal in the $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra, suggesting B-O-B connectivity with the absence of hydroxyl groups (see below). However, the overall observed ^{11}B DQ-SQ NMR signal intensity for B-MWW was *ca.* 70-80 % less than that observed for B/SiO₂ (Figure 7D). This suggest that most of the boron in B-MWW is substituted into the zeolite framework with relatively few extra-framework oxidized boron clusters, whereas B/SiO₂ contains significant oxidized boron clusters. It is worth noting that the complete 2D ^{11}B DQ-SQ NMR spectrum of B-MWW was recorded in only 40 minutes despite the fact that it only contains 1 wt. % B, and further, only a small fraction of the boron is clustered or aggregated. In comparison, *ca.* 9 hours was required to record a 1D ^{11}B DQ-SQ NMR spectrum of B-MWW at $B_0 = 9.4$ T with signal-to-noise of *ca.* 7.¹⁷ This comparison illustrates the dramatic sensitivity gains provided by the 35.2 T SCH magnet.

Plausible Boron Molecular Structure & Connectivity

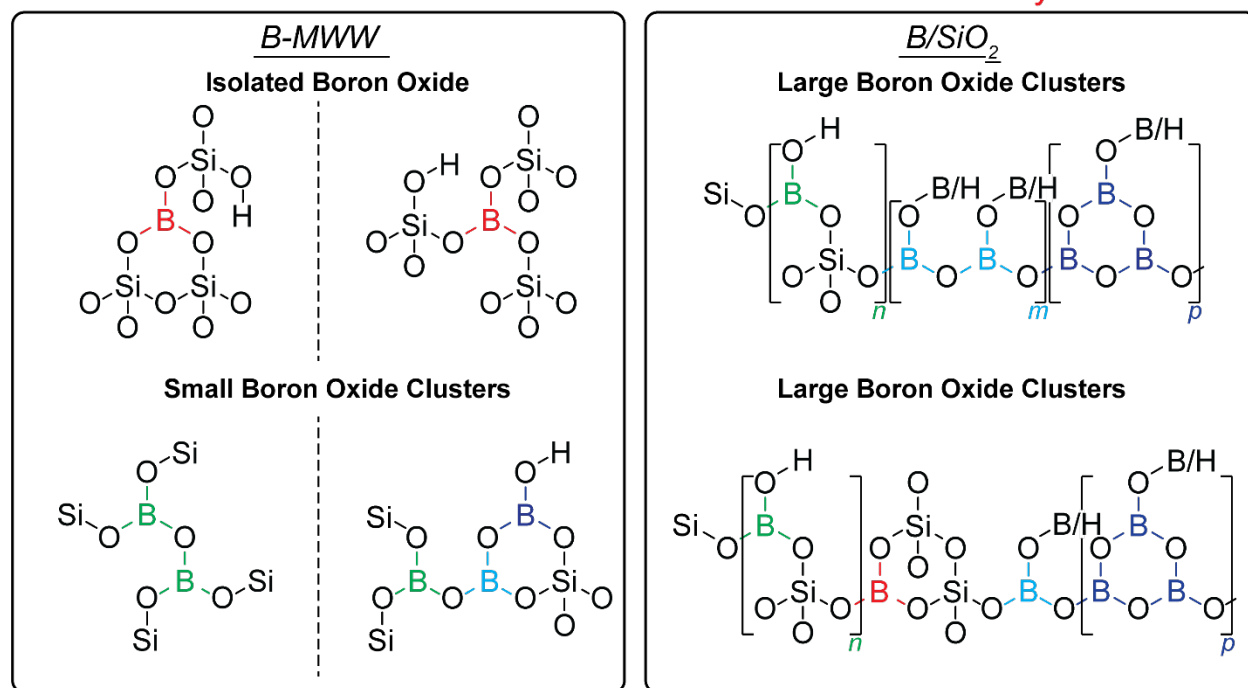


Figure 8. Plausible boron molecular structure and connectivity present in (left) B-MWW and (right) B/SiO₂. The color of the boron atoms corresponds to the colors in the analytical simulations of the 1D direct excitation ¹¹B NMR spectrum shown in Figure 6.

Ultra-high field 2D ¹¹B homonuclear and ¹H-¹¹B heteronuclear correlation SSNMR experiments probed boron functionality and connectivity within the B-MWW and B/SiO₂ catalysts, ultimately allowing for the identification of boron molecular structure. For B-MWW, the majority of the boron species can be assigned to isolated B(OSi)₃ ($\delta_{\text{iso}} \sim 10.5\text{--}12$ ppm) in the zeolite framework where there is an adjacent silanol group *ca.* 3.5 Å away (Figure 8, top left; highlighted red atoms). The ¹¹B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 13\text{--}14$ ppm did not show any appreciable ¹H-¹¹B heteronuclear correlations but did exhibit strong ¹¹B DQ-SQ autocorrelations and weaker off-diagonal correlations with higher frequency ¹¹B NMR signals. Taking into account these observations, the ¹¹B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 13\text{--}14$ ppm likely correspond to B(OSi)₂(OB) exhibiting one B-O-B bond and two B-O-Si bonds (Figure 8, bottom left; highlighted green atoms). The ¹¹B NMR signals with higher δ_{iso} in the range of 15-18 ppm have both B-OH functionality and boron-boron connectivity. We also note a lack of strong ¹¹B DQ-SQ autocorrelations for these higher frequency ¹¹B NMR signals. Therefore, we propose that the ¹¹B NMR signals with an $\delta_{\text{iso}}(^{11}\text{B}) \sim 15\text{--}18$ ppm correspond to small oxidized boron clusters containing only a few boron

atoms with multiple B-O-B and or B-OH bonds (Figure 8, bottom left; highlighted blue atoms). We note that it is possible to form $\text{B}(\text{OSi})(\text{OH})_2$ species within B-MWW (yield high frequency ^{11}B NMR signals),⁸²⁻⁸³ however, they would compose only a small fraction (near negligible amount) of boron present in B-MWW based on the NMR characterization presented here.

The ^{11}B NMR spectra (1D and 2D) of B-MWW and B/SiO₂ clearly highlight similarities and differences in boron molecular structure between the two catalysts. For B/SiO₂, the 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra suggest the ^{11}B NMR signal at $\delta_{\text{iso}}(^{11}\text{B}) = 13.5$ ppm is a $\text{B}(\text{OSi})_2(\text{OH})$ species (Figure 8, right; highlighted green atoms). The ^{11}B DQ-SQ spectrum revealed correlations between these boron species and both the lower and higher frequency ^{11}B NMR signals, illustrating close spatial proximity to all types of boron. The lowest frequency ^{11}B NMR signals can be assigned to $\text{B}(\text{OSi})_3$ just as they were in B-MWW. However, contrary to B-MWW, these $\text{B}(\text{OSi})_3$ units are not completely isolated as they show significant ^{11}B NMR signal intensity in the DQ-SQ spectrum and correlations to both $\text{B}(\text{OSi})_2(\text{OH})$ and the higher frequency ^{11}B NMR signals (Figure 8, bottom right; highlighted red atom). The higher frequency ^{11}B NMR signals show significant DQ-SQ correlations and can therefore be assigned to oxidized/hydrolyzed boron species with extensive B-O-B connectivity. Previously, we proposed these ^{11}B NMR signals could be assigned to both linear chain-type metaborates and boroxol rings based on their $\delta_{\text{iso}}(^{11}\text{B})$ and the presence of a Raman spectroscopy vibration at 807 cm^{-1} (boroxol ring breathing mode^{73, 76}).⁷ In addition, as mentioned above, multiple groups have previously investigated the effects on the $\delta_{\text{iso}}(^{11}\text{B})$ for linear chain-type metaborates and boroxol rings in boron oxide-based glasses.^{35, 61, 72-75} Therefore, we can assign the ^{11}B NMR signals at ~ 14 -15 ppm to chain-type metaborates (light blue atoms in Figure 8) and the ^{11}B NMR signals at ~ 16 -18 ppm to boroxol rings (dark blue atoms in Figure 8), both forming relatively large clusters on the silica surface.

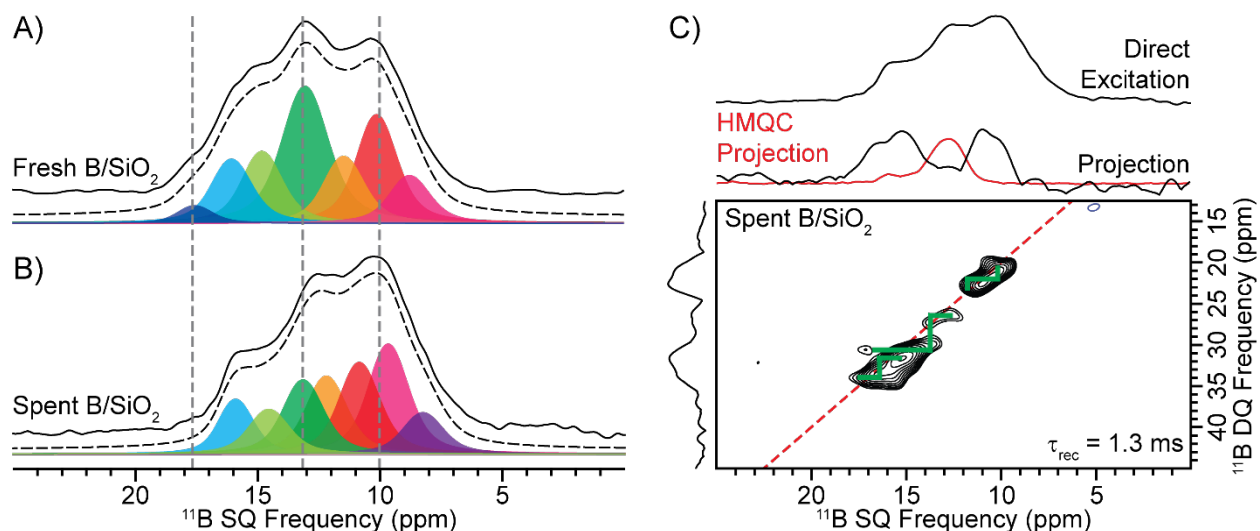


Figure 9. 1D direct excitation small tip angle (30°) ^{11}B SSNMR spectra of (A) fresh and (B) spent B/SiO_2 . (C) 2D ^{11}B dipolar DQ-SQ spectrum of spent B/SiO_2 recorded at $B_0 = 35.2$ T with 18 kHz MAS and 1.3 ms of total $BR2\frac{1}{2}$ homonuclear dipolar recoupling. A 1D direct excitation ^{11}B NMR spectrum and 2D ^{11}B projection from a $^{11}\text{B}\{^1\text{H}\}$ D-HMQC recoded with 1.1 ms of total $SR4\frac{1}{2}$ heteronuclear dipolar recoupling (Figure S12) is overlaid above the 2D SQ projection. The solid green line illustrates the correlations observed between different boron species. The dashed red line indicates the diagonal (autocorrelations).

We have previously hypothesized that some degree of oxidized/hydrolyzed boron clustering is required for active ODH catalysts because B-MWW did not exhibit significant ODH activity (unlike B/SiO_2) and most of the boron is isolated in the zeolite framework. The clustering of oxidized/hydrolyzed boron on the surface of B/SiO_2 therefore likely explains why it is an active ODH catalyst. We have previously shown that during catalysis with B/SiO_2 the propane conversion decreases by *ca.* 50 % over a 24 hour period before stabilizing (Figure 1); consequently the boron loading also decreases by *ca.* 50 % when the boron loading is *ca.* 1 wt. %.⁷ The decrease in propane conversion was hypothesized to result from the restructuring and leaching of surface oxidized/hydrolyzed boron species before steady-state conversion is reached. However, precise identification of which boron species leached and/or restructured under reaction conditions was not well understood. Therefore, we performed similar sets of 2D ^{11}B homonuclear and ^1H - ^{11}B heteronuclear correlation NMR experiments on a B/SiO_2 sample after being used for ODH catalysis to identify the boron species present in B/SiO_2 after ODH. The spent B/SiO_2 material has an *ca.* 0.5 wt. % boron loading, a 50 % decrease compared to the fresh catalyst.

Comparison of quantitative 1D direct excitation ^{11}B NMR spectra of fresh and spent B/SiO_2 illustrate distinct differences in the boron speciation after ODH catalysis (Figure 9A and 9B, respectively). Notably, there is a significant decrease in signal intensity for the higher frequency ^{11}B NMR signals ($\delta_{\text{iso}} \sim 13\text{-}18$ ppm) in the spent material, which were assigned to $\text{B(OSi)}_2(\text{OH})$ ($\delta_{\text{iso}} \sim 13.5$ ppm), linear chain-type metaborates ($\delta_{\text{iso}} \sim 14\text{-}15$ ppm) and boroxol rings ($\delta_{\text{iso}} \sim 16\text{-}18$ ppm) that cluster on the silica surface. There is also a minor amount of four-coordinate boron in the spent catalyst ($\sim 11\%$, Figure S9). A 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectrum of spent B/SiO_2 displays similar features to that observed for the fresh material (Figure S12). However, the highest frequency ^{11}B NMR signal ($\delta_{\text{iso}} \sim 17\text{-}18$ ppm) observed in the D-HMQC spectrum of fresh B/SiO_2 (B-OH group in boroxol ring) did not appear in the HMQC spectrum of spent B/SiO_2 . This is not surprising as the NMR signal intensity for the peak at $\delta_{\text{iso}}(^{11}\text{B}) \sim 18$ ppm is significantly reduced in the 1D ^{11}B direct excitation spectrum (dark blue fit in Figure 9). Two 2D ^{11}B dipolar DQ-SQ NMR spectra of spent B/SiO_2 were recorded with 1.3 ms or 2.7 ms of total $BR2\frac{1}{2}$ homonuclear dipolar recoupling (Figure 9C and S13, respectively). We note that the ^{11}B DQ-SQ NMR sensitivity was at least an order of magnitude lower for the spent material, suggesting less B-O-B connectivity, and this observation is consistent with the reduced B loading in the spent material and the reduction in intensity of the highest frequency ^{11}B NMR signals. However, we could not directly compare the DQ-SQ NMR efficiencies as the total amount of spent B/SiO_2 in the NMR rotor was less than that of fresh B/SiO_2 (i.e. the spent B/SiO_2 rotor was not fully packed). The 2D ^{11}B DQ-SQ NMR spectrum of spent B/SiO_2 recorded with 1.3 ms of total homonuclear dipolar recoupling displays strong autocorrelations for the ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 10\text{-}12$ ppm [B(OSi)_3] and $\delta_{\text{iso}}(^{11}\text{B}) \sim 15\text{-}18$ ppm [linear chain-type metaborates and boroxol rings], in addition to an off-diagonal correlation between the ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 13.5$ ppm [$\text{B(OSi)}_2(\text{OH})$] and $\delta_{\text{iso}}(^{11}\text{B}) \sim 14$ and 17 ppm [linear chain-type metaborates and boroxol rings]. These sets of correlations are relatively similar to that observed in the 2D ^{11}B DQ-SQ spectrum of the fresh catalyst. As the duration of homonuclear dipolar recoupling was increased to 2.7 ms, autocorrelations were observed for the ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 13.5$ ppm [$\text{B(OSi)}_2(\text{OH})$] in addition to off-diagonal correlations between ^{11}B NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 10\text{-}12$ ppm [B(OSi)_3] and $\delta_{\text{iso}}(^{11}\text{B}) \sim 13.5$ ppm [$\text{B(OSi)}_2(\text{OH})$]. We note that the higher frequency ^{11}B NMR signals (δ_{iso}

~ 14 and 17 ppm) [linear chain-type metaborates and boroxol rings] do not appear in the 2D ^{11}B DQ-SQ spectrum recorded with 2.7 ms of total homonuclear dipolar recoupling.

The 2D ^{11}B homonuclear and ^1H - ^{11}B heteronuclear correlation NMR spectra confirmed that similar boron connectivity is present in both fresh and spent B/SiO₂ while the quantitative 1D ^{11}B direct excitation NMR spectra identified relative populations of each species. The 1D ^{11}B direct excitation spectrum of spent B/SiO₂ reveals a significant decrease in B(OSi)₂(OH) and boroxol ring species with a slight decrease in linear chain-type metaborates, suggesting these species leached during ODH. H₂O is a co-product of the ODH reaction and likely hydrolyzes labile surface oxidized/hydrolyzed boron species under reaction conditions. Previously, it has been shown that H₂O can leach oxidized/hydrolyzed boron in a zeolite to form B(OH)₃ on the zeolite surface.^{78-79, 81, 84} Therefore, we suggest that clusters of B(OSi)₂(OH), linear chain-type metaborates and boroxol rings on the silica surface hydrolyze during ODH. We note that the hydrolyzed boron oxide is likely removed under reaction conditions. The B(OSi)₂(OH), linear chain-type metaborate and boroxol ring species observed in B/SiO₂ after catalysis are likely associated with smaller oxidized/hydrolyzed boron clusters and/or oxidized/hydrolyzed boron clusters directly bonded to the silica surface that are more difficult to hydrolyze. This allows us to draw the conclusion that large networks of B(OSi)₂(OH), linear chain-type metaborates and boroxol rings on the surface of the silica are the “most” catalytically active boron species for the ODH of propane to propylene. However, these “most catalytically active” large oxidized/hydrolyzed boron clusters are the easiest to remove during ODH, which likely occurs through hydrolysis. This implies that the smaller, more stable oxidized/hydrolyzed boron clusters are responsible for the long-term activity of B/SiO₂, as this material reaches a steady-state propane conversion of ~ 10% (Figure 1).⁷ Therefore, it can be hypothesized that by modifying the silica support so that it becomes more hydrophobic, it may be possible to hinder the hydrolysis of the large oxidized/hydrolyzed boron clusters and produce a more stable catalyst.

Conclusions

35.2 T ultra-high field ^{11}B SSNMR spectroscopy enabled the determination of molecular structure in boron-based heterogeneous catalysts for the ODH of light alkanes to olefins. The 35.2 T magnetic field significantly reduces the second-order quadrupolar broadening for ^{11}B NMR

signals with $C_Q < 3$ MHz, resulting in ^{11}B NMR signals that are near isotropic. The enhanced resolution provided by $B_0 = 35.2$ T enabled 2D ^1H - ^{11}B heteronuclear and ^{11}B homonuclear correlation SSNMR experiments to be performed to unambiguously determine boron structure and connectivity within spent *h*-BNNT, fresh B-MWW, fresh B/SiO₂ and spent B/SiO₂. The 1D direct excitation ^{11}B SSNMR spectrum of spent *h*-BNNT allowed for the easy identification of all boron sites (BN₃, BN₂O, BNO₂, BO₃ and BO₄). Integration of the 1D spectrum revealed that *ca.* 50 % of boron in *h*-BNNT was either fully (28 %) or partially (22 %) oxidized after two hours of ODH. 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra probed ^1H - ^{11}B local proximities and revealed that most B-OH functionality was constrained to the oxidized/hydrolyzed boron phase [BO_{*x*}(OH)_{3-*x*}]. 2D ^{11}B dipolar DQ-SQ homonuclear correlation NMR spectra probed boron-boron connectivity between bulk BN and the surface boron oxide phase. Ultimately, the 2D ^{11}B dipolar DQ-SQ NMR spectra showed that the oxidized/hydrolyzed boron phase is connected to the BN framework through BN₂O species, where the two nitrogen atoms are covalently bonded to the BN framework and the oxygen atom is covalently bonded to the oxidized/hydrolyzed boron phase (i.e. bridging).

Ultra-high field ^{11}B NMR spectroscopy of fresh B-MWW, fresh B/SiO₂ and spent B/SiO₂ allowed for a more precise identification of supported boron oxide species. 1D direct excitation ^{11}B SSNMR spectra of B-MWW and B/SiO₂ showed distinct differences in the relative populations of all ^{11}B NMR signals. 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC spectra of B-MWW showed that boron species containing B-OH functionality resonated at the highest observed ^{11}B NMR frequencies in the direct excitation experiment ($\delta_{\text{iso}} \sim 15\text{-}18$ ppm). Alternatively, B/SiO₂ displayed a very intense $^{11}\text{B}\{^1\text{H}\}$ D-HMQC NMR signal at $\delta_{\text{iso}}(^{11}\text{B}) \sim 13.5$ ppm (in addition to NMR signals at $\delta_{\text{iso}}(^{11}\text{B}) \sim 15\text{-}18$ ppm) which could be assigned to B(OSi)₂(OH). 2D ^{11}B dipolar DQ-SQ NMR spectra of B/SiO₂ revealed large oxidized/hydrolyzed boron clusters consisting of mostly B(OSi)₂(OH), linear chain-type metaborates and boroxol rings, in addition to some B(OSi)₃ in close proximity to the oxidized/hydrolyzed boron clusters. Alternatively, a ^{11}B dipolar DQ-SQ NMR spectrum of B-MWW showed that only small oxidized/hydrolyzed boron clusters are present [mainly B₂(O)(OSi)₄], however, a majority of the boron species are isolated framework B(OSi)₃. In addition, the lack of ^{11}B DQ-SQ autocorrelations for the higher frequency ^{11}B NMR signals ($\delta_{\text{iso}} \sim 15\text{-}18$ ppm) suggested the absence of linear chain-type metaborates and boroxol ring species. These results are consistent with our previous hypothesis that large oxidized/hydrolyzed boron clusters [B(OSi)₂(OH), linear chain-type metaborates and boroxol rings] are required for ODH.

Lastly, 1D direct excitation ^{11}B , 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC and 2D ^1H dipolar DQ-SQ NMR spectra were recorded for B/SiO₂ after 24 hours of ODH of propane to propylene. As previously mentioned, the propane conversion decreases by *ca.* 50 % over a 24-hour period before stabilizing; consequently, the boron loading also decreased by *ca.* 50 %. The 2D $^{11}\text{B}\{^1\text{H}\}$ D-HMQC and 2D ^{11}B dipolar DQ-SQ NMR spectra showed that similar types of boron species are present in B/SiO₂ after 24 hours of ODH; however, the DQ-SQ experiments suggested only smaller oxidized/hydrolyzed boron clusters were present. Comparison of the quantitative 1D direct excitation ^{11}B NMR spectra for the fresh and spent B/SiO₂ material allowed us to conclude that a major portion of the large B(OSi)₂(OH), linear chain-type metaborates and boroxol ring oxidized/hydrolyzed boron clusters were hydrolyzed during ODH and therefore leached from the catalyst, explaining the decrease in ODH activity. This conclusion further supports that large clusters of B(OSi)₂(OH), linear chain-type metaborates and boroxol rings are the most catalytically active species in B/SiO₂; however, they are readily susceptible to hydrolysis under reaction conditions.

The more precise identification of ODH active boron species and the determination of boron molecular structure in these boron-based heterogeneous catalysts will allow for the future design and development of next-generation boron-based ODH catalysts. Furthermore, this work illustrates the necessity of using ultra-high magnetic field strengths to precisely probe molecular structure in disordered materials containing many inequivalent quadrupolar nuclei. We anticipate that this work and other recent demonstrations^{44, 52-54, 63-71} will prompt the continuing use of ultra-high field SSNMR to study molecular structure in other important materials containing quadrupolar nuclei.

Supporting Information

The Supporting Information is available free of charge at

Solid-state NMR experimental parameters, magnetic field strength dependence on ^{11}B NMR signal broadening, additional solid-state NMR spectra, Raman spectra.

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TOC Graphic

