

Tracking Active Phase Behavior on Boron Nitride during the Oxidative Dehydrogenation of Propane Using Operando X-ray Raman Spectroscopy

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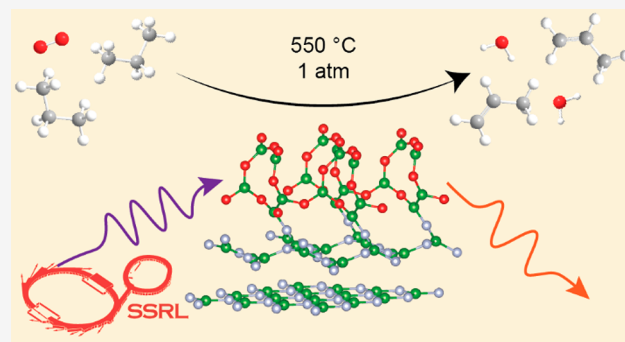


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ABSTRACT: Hexagonal boron nitride (hBN) is a highly selective catalyst for the oxidative dehydrogenation of propane (ODHP) to propylene. Using a variety of *ex situ* characterization techniques, the activity of the catalyst has been attributed to the formation of an amorphous boron oxyhydroxide surface layer. The ODHP reaction mechanism proceeds via a combination of surface mediated and gas phase propagated radical reactions with the relative importance of both depending on the surface-to-void-volume ratio. Here we demonstrate the unique capability of *operando* X-ray Raman spectroscopy (XRS) to investigate the oxyfunctionalization of the catalyst under reaction conditions (1 mm outer diameter reactor, 500 to 550 °C, $P = 30$ kPa C_3H_8 , 15 kPa O_2 , 56 kPa He). We probe the effect of a water cofeed on the surface of the activated catalyst and find that water removes boron oxyhydroxide from the surface, resulting in a lower reaction rate when the surface reaction dominates and an enhanced reaction rate when the gas phase contribution dominates. Computational description of the surface transformations at an atomic-level combined with high precision XRS spectra simulations with the OCEAN code rationalize the experimental observations. This work establishes XRS as a powerful technique for the investigation of light element-containing catalysts under working conditions.



INTRODUCTION

Hexagonal boron nitride (hBN) and other boron-containing materials (e.g., metal borides, B_4C , elemental boron, and boron supported on silica, carbon, and alumina) are highly selective catalysts for the oxidative dehydrogenation of propane (ODHP), exhibiting exceptionally high propylene selectivity.^{1–4} Propylene is the second largest organic chemical by mass (2017 global market: 130 Mt/y),⁵ currently produced in endothermic cracking or dehydrogenation processes. Exothermic technologies such as ODHP with the potential to produce propylene at a lower energy cost are therefore greatly desired.⁶ The high alkene selectivity displayed by B-based catalysts compared to hitherto investigated materials has made the origin of their catalytic performance a subject of significant interest.

Catalytic activity on these boron materials is attributed to the formation of an amorphous boron oxyhydroxide phase with the general formula $B_2(OH)_{2x}O_{3-x}$ ($x \leq 3$).^{7,8} For hBN, the formation of this oxyhydroxide phase is associated with an induction period during which the propane conversion steadily increases before reaching steady state.^{8,9} The oxyfunctionalized

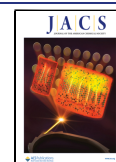
boron phase is highly dynamic under ODH reaction conditions, acting as a liquid phase catalyst supported on hBN.¹⁰ This molten phase readily restructures and can generate metastable boron sites that are not accessible at room temperature.^{11,12} Extensive *ex situ* characterization has been conducted with the aim of identifying structure–performance relationships.^{7–9,13–22} For example, B–OH content has been correlated with catalytic activity²⁰ while the details of the extended boron structure (e.g., ring or linear) continue to be the subject of ongoing research. However, the nature of the active phase is such that the species present under the reaction conditions are distinct from those present on the thermally relaxed surface as observed with *ex situ* techniques, making *operando* studies imperative.

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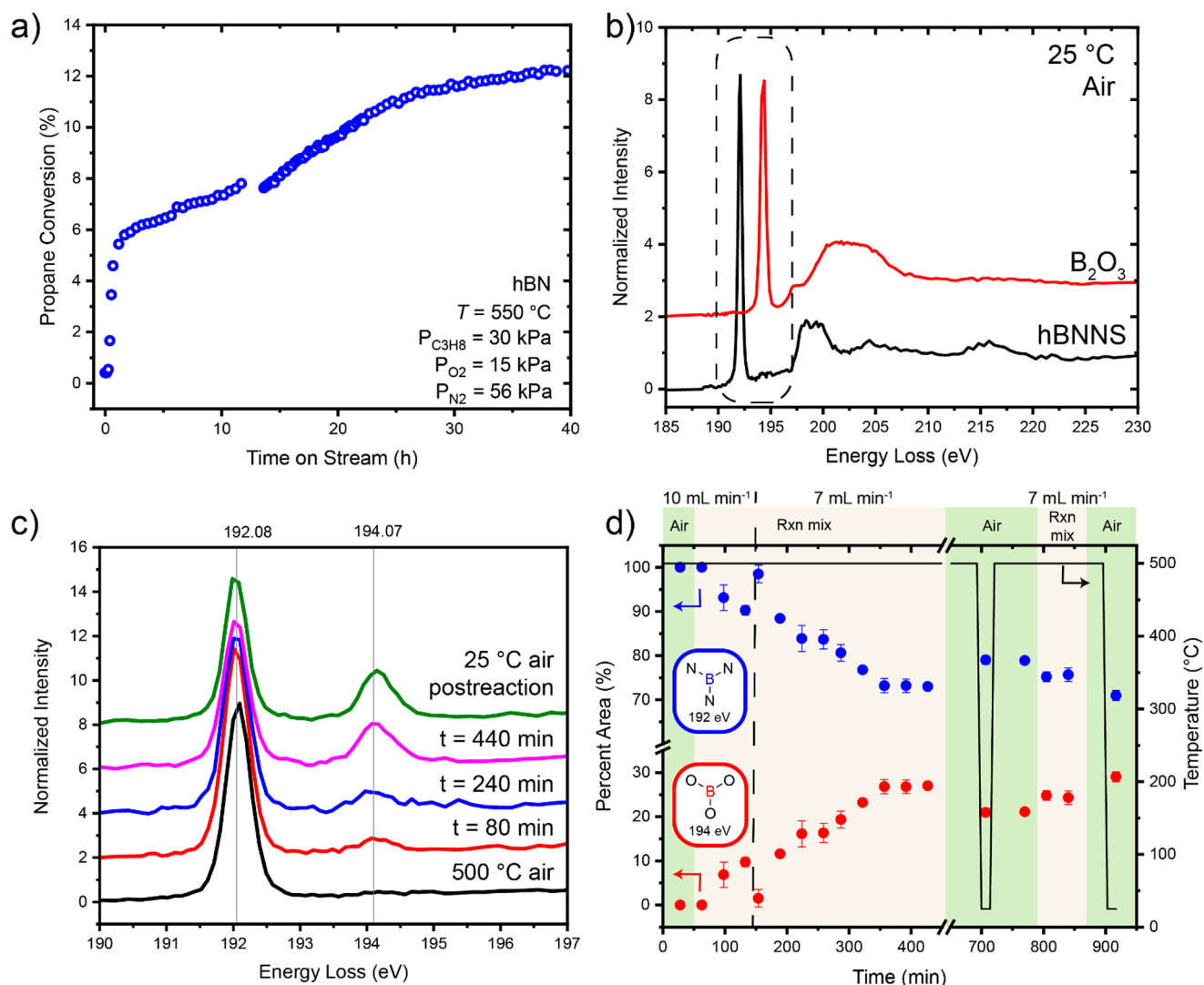


Figure 1. (a) Plot of propane conversion as a function of time on stream for hBN during propane ODH measured in a laboratory reactor (7 mm internal diameter). (b) Room temperature X-ray Raman spectrum of the B K-edge of hBNNS and B_2O_3 . The dashed box indicates the portion of the spectra shown in panel c. (c) Representative normalized *operando* X-ray Raman spectra of the B K-edge of hBNNS during propane ODH. (d) Percent areas of the $[\text{BN}_3]$ (blue dots) and $[\text{BO}_3]$ (red dots) peaks over the course of the *operando* reaction. The green shaded areas are spectra recorded in synthetic air (20% O_2/He) and the beige shaded areas are recorded under reaction conditions (2:1 $\text{C}_3\text{H}_8/\text{O}_2$). The dashed black line indicates a change in flow rate from 10 mL min^{-1} to 7 mL min^{-1} and the solid black line shows the reaction temperature. The error bars in panel d are the standard deviation from averaging 3 to 5 individual scans.

The reaction kinetics of ODH over hBN have been well established as a foundation to investigate the underlying mechanism.^{2,23–27} The reaction proceeds via a radical mechanism, presumably initiated by the surface.^{24–27} Reactor parameters (e.g., geometry and void space) have a large effect on the reaction rate.²⁴ Notably, when the amount of hBN is kept constant, the reactivity scales linearly with the catalyst bed volume, with larger volumes affording higher activity. The addition of 1% to 20% water vapor by volume to the reaction feed enhances the reaction rate without impacting product selectivity, indicating that water enhances the flux of existing reaction pathways.²⁵ Therefore, it was hypothesized that a main role of water is to increase the radical pool concentration.²⁵ Additionally, the reaction shows a first-order rate dependence in water, and it was suggested that water can help dehydrate the surface to regenerate active species, playing a role in the rate-determining step. Previous work showed that boron oxide can be hydrolyzed from the surface of silica-

supported boron materials in a postreaction washing step, resulting in deactivated catalysts with greatly decreased boron content.¹³ However, the effect of water vapor on the surface of hBN during the reaction has not yet been experimentally investigated and is addressed in this work.

Only a few *in situ* studies of this catalytic system have been reported, owing to harsh reaction conditions ($>450\text{ }^{\circ}\text{C}$, O_2 , C_3H_8) in combination with the difficulties of analyzing the light elements that comprise the active phase (i.e., oxygen and boron).^{3,4,28,29} *In situ* vibrational spectroscopy (IR and Raman) has been used with limited success, correlating B–O and B–OH features with catalytic activity.^{3,4} Synchrotron vacuum ultraviolet (SVUV) radiation has also been used to confirm the presence of radical species during ODHP.^{28,29} However, the conditions used in the SVUV experiment (i.e., pressure) are far from those used in actual catalytic testing, complicating the connection to the observed reaction kinetics. Moreover, the need for UV irradiation can likely trigger undesired side

reactions like the dissociation of propyl radicals, leading to perturbed observations. The analytical methods applied to this catalyst system thus far have been limited due to (i) their insensitivity to light elements, (ii) their inability to obtain site-specific information, and (iii) their inability to mirror laboratory testing conditions.

X-ray absorption spectroscopy (XAS) is a powerful tool for studying heterogeneous catalysts under realistic working conditions. Such studies provide detailed element-specific atomistic information about the average local geometry, oxidation state, and coordination environment of the element being probed. Light elements, such as B, N, C, and O, have their absorption edges in the soft X-ray (<1 keV) regime. The need for soft X-rays limits the types of experiments that can be performed, as their short path length coupled with the short mean free path of the emitted electrons, necessitates measurements in (near-)vacuum environments.

X-ray Raman spectroscopy (XRS) measures the energy loss (inelastic scattering) of a monochromatic hard X-ray (ca. 6.5 keV in our case) and, for low momentum transfers, provides XAS-equivalent information.^{30–33} Because the energy transfer from a hard X-ray is measured, XRS enables the measurement of the K-edge of light elements under actual catalytic reaction conditions instead of vacuum. Thus, XRS allows for studies of light element-containing catalysts under true working conditions while simultaneously monitoring the reaction products (i.e., *operando*). The use of XRS has been limited, owing to the small inelastic scattering cross section, and is only made possible by high flux beamlines at synchrotrons as well as the development of high efficiency and high-energy-resolution spectrometers with a large solid angle. This technique is at the forefront of *in situ* spectroscopy and has been used to study intercalation in hydrogen sorption and battery materials.^{34–38} The application of XRS in the *operando* study of heterogeneous catalysts is still in its infancy but holds great promise.³⁹

In this study, we track boron oxyhydroxide formation and behavior on hBN during catalyst induction, steady state operation, and water cofeeding cycles using *operando* XRS. We probe the effect of a water cofeed on the surface of the activated catalyst and find that water removes bulk oxide from the surface, resulting in a lower reaction rate when the surface reaction dominates and an enhanced reaction rate when the gas phase contribution dominates. X-ray Raman spectra of oxyfunctionalized hBN at room temperature and elevated temperatures show subtle spectral changes to both the hBN and oxide features. We rationalize these subtle changes in X-ray Raman spectra using systematic *ab initio* calculations of XRS for metastable structure candidates determined from grand canonical simulations of boron oxyhydroxide species present under the ODHP reaction conditions.

RESULTS AND DISCUSSION

Observing hBN Oxyfunctionalization During the Catalyst Induction Period. hBN undergoes a sample-dependent induction period of up to several hours during which the propane conversion steadily increases before reaching a steady state (Figure 1a).^{9,10} The exact shape and duration of the induction period depend on the reaction conditions. Based on *ex situ* characterization, this induction period can be attributed to the formation of the boron oxyhydroxide phase ($B_2(OH)_{2x}O_{3-x}$ ($x \leq 3$)) necessary for catalytic activity.^{8,10} While there has been much debate about the active site structure, there is a general agreement that

amorphous boron oxyhydroxide is required to achieve the catalytic activity typical for boron-based catalysts. Therefore, understanding the formation and behavior of the oxyhydroxide phase is crucial to understanding this exciting class of catalysts. We first use *operando* XRS to observe the formation of boron oxyhydroxide during the catalyst induction period of hBN.

Since XRS is a bulk-sensitive probe, while catalysis is a surface phenomenon, a study of traditional bulk hBN would be entirely dominated by its bulk contribution. Previous studies have shown that ODHP over hBN and nanostructured hBN proceeds via the same mechanism and that the same boron oxyhydroxide species are generated on the different catalyst materials.^{1,8} To increase the active surface area and achieve enhanced signal from the surface, exfoliated hBN nanosheets (hBNNSs, Figure S1) were used in this study (see Supporting Information). The hBNNS sample (2 mg of undiluted powder) was packed into a 1 mm outer diameter (o.d.) quartz capillary tube to give a 5 mm length catalyst bed. Detailed reactor parameters are given in Table S1. The packed quartz capillary (Figure S2) was placed in the flow cell⁴⁰ and mounted at beamline 15-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) with a mass spectrometer (MS) attached to the reactor outlet.

At room temperature under a flow of synthetic air (20% O₂ by volume in He), the X-ray Raman spectrum of hBNNSs exhibits a strong, sharp peak at 192.08 eV and a set of broader features above 197 eV (Figure 1b black spectrum).

The 192.08 eV feature is attributed to B 1s $\rightarrow \pi^*$ transition in hBN ([BN₃] species); transitions to σ^* and π^* states contribute to the features above 197 eV.⁴¹ This spectrum agrees well with results from XRS, soft XAS, and electron energy loss spectroscopy (EELS) reported in the literature.^{8,41} Furthermore, the relative spectral weights of the sharp peak at 192.08 eV and the broader feature above 197 eV are a clear indication that the XRS exhibit a dominant contribution of the momentum transfer vector q parallel to the c axis.^{41,42} B₂O₃ (Figure 1b, red spectrum) exhibits a strong sharp peak at 194.37 eV ([BO₃] species) and a set of broader features above 196 eV.

The sample was heated from room temperature to 500 °C (at 10 °C min⁻¹) under a flow of synthetic air (black trace in Figure 1c). After the temperature stabilized, propane was added into the feed in a 2:1 C₃H₈/O₂ ratio to give a total flow rate of 10 mL min⁻¹ (3 mL min⁻¹ C₃H₈, 7 mL min⁻¹ 20% O₂/80% He by volume), and spectra were continuously recorded. Representative normalized spectra at 80, 240, and 440 min on stream and after reaction are shown in Figure 1c. After 120 min on stream, the total flow rate was decreased to 7 mL min⁻¹ (2 mL min⁻¹ C₃H₈, 5 mL min⁻¹ air) to increase the contact time. The reaction proceeded until a steady amount of oxidized boron had formed (8 h total reaction time). The sample was then cooled to room temperature in air, heated back up to 500 °C, and re-exposed to reaction conditions for an additional 105 min before being cooled to end the experiment. When propane was added to the hot catalyst, the MS signal for the ODHP reaction product H₂O ($m/z = 18$) appeared with a slight delay relative to the signals for propane ($m/z = 28$ and 44), indicating that ODHP was occurring (Figure S3). The MS signals for propylene overlap with those for propane and are thus not a clear indicator of the reaction proceeding.

Two features at 192 and 194 eV are observed in the postreaction spectrum (green trace in Figure 1c). As seen in

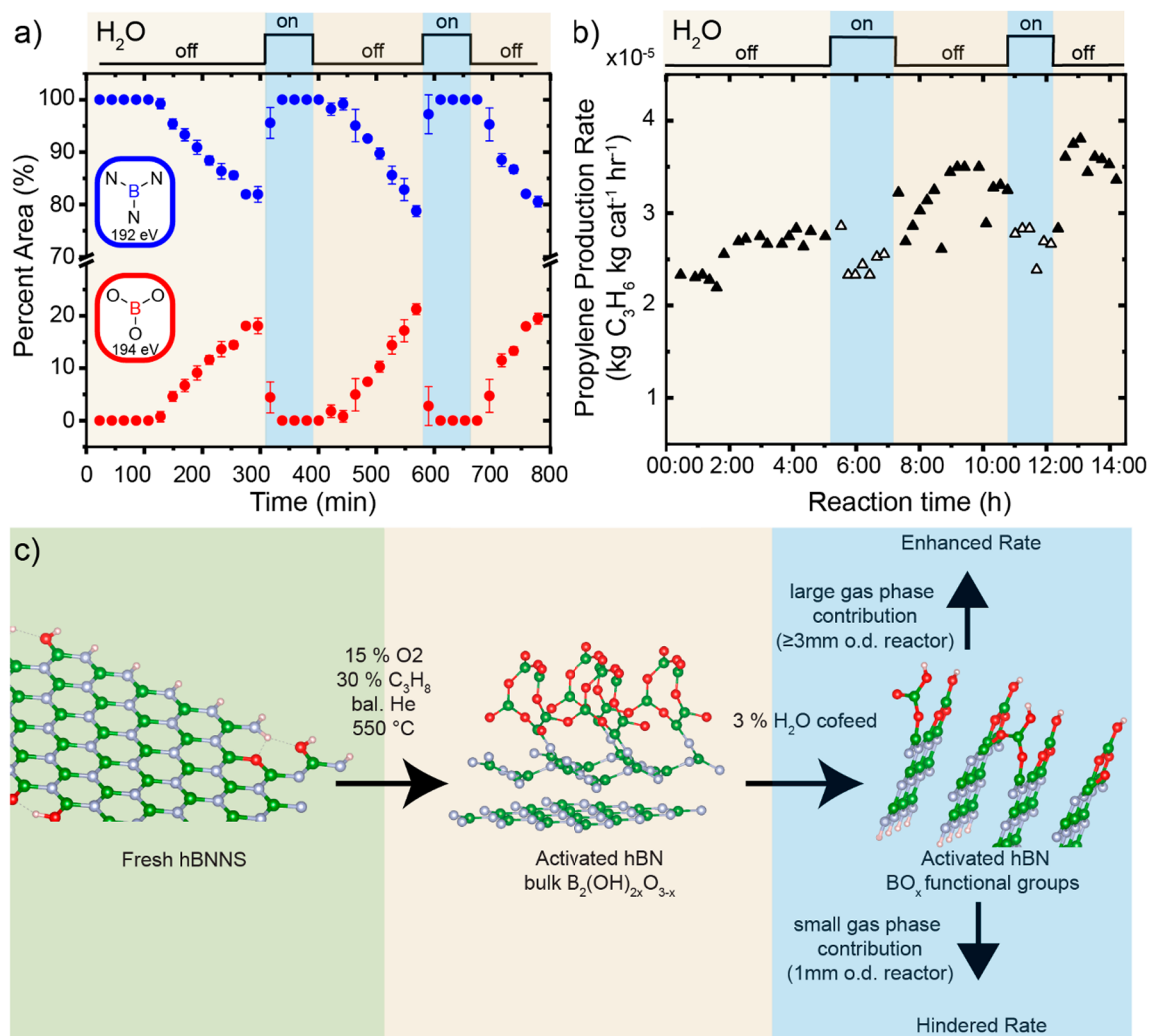


Figure 2. (a) Integrated areas of the $[\text{BN}_3]$ (blue circles) and $[\text{BO}_3]$ (red circles) features over the time of the experiment; and (b) propylene production rate over time. Reaction conditions: $T = 550^\circ\text{C}$, 10 mL min^{-1} total flow rate ($1.4\text{ mL min}^{-1}\text{ C}_3\text{H}_8$, $3.5\text{ mL min}^{-1}\text{ 20\% O}_2/\text{He}$, and $5.1\text{ mL min}^{-1}\text{ He}$). The beige shaded regions indicate a dry cycle (no added water), and the blue shaded regions indicate a wet cycle (with 3% cofed water). (c) Scheme summarizing the surface response to the conditions probed in the water cofeed experiments. The error bars in panel a are the standard deviation determined from averaging 3 to 5 individual scans.

Figure 1b, the peak at 192 eV corresponds to the $[\text{BN}_3]$ species and the peak at 194 eV corresponds to the $[\text{BO}_3]$ -type species. The intensity of the $[\text{BO}_3]$ feature increased over the course of the reaction. The area under the 192 and 194 eV signals was integrated, and the resulting percentage areas over the course of the experiment are plotted in Figure 1d (plot of integrated area over time is shown in Figure S4). With a total flow rate of 10 mL min^{-1} , there is a slow increase in the amount of oxidized boron. When the flow rate is decreased to 7 mL min^{-1} , increasing the contact time, the amount of oxide initially decreases and then quickly increases, eventually reaching a maximum of ca. 25% of the total integrated area. This value is in line with previous quantification by solid state NMR (SSNMR), which shows that hBN after reaction contains 30% $[\text{BO}_3]$ -type species.⁸ There is little change in surface composition upon re-exposure to reaction conditions, indicating that the surface has reached a steady state composition.

Linear combination fitting (LCF) analysis was applied to quantify the relative amounts of the two species present using the spectra of hBNNSs and B_2O_3 acquired at room

temperature as standards. The LCF results (Figure S5) show the same trend as the percentage areas in Figure 1. Fitting the $[\text{BO}_3]$ peak at 194 eV with the B_2O_3 standard consistently shows a residual at the lower energy side of the experimental peak (Figure S6). This residual is present at both room and reaction temperatures, although the intensity of the residual peak is larger at elevated temperatures (Figure S6a). The residual in the oxide feature suggests the presence of boron oxyhydroxide species with geometry and coordination distinct from those of the boron species in B_2O_3 . The presence of distinct boron oxyhydroxide species is in line with proposed structures from SSNMR as well as with theory-predicted metastable BO_x species. The $[\text{BN}_3]$ peak at 192 eV also exhibits residuals, but only at elevated temperatures (Figure S6b). These residuals are associated with distortions in the hBN layer due to oxidation of facial sites (as opposed to edge sites; Figure S7), especially the highly restructured facial species, whose populations become significant only at reaction temperatures. Proposed structures from theory which may account for the subtle spectral changes observed under reaction conditions are discussed in detail below.

Interestingly, when the flow rate is decreased, the oxide temporarily disappears (at 160 min), reappearing in the next averaged spectral time (i.e., the oxide was not present for ca. 40 min.). Decreasing the gas flow rate increases the contact time and therefore the conversion, leading to an increased local concentration of water. As water has been shown to hydrolyze boron oxide, an explanation for the temporary loss of the $[\text{BO}_3]$ signal is that the species were hydrolyzed, and the reoxidation of hBN is slow at this stage of the reaction.

We confirmed our observations in a second repeat experiment (Figure S8). Our results show that once the oxidized boron layer is formed, the surface structure, though dynamic on the short time scale,¹¹ is stable on the time scale of XRS. The success of XRS in tracking oxyfunctionalization allowed us to design experiments that could reveal more about the behavior of the active phase, such as the effect of a water cofeed on the surface. Therefore, to better understand the active oxide phase, we perturbed the system by modulating the addition of water to the reaction mixture.

Probing the Effect of Water Vapor on the Catalyst Surface. As mentioned above, the addition of water vapor to the ODH feed has previously been shown to enhance the rate of propane conversion.²⁵ The enhancement effect is reversible, and it was hypothesized that the main roles of water are to (i) increase the radical pool concentration and (ii) assist in the rate-determining step of active site regeneration. Here, we probe the effect of water vapor on the hBN catalyst while simultaneously monitoring the reaction products by gas chromatography (GC).

hBNNSs (7 mg, powdered and undiluted, from the same batch used in Figure 1) were packed into a 1 mm o.d. capillary tube to give a 10 mm catalyst bed length and mounted at BL 15-2 at SSRL (detailed reaction parameters in Table S1). The sample was heated in synthetic air (at 10 °C/min) to 550 °C before switching to a dry reaction gas mix (i.e., without any added water) until a stable amount of $[\text{BO}_3]$ (194 eV feature) formed. Following the induction period, the gas was routed through a room temperature water saturator to start the first wet cycle. After about 80 min, the gas feed was switched back to the dry feed. The wet and dry cycles were performed twice.

Normalized B K-edge X-ray Raman spectra collected throughout the cofeeding experiment are shown in Figure S9. The area under the peaks at 192 and 194 eV of the individual normalized B K-edge XRS scans were integrated, and the resulting percentage areas are plotted over time in Figure 2a (integrated areas shown in Figure S10). Figure 2b shows the propylene production rate over the course of the reaction. Representative GC traces are shown in Figure S11. In each of the plots in Figure 2, the blue shading indicates a wet cycle and the beige shading indicates a dry cycle. LCF analysis was also performed on these spectra (Figure S12). As in the previous experiment, there is a residual present at the lower energy side of the 194 eV peak that corresponds to a $[\text{BO}_3]$ -type species (Figure S13).

As shown in Figure 1 for the dry feed, there is again a gradual increase in the 194 eV feature ($[\text{BO}_3]$ -type species) during the induction period until a stable surface composition is formed (first beige segment in Figure 2a). When water is added to the feed (the first blue segment in Figure 2), the oxide feature at 194 eV quickly disappears. Upon the removal of water from the gas feed, the 194 eV signal gradually returns, showing that the removal of boron oxyhydroxide can be cycled. Oxide removal occurs faster than oxide growth, with removal

occurring within the first 10 min of a wet cycle and growth occurring after at least 15 min of a dry cycle (Figure 2a). The propylene production rate (Figure 2b) is lower in the wet cycles than in the dry cycles, a trend opposite to that observed by Venegas et al.²⁵

The removal of boron oxyhydroxide by water is consistent with a previous study where the active boron oxyhydroxide layer is hydrolyzed from silica-supported catalysts in a postreaction washing step.¹³ However, the catalytic response to the addition of water was initially surprising, as lab-based results show an increase in propylene production as a result of the water cofeed. Based on the inverse relationship to water addition seen in our reactivity results measured at BL 15-2 and the hypothesis that a role of water is to increase the radical pool concentration, we hypothesize that the differing response is an effect of minimal gas phase contribution in the 1 mm reactor configuration used for the XRS study. Work from Venegas et al. demonstrated the importance of reactor parameters on the reaction rate for ODHP over hBN.²⁴ They observed a drastic decrease in ODHP activity for hBN in a 4 mm inner diameter (i.d.) reactor compared to an 8 mm i.d. reactor tube at similar contact times and showed that propane conversion scales linearly with the void volume of the catalyst bed.

In our cofeed experiment at BL 15-2, the catalyst was packed into a 1 mm outer diameter (o.d.) capillary to give a 10 mm length bed (bed volume $\approx 8 \text{ mm}^3$), a volume that is 2 orders of magnitude smaller than that in typical laboratory-based reactors (bed volume for the 6 mm i.d. reactor used in Venegas et al.: 570 mm^3).²⁵ To test our hypothesis, we performed water cofeeding experiments using a 3 mm o.d. capillary tube (10 mm length bed, bed volume $\approx 71 \text{ mm}^3$). Similar to our beamline experiments, the hBN catalyst was treated at 550 °C under a dry reaction mix for 8 h to form the stable oxide phase. When water was cofed into the reactor, we observed the expected enhancement to the reaction rate (Figure S14). Notably, there was a visible white deposit at the outlet of the 3 mm capillary reactor at the end of the water cofeed experiments, indicating that boron was hydrolyzed from the surface as in the 1 mm capillary reactor (Figure S15). The observed enhancement by water along with boron oxide hydrolysis in the larger volume catalyst bed supports our hypothesis of minimal gas phase contribution in the 1 mm capillary reactor. We can therefore ascribe the reactivity that we observe in the 1 mm reactor to the surface alone. Thus, when the reactor volume is sufficiently large and gas phase chemistry is present, water enhances the reaction rate; when the reactor volume is small and gas phase chemistry is not present, the surface reactivity dominates and water hinders the reaction rate. In both cases, water removes oxidized boron from the catalyst.

Propylene production does not completely stop with the loss of the $[\text{BO}_3]$ XRS signal, indicating that there are residual $[\text{BO}_3]$ functional groups that can perform the reaction. However, the loss in propylene production rate is not proportional to the loss of oxide content, which is likely an effect of the ability of water to assist in the rate-determining step of active site regeneration. So, although water has removed the bulk boron oxyhydroxide, leading to decreased propylene production, functional groups which can perform the reaction remain and their regeneration is aided by the presence of water. To confirm the presence of residual boron oxyhydroxide, ¹¹B SSNMR of activated hBN treated with a

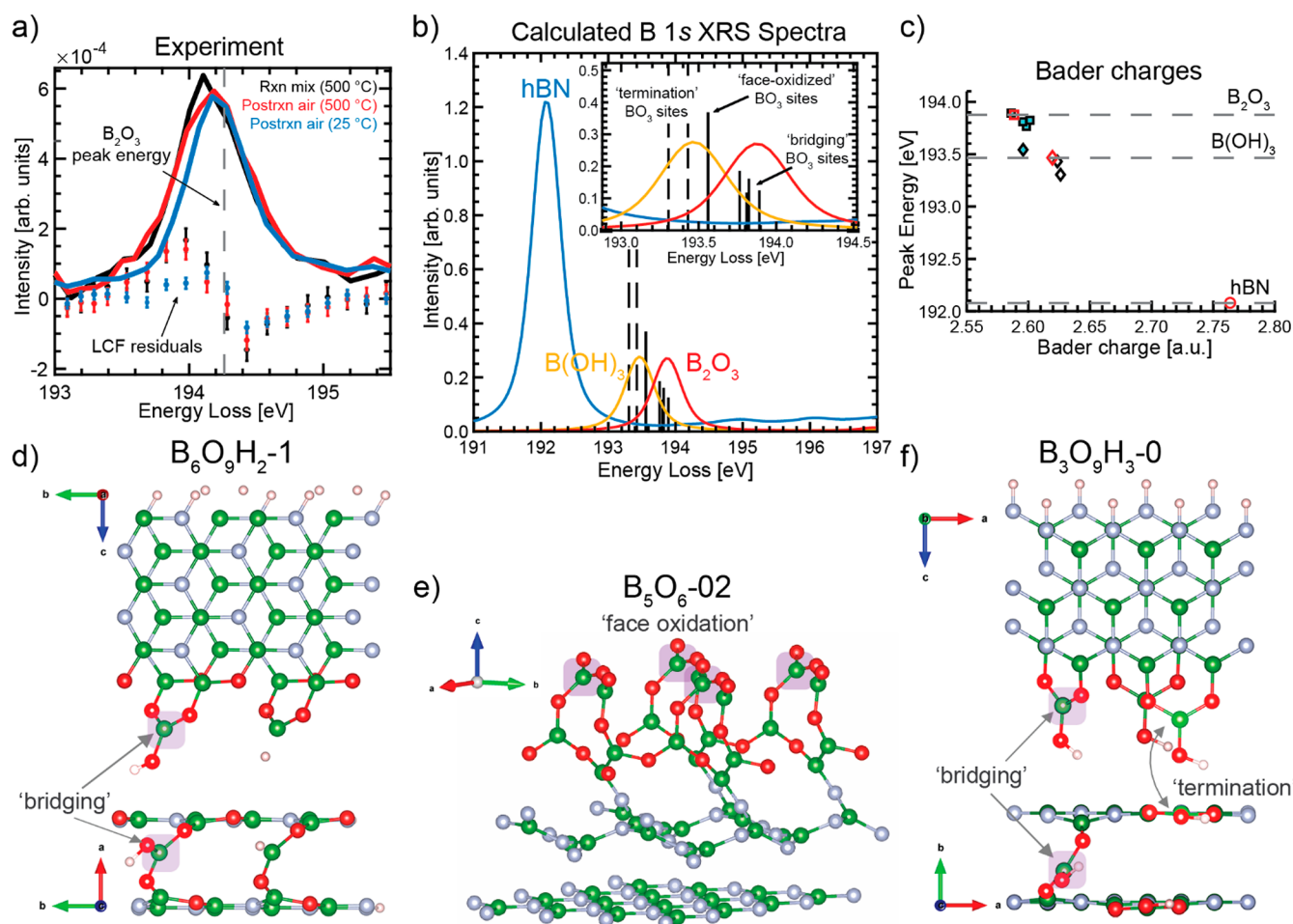


Figure 3. (a) Experimental B 1s XRS spectra zoomed in on the 194 eV feature ([BO₃]-type species) of hBNNS under the reaction gas mix (30% C₃H₈, 15% O₂, bal. He) at 500 °C (black line), under air at 500 °C (red line), and under air at 25 °C (blue line); markers with error bars are the corresponding LCF residuals. The black dashed line indicates the reference B₂O₃ peak energy from experiment. (b) Calculated B 1s XRS spectra of hBN, B(OH)₃, and B₂O₃ along with peak energies of [BO₃]-type sites within relevant structures under the ODH of propane. (c) Bader charges and peak energies of candidate boron structures and references. References—red markers: hBN (open red circle), B(OH)₃ (open red diamond), and B₂O₃ (open red square). Candidate structures [BO₃]-sites: “termination” (open black diamond), “face-oxidized” (filled cyan diamond), “bridging” (filled cyan squares). (d–f) Representative candidate structures.

water cofeed (in a 7 mm i.d. reactor) shows the presence of ca. 10% [BO₃]-type species (Figure S16), a relative oxide contribution much lower than the 30% [BO₃]-type species previously reported for activated hBN without a water cofeed.⁸ Additionally, the volume-dependent response to water indicates that under typical laboratory reactor conditions the gas phase chemistry is more kinetically relevant than the surface chemistry.

Structural Insights from Theory. As mentioned above, LCF analysis using hBN and B₂O₃ standards results in residuals around both the [BN₃] peak at 192 eV and the [BO₃] feature at 194 eV. For the [BN₃] peak, residuals are observed only at high temperatures, whereas for the [BO₃] feature, a small residual is present at room temperature, which becomes more prominent at elevated temperatures (Figure 3a). To understand this behavior, we investigated the surface reconstruction of hBN edges and faces under ODHP conditions by performing systematic simulations of X-ray Raman spectra for several candidate structures and references (Figure 3b, see SI for calculation details). The peak energy as a function of Bader charge is shown in Figure 3c. The candidate structures (Figure 3d–f) are partially oxidized/hydroxylated

and restructured hBN terminations (armchair edge, zigzag edge, and face) from grand canonical global optimization sampling with varying surface stoichiometry of B_xO_yH_z. Notably, this method captures not only the structures of the most stable surface phase (global minimum) but also the metastable structures (local minima) which are only accessible in the catalytic conditions, such as the bridged O–B–O over the hBN edges and the unsaturated B–B motifs on restructured hBN faces.

The obtained ensemble of reconstructed face-oxidized structures predicts the formation of different boron species on top of the hBN layer, introducing structural changes and distortions in the upper hBN lattice (Figure 3e). Therefore, the overall distance between the undistorted and top (oxidized) layer becomes smaller as compared to edge-oxidation or pristine hBN (Figure S7b,c). Particularly, the distance between nearest boron atoms at adjacent layers for hBN and edge-oxidation structures is ≈3.62 and ≈3.65 Å, respectively, whereas for face-oxidation structures this distance can get as short as ≈2.78 Å. Such reduction in the interlayer distance yields additional spectral features on the low- and high-energy sides of the [BN₃] peak, distorting the characteristic single

peak observed in hBN and edge-oxidation candidates (Figure S7b–d). In edge-oxidation structure candidates, we found that the only species giving additional features in the near vicinity of the $[\text{BN}_3]$ energy peak are the $[\text{BO}_2\text{H}]$ and $[\text{BN}_2\text{O}]$ sites for the armchair-edge and zigzag-edge structures, respectively. From the above results, we found that the reduction in the interlayer distance due to face-oxidation and the presence of $[\text{BO}_2\text{H}]$ and $[\text{BN}_2\text{O}]$ species in edge-oxidation candidates, both occurring at reaction conditions and/or high temperatures, are the most probable cause accounting for the experimental changes observed at the $[\text{BN}_3]$ feature at high temperatures.

Several boron species are formed at the reconstructed hBN termination edges. Energy positions of the first resonance (peak energies) vs Bader charges of these boron sites along with reference structures are shown in Figure S17. An almost linear relation is observed between the peak energies and Bader charges of the different boron sites, particularly for the armchair-edge candidates, and a relatively larger dispersion on the results for the zigzag-edge structures (Figure S17b). Overall, the calculations exhibit a remarkable consistency across all considered structures, showing the reliability of the DFT-BSE approach implemented in OCEAN⁴³ for predicting relative energy positions of spectral features between different systems. From all oxidized boron species present within these structures, only $[\text{BO}_3]$ sites have peak energies with values ranging from the vicinity of $\text{B}(\text{OH})_3$ to B_2O_3 reference systems. The more symmetric and strained ones, those $[\text{BO}_3]$ sites where two oxygens are bonded to boron atoms of the same hBN layer, labeled as “termination” sites (Figure 3f), have peak energies below the $\text{B}(\text{OH})_3$ peak. More interestingly, only those $[\text{BO}_3]$ sites “bridging” between two adjacent layers (Figure 3d,f), where two of the oxygens are bonded to boron atoms in different hBN layers, have peak energies above $\text{B}(\text{OH})_3$ and close to B_2O_3 . It is precisely in this energy range where the experiment shows the largest residuals of the LCF fitting around the oxide peak under the reaction conditions (Figure 3a).

The difference between the “bridging” species in the zigzag-edge and armchair-edge candidate structures is in the chemical environment of the termination layer boron site where the bridge is connected. For armchair-edge and zigzag-edge the termination boron atoms linking the bridging species are $[\text{BO}_2\text{N}]$ and $[\text{BN}_2\text{O}]$ sites, respectively. This difference becomes very relevant when considering that according to our calculations, $[\text{BO}_2\text{N}]$ sites would yield spectral features at ≈ 1 eV above the $[\text{BN}_3]$ peak (Figure S17b). However, in the experiment there is no evidence of such features at any measured condition. Hence, these observations allow us to rationalize that, during *operando* conditions, only $[\text{BO}_3]$ “bridging” sites between zigzag-edge terminations are fully compatible with the evolution of the observed experimental features at both $[\text{BN}_3]$ and $[\text{BO}_3]$ peaks and accounts for spectral the changes during reaction. Another structure yielding boron oxides with peak energies in this energy region, though slightly below $[\text{BO}_3]$ “bridging” species, are those $[\text{BO}_3]$ sites formed in the upper layer during “face-oxidation” (Figure 3e). These results are summarized in Figure 3.

CONCLUSIONS

We performed an *operando* X-ray Raman spectroscopy study to observe the oxyfunctionalization of hBN during the catalyst startup in the ODH of propane. We then used *operando* XRS

to clarify the role of cofed water in hBN-catalyzed ODHP. When water is added into the reaction gas feed, the peak for $[\text{BO}_3]$ disappears, and the rate of propylene formation decreases. The reactivity response is the opposite of the rate enhancement effect by water addition previously reported in the literature. We show that the different response in activity is an effect of the smaller reactor volume which minimizes the gas phase contribution. Therefore, the reactivity observed during the *operando* XRS study is dominated by the surface, with minimal contributions from the gas phase. When gas phase chemistry participates, water enhances the rate of reaction; when the gas phase chemistry does not participate, water hinders the reaction rate. In both cases, water removes oxidized boron from the surface. Under typical laboratory reactor conditions, the effect of water on the gas phase is greater than its effect on the surface, and the gas phase chemistry is responsible for the majority of the observed conversion. These novel results showcase the unique ability of XRS for the *operando* characterization of boron-based (or other low-Z) catalysts under relevant reaction environments. Importantly, the demonstrated high accuracy of the simulated XRS spectra highlights the unprecedented value of state-of-the-art theoretical approaches. Altogether, such experimental–theoretical tools are now setting a new era for *operando* catalysis research as they can rationalize with high fidelity spectral fingerprints originating from transient complex structures that cannot be obtained experimentally from standard materials or *ex situ* studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c08679>.

Experimental methods, computational details, and additional characterization and results (PDF)

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Notes

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