

Transforming Boron Carbon Nitride: A Carbon-to-Oxygen Switch to Boost Propane Oxidative Dehydrogenation

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Supporting Information Placeholder

ABSTRACT: Hexagonal boron nitride (h-BN) catalysts exhibit promising olefin selectivity in the oxidative dehydrogenation of propane (ODHP). However, their catalytic activity is limited by the intrinsically low density of active B–O sites in the h-BN scaffolds. An in situ carbon-to-oxygen switch strategy with a well-defined boron carbon nitride (BCN) skeleton was developed to afford h-BN catalysts with abundant BO₃ units, leading to enhanced catalytic performance in ODHP. An ionothermal procedure was adopted for BCN construction from molten salt precursors (NaNH₂, NaBH₄, and CaC₂), in which the uniformly embedded B–C₃ was transformed into B–O₃ via oxidative calcination (denoted as BON). The structural evolution from BCN to BON was well characterized by spectroscopy and soft X-ray-based techniques. The abundant number of BO₃ units in the as-afforded BON catalysts led to significantly enhanced catalytic performance in ODHP, outperforming the commercial and molten salt-derived h-BN catalysts, with 50.4% conversion of propane and 32.7% yield of olefins achieved at 500 °C. Theoretical simulations further revealed that these B–O₃ species ensure the preferential adsorption and dissociation of the C–H bonds of propane, making the process more thermodynamically favorable. The ionothermal and in situ restructuring approach developed herein provides an efficient strategy to afford high-quality heteroatom-doped h-BN catalysts with enhanced performance in diverse catalysis procedures.

Propylene is a crucial chemical building block in the petrochemical industry and is traditionally produced through fluid catalytic cracking, steam cracking of hydrocarbons in naphtha, and the methanol-to-olefin process.¹⁻³ Propane dehydrogenation (PDH) has emerged as a promising industrial method for propylene production, particularly following the “shale revolution,” which offers the additional benefit of sustainable hydrogen recycling.⁴⁻⁷ Nevertheless, PDH faces challenges, including the formation of undesired byproducts from cracking and coke formation.

These issues arise from the endothermicity of the reaction, which requires high temperatures.⁸ In contrast, the oxidative dehydrogenation of propane (ODHP) offers a competitive alternative for propylene production. The ODHP is favored for its exothermicity and ability to suppress coking. Extensive research has focused on metal oxide-based catalysts for ODHP. However, olefins tend to overoxidize, resulting in byproducts such as monoxide (CO) and carbon dioxide (CO₂). This overoxidation is a critical limitation for the industrial implementation of the ODHP.⁹⁻¹¹

Hexagonal boron nitride (h-BN), one of the most promising materials composed of alternating B and N atoms via strong B–N bonds, has emerged as a vital two-dimensional (2D) nanomaterial analogous to graphene with planar structures.^{12,13} The unique linking pattern endows h-BN with adjustable chemical, electrical, and optical properties, enabling high performance in various fields.¹⁴⁻¹⁶ In 2016, h-BN and boron nitride nanotubes (BNNTs) were identified as promising catalysts for ODHP, exhibiting unprecedented olefin selectivity.^{17,18} Research has demonstrated that the formation of boron-oxygen active phases, such as BO₃ and >BO–OB< species, during ODHP pretreatment is crucial for catalytic activity.¹⁹⁻²² However, the intrinsic limitation in the number of active sites typically formed at unsaturated B sites at the edges and defects in h-BN results in low catalytic activity.²³ To address this issue, a progressive substitution strategy was introduced under high-temperature conditions (>1,500 °C) to develop boron-oxygen-nitrogen nanotubes (BONNTs) enriched with in situ formation of B–O₃ and O–O species as highly active, selective, and stable catalysts for ODHP.²⁴ Further studies on supported boron oxide catalysts (B₂O₃/SiO₂) have presented promising results for ODHP featuring BO₃ and BO–H species.²⁵ Additionally, an economically viable oxidized activated carbon-supported boron (B/OAC) with stable 3-coordinate BO₃-containing species showed high activity in ODHP,²⁶ followed by rapid loss of bulky B₂O₃. Consequently, the construction of stable B–O active sites plays a crucial role in enhancing ODHP performance. Therefore, developing a

simple and controllable method for preparing h-BN nanomaterials enriched with B–O active sites for ODHP remains both essential and challenging.

In this study, we present an in situ carbon-to-oxygen switch strategy in a well-defined boron carbon nitride (BCN) skeleton, in which the uniformly embedded B–C₃ was transformed into B–O₃ via oxidative calcination (denoted as BON). The incorporation of C was achieved through a thermal method involving inorganic molten salts, utilizing NaNH₂, NaBH₄ and CaC₂ as precursors to produce h-BCNs, in which the C atoms act as B–C₃ in h-BN²⁷. Subsequently, the C atoms in BCN were substituted with O atoms via pyrolysis in O₂ atmospheres, successfully yielding abundant B–O₃ sites in the h-BN skeleton, offering a significant improvement in ODHP activity. The as-afforded boron-oxygen-nitride (h-BON-1) offers an olefin yield of 32.7% and a propane conversion of 50.4% under a WHSV of 7200 h⁻¹ at 500 °C, which is 2.4 times greater than that of commercial h-BN. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and density functional theory (DFT) calculations revealed that the in situ formation of B–O₃ active species facilitates the preferential adsorption and activation

of C–H bonds and is thermodynamically favorable for the formation of C=C bonds during ODHP. The controlled incorporation of C atoms into the h-BN framework provides a promising avenue for designing highly efficient catalysts for ODHP and constructing BCN nanostructures with tunable compositions and good crystallinity.

The h-BCN materials were constructed using NaBH₄, NaNH₂, and CaC₂ as starting materials, followed by pyrolysis under O₂ atmospheres to substitute C atoms with O atoms in situ to synthesize h-BON, which resulted in the formation of abundant B–O₃ active species in h-BON (see Figure 1A and the experimental procedures in the Supporting Information). The presence of C domains typically led to darker composites, so the color of the product deepened with increasing amounts of CaC₂²⁸ (Figure S1). Thermogravimetric analysis (TGA) revealed that the C contents in h-BCN-1, h-BCN-2, and h-BCN-3 were 3.7 wt%, 6.5 wt%, and 12.0 wt%, respectively (Figure S1). X-ray diffraction (PXRD) results of the synthesized h-BCN materials revealed a prominent diffraction peak at 2θ = 26.31°, corresponding to the (002) crystal plane of h-BN.

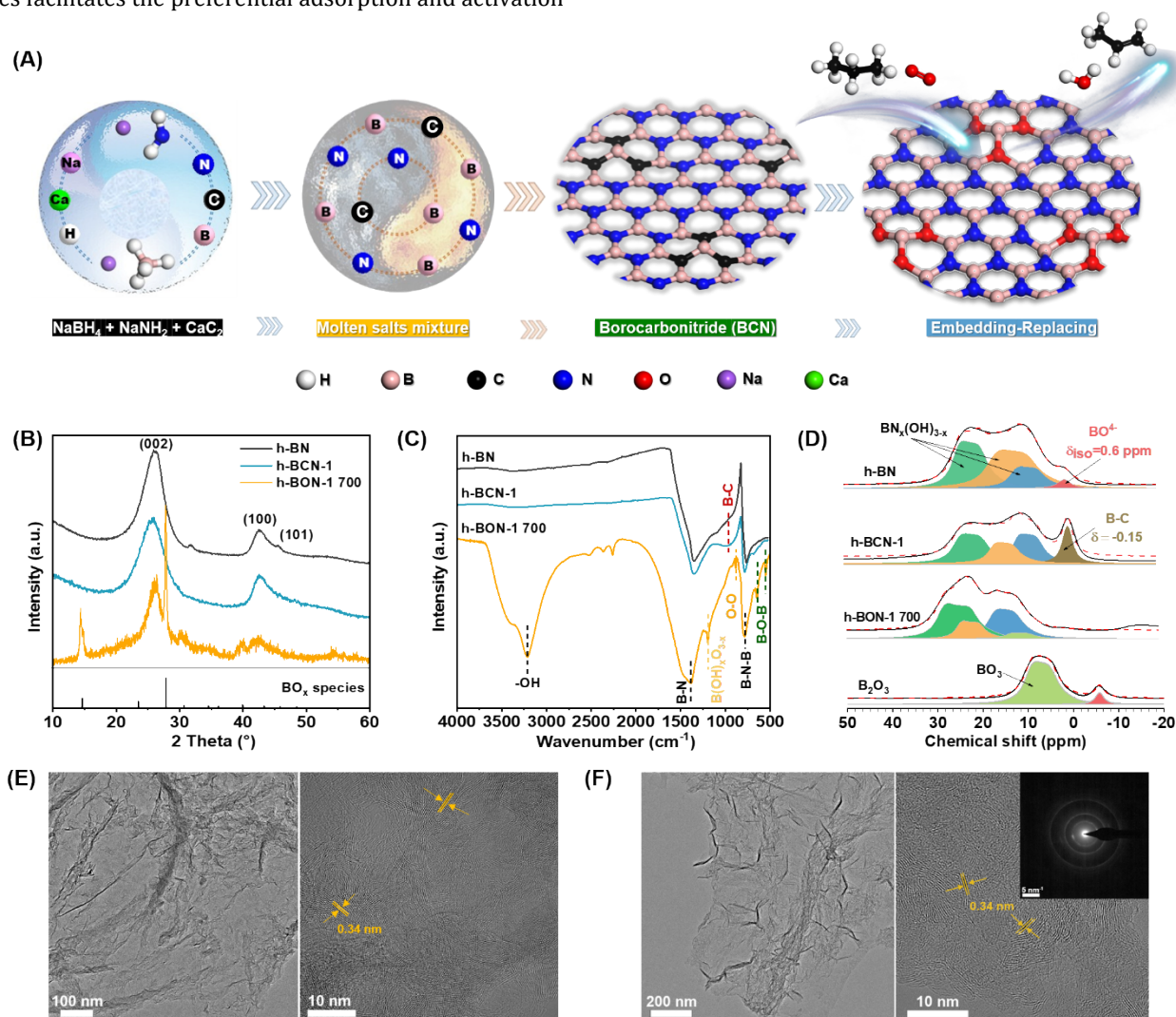


Figure 1. (A) Schematic illustration of the synthesis of h-BCNs and h-BON through a carbon embedding-oxygen replacing strategy to transfer B–C₃ to B–O₃ in boron nitride. (B) XRD patterns and (C) FTIR spectra of h-BN, h-BCN-1 and h-BON-1. (D) ¹¹B solid-state NMR spectra of h-BN, h-BCN-1, h-BON-1, and B₂O₃. HR-TEM images of (E) h-BCN-1 and (F) h-BON-1.

Additionally, two weaker peaks attributed to the (100) and (101) crystal planes at $2\theta = 42.4^\circ$ and 45.5° , respectively, diminished with increasing embedded C content, ultimately indicating a decrease in crystallinity (Figure 1B, Figure S2). These results confirmed that the introduction of C atoms into the h-BN lattice induced an amorphization effect.²⁹ Furthermore, the h-BON-1 pattern exhibited a broad peak corresponding to lower crystalline h-BN and expansion of the interplanar crystal spacing, which was attributed to the substitution of O atoms in the h-BN lattice.³⁰ Notably, diffraction peaks at $2\theta = 27.8^\circ$ and 39.9° corresponding to BO_x were observed.

The Fourier transform infrared (FTIR) spectra of both h-BN and h-BCNs showed two characteristic peaks at $1,360.2\text{ cm}^{-1}$ and 783.1 cm^{-1} , corresponding to the in-plane stretching and out-of-plane bending vibrations of B-N bonds, respectively. (Figure 1C, Figure S3). An additional peak at 916.2 cm^{-1} , which intensified with increasing C content, was assigned to the B-C bond.^{31,32} Moreover, a small peak at $1,643.4\text{ cm}^{-1}$ in h-BCN-3 indicated the formation of C=N bonds.³³ These results confirmed the successful incorporation of C atoms into the BN lattice to create h-BCN hybrid materials. The FTIR spectrum of h-BON-1 indicated that the h-BN skeleton remained well preserved, even after O_2 activation of h-BON-1 (Figure S4). Additionally, the B-C bonds in the FTIR spectra disappeared after pyrolysis at temperatures higher than $700\text{ }^\circ\text{C}$, and additional absorption peaks assigned to different kinds of B-O active species for ODHP were observed (Figure S5, Figure 1C).³⁴ Specifically, two absorption peaks at approximately 548.2 cm^{-1} and 647.3 cm^{-1} corresponding to the B-O-B bond were derived from the in situ construction of O-containing terminal groups.²⁴ Furthermore, the $\text{B(OH)}_x\text{O}_{3-x}$ species at $\sim 1,195.9\text{ cm}^{-1}$ and O-O species at 926.3 cm^{-1} were detected, indicating that C primarily existed as B-C₃ in the h-BN framework, with neighboring C atoms substituted by O atoms.^{18,24} In contrast, the vibrations of O-O species and $\text{B(OH)}_x\text{O}_{3-x}$ species were difficult to recognize in commercial h-BN and h-BN without

any C-to-O switching (Figure S6). Thus, C embedding was a crucial step for constructing B-O₃ active species. In addition, the strong and broad peaks centered at 3220 cm^{-1} and 3400 cm^{-1} were related to O-H and N-H stretching vibrations, which are features of hydroxylation under the ODHP process commonly observed in the BN system. The ¹¹B solid-state nuclear magnetic resonance (¹¹B SSNMR) spectra revealed three major characteristic signals attributed to B atoms with three coordinating N/O atoms ($\text{BN}_x(\text{OH})_{3-x}$ ($0 \leq x \leq 3$)) that can be simulated with a chemical shift (δ_{iso}) between 31.5 ppm and 14.0 ppm (Figure 1D).^{18,35,36} The new signal at 0.60 ppm was attributed to B with hydroxyl groups and B-containing complexes (BO^+), which is consistent with previous studies on h-BN.²⁷ Notably, h-BCN-1 exhibited an additional peak at -0.15 ppm belonging to the B-C bonds.³⁷ In addition, from h-BCN-1 to h-BCN-3, the intensity of the B-C peak increased as the C content gradually increased, as shown in Figure S7, indicating that more B-C bonds formed. The difference in the ¹¹B SSNMR data of h-BON-1 and commercial B_2O_3 suggested that the fine structure of the BO_3 species in h-BON-1 did not match that of bulk B_2O_3 . These BO_3 species increase with increasing pyrolysis temperature, following the loss of some boron sites (Figure 1D, Figure S8). Hence, these BO_x species were B-O₃ in the h-BN structure, not bulk B_2O_3 , as confirmed by the FTIR and ¹¹B SSNMR results (Figure S8-S9).

High-resolution transmission electron microscopy (HR-TEM) images revealed a curled nanosheet-like structure in h-BCN-1 (BN: C = 1: 0.05) with an interlayer crystal lattice spacing of 0.34 nm, which is consistent with h-BN synthesized without CaC_2 (Figure 1E, Figure S10). The morphology of the h-BON-1 nanosheets was clearly preserved even after gradual oxidation, as shown in Figure 1F. However, the presence of excessive C led to the aggregation of the h-BN structure and induced a disordered configuration, which was confirmed by N_2 adsorption-desorption analysis and electron paramagnetic resonance (EPR) spectroscopy (Figure S11-S12).

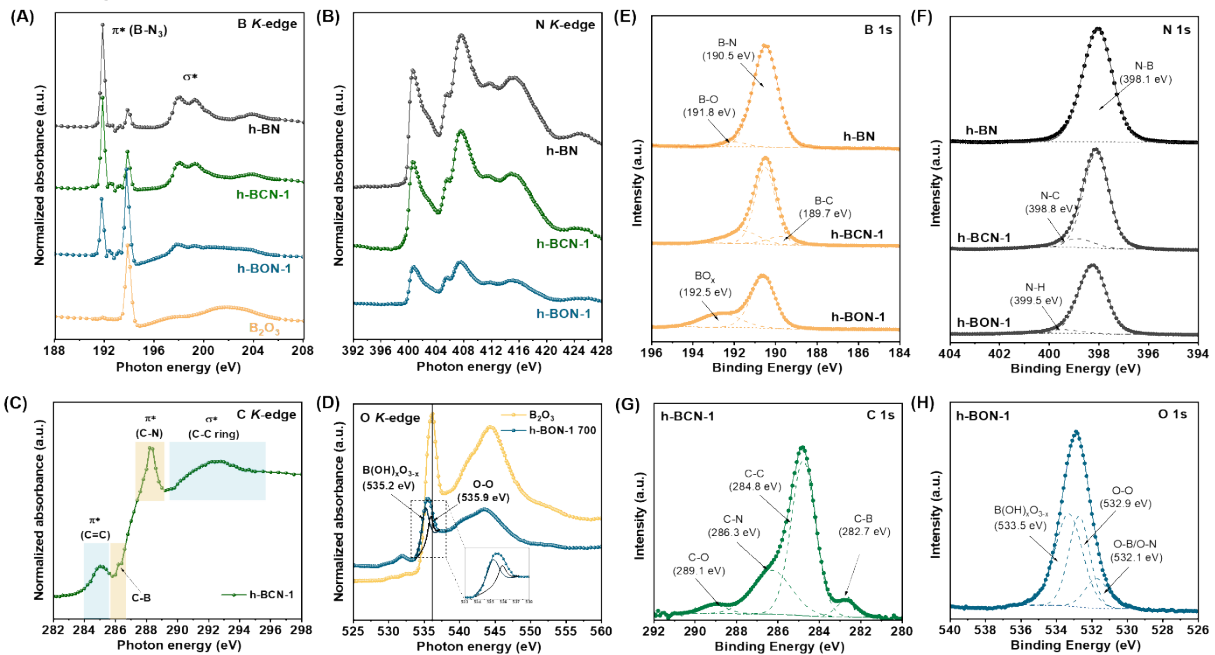


Figure 2. XANES spectra for (A) B K-edges of h-BN, h-BCN-1, h-BON-1, and B_2O_3 . (B) N K-edges of h-BN, h-BCN-1, and h-BON-1. (C) C K-edge of h-BCN-1. (D) O K-edge from h-BON-1 and reference B_2O_3 . (E) B 1s XPS spectra and (F) N 1s XPS spectra of h-BN, h-BCN-1, and h-BON-1. (G) C 1s XPS spectra of h-BCN-1. (H) O 1s XPS spectra of h-BON-1.

The transformation of B-C₃ to B-O₃ in the h-BCN framework led to the formation of h-BON-1 nanosheets. X-ray absorption near edge structure (XANES) and X-ray photoelectron spectroscopy (XPS) were employed to gain more insight into the local electronic structures. In the case of the B K-edge, the h-BN, h-BCN-1, and h-BON-1 spectrum curves contained a B 1s- π^* transition resonance at 191.8 eV, indicating the existence of a high concentration of sp²-hybridization B-N bonds (BN₃), and the broad feature at 197.5 eV corresponded to the B 1s- σ^* transition resonance (Figure 2A). Comparatively, the intensity of the B 1s π^* features in h-BCN-1 decreased compared with that in h-BN (0.25:0.22), indicating that the incorporation of C into the h-BN skeleton significantly reduced the π bonding states by forming defective pyridine-like C-N structures.³⁸ The peak at 194 eV in fresh h-BON-1 corresponded to a B-O₃

coordination environment, which offered a greater number of reactive sites for ODHP. In contrast, B₂O₃ exhibited a sharp peak at 194 eV (BO₃ species) and broader features above 196 eV, which were considerably different from those of the B-O₃ species in h-BON-1. An intensity decrease trend and assignment was observed in the N K-edge spectrum, which was composed of N 1s- π^* transitions (2p_z) at 401.7 eV and N 1s σ^* transitions (2p_{x,y}) above 408.6 eV with increased intensity (Figure 2B).³⁹ Additionally, the C K-edge spectrum of h-BCN-1 is shown in Figure 2C, which provides clear evidence of C incorporation into the h-BN skeleton. The presence of the peak at 285.4 eV (π^* C-C), corresponding to the π^* state of graphite, indicates that there was adjacent C in h-BCN-1. The peak located at 286.5 eV and 288.5 eV assigned to C-B bonds and C-N bonds, respectively, were related to the formation of a ternary B-C-N compound.

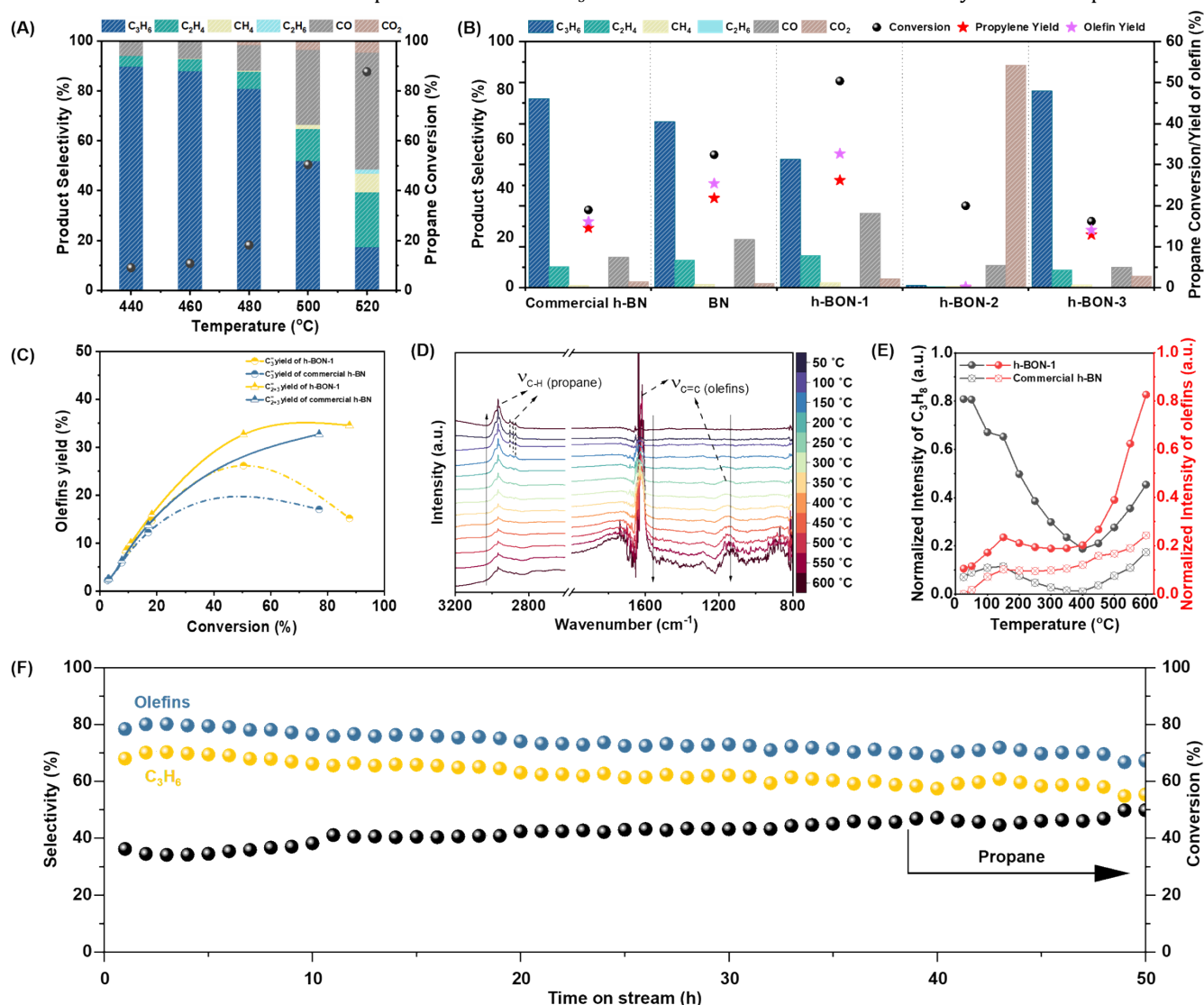


Figure 3. (A) Propane conversion and propylene selectivity with increasing reaction temperature over h-BON-1. (B) Propane conversion, propylene yield, total olefin yield, and product selectivity when different catalysts are deployed at 500 °C (commercial h-BN, h-BN, h-BON-1, h-BON-2, and h-BON-3). (C) Propylene yield and olefin yield as a function of propane conversion. (D) In situ DRIFTS observation of h-BON-1 collected under simulated reaction conditions from 25 °C to 600 °C with a ramping rate of 50 °C/min. (E) Normalized intensities of the C-H vibration peak and C=C vibration peak. (F) Stability test of h-BON-1 at 500 °C. Reaction conditions: catalyst weight, 200 mg; gas feed, 240 mL min⁻¹; C₃H₈/O₂/N₂ with a molar ratio of 1/1.5/3.5; WHSV = 7200 h⁻¹. Propylene selectivity and olefin selectivity as a function of propane conversion.

The broad peak at approximately 291 eV corresponded to the transitions from C 1s to σ^* states (σ^* C-C) and the empty higher-energy states, indicating the presence of *p*-symmetry components projected onto the C sites.⁴⁰ The O K-edge XANES spectra of h-BON-1 provided additional evidence that the B-O species in h-BON-1 were B-O₃ structures that were structurally distinct from the bulk B₂O₃ on the surface (Figure 2D). The O K-edge XAS spectra of fresh h-BON-1 showed a minor signal at ~532 eV attributed to a B-O bond, which differed from the B-O bond in B₂O₃ (~536 eV), in agreement with a previous report.^{18,41} In contrast, except for the B-O peak at 532 eV, there was a peak centered at 535.5 eV, which split into two peaks: B(OH)_xO_{3-x} species (likely BO₃) at 535.2 eV and O-O species at 535.9 eV. The chemical compositions and coordination states were further characterized by XPS, and the results are shown in Figure 2E-2H and Figure S13- S16. The existence of B-N bonds in h-BCN was verified by the peak in the XPS spectra of B 1s at a binding energy (BE) of 190.5 eV and N1s at a BE of 398.1 eV. Additionally, a peak at a BE of 189.7 eV in the B1s XPS spectrum was attributed to the formation of B-C bonds, and the peak at a BE of 398.8 eV in the N1s XPS spectrum was attributed to the C-N bond (Figure 2E-2F).^{38,42} Surface C was incorporated in the form of C-B, C-C, C-N, and C-O bonds, with BEs of 282.7, 284.8, 286.3, and 288.9 eV, respectively, as shown in the C1s XPS spectrum (Figure 2G).⁴³ XPS results of h-BON-1 revealed the presence of both B-N and N-B in the B 1s and N 1s spectra, respectively, confirming that the h-BN skeleton composed of B and N atoms remained dominant. The doped C atoms in the terminal groups and adjacent locations of h-BCN-1 were substituted by O atoms after oxidation, resulting in oxygen-functionalized h-BON-1, which was confirmed by the appearance of abundant BO_x species. As shown in Figure 2H, the peak at 533.5 eV in the O 1s XPS spectrum was assigned to the B(OH)_xO_{3-x} species, and the peak at 532.1 eV was attributed to B-N/B-O.²⁴ Notably, another peak at ~532.9 eV belongs to the O-O species, which is likely generated from the O-substitution of adjacent C-C atoms, as corroborated by the FTIR and XPS spectra (Figure 1C, Figure S15-S16).

The ODHP is a vital alternative to traditional propylene production procedures because of its reaction endothermicity and cost-effectiveness. The B-based catalysts played a crucial role in this process, as the B-O active species accounted for propane activation and the unique behavior of O₂ activation on the active surface, leading to high olefin selectivity. To increase the catalytic activity, maximizing the B-O species was essential. We employed h-BON-*x* catalysts, which utilize a flexible C embedding-O replacement strategy to transfer B-C₃ to B-O₃ active species, for efficient ODHP within a temperature range of 440–520 °C. Notably, h-BON-*x* catalysts function effectively for ODHP without requiring additional activation. As illustrated in Figure 3A and Figure S17, commercial h-BN, h-BN and h-BON-1 catalysts exhibited poor propane conversion at lower reaction temperatures. This limitation arose from the difficulty in overcoming the energy barrier for the homolytic dissociation of the BO-H bond at low reaction temperatures (<460 °C). Increasing the reaction temperature drastically enhanced propane conversion, yielding remarkable propylene and olefin yields of 26.2% and 32.7%, respectively, and a propane conversion of 50.4% over h-BON-1 at 500 °C under a WHSV of 7,200 h⁻¹,

which was much greater than that of commercial h-BN (16.9% propane conversion and 13.7% olefin yield) and h-BN without any C-to-O switch (35.8% propane conversion and 27.1% olefin yield) under the same conditions (Figure 3B-3C). Importantly, the CO₂ selectivity was less than 5% throughout the whole process, and the products were mainly propylene and ethylene. Thus, it was concluded that the flexible and controllable C embedding-O replacement strategy used to transfer B-C₃ to B-O₃ in the h-BN skeleton contributed to the enhanced ODHP performance. When h-BON-2 was tested, minimal propylene with a majority of CO₂ was detected, where a propane conversion of 20.0% and only a low olefin yield of 0.169% were obtained at 500 °C. However, further increasing the C content induced carbonization. h-BON-3 only showed an olefin yield of 14.0%, with a propane conversion of 16.2%. These results confirmed that the incorporation of a suitable number of C atoms was beneficial for constructing h-BON nanostructures that enhanced ODHP activity. Conversely, an excess of C atoms may lead to reduced activity, likely due to surface blockage of the agglomeration of h-BON-2 and h-BON-3 (Figure S17).

To further investigate the mechanism of propane activation and propylene formation, in situ DRIFTS was conducted (Figure 3D). In the absorption stage for introducing C₃H₈, the characteristic vibration peak at approximately 3,060–2,850 cm⁻¹ was attributed to the C-H stretching of the methyl and methylene groups in C₃H₈.⁴⁴ The intensities of these characteristic peaks were used to assess the C₃H₈ adsorption capacity of h-BON-1, which outperformed that of commercial h-BN (Figure S18). As the treatment temperature increased, the intensity of C-H in C₃H₈ for h-BON-1 decreased more rapidly than that of commercial h-BN. In addition, all the catalysts generated olefins, as indicated by peaks at 1,200–1,000 cm⁻¹ and 1,500–1,650 cm⁻¹, corresponding to the stretching vibration of =CH₂.⁴⁵ The generation rate of =CH₂ was relatively fast on the h-BON-1 catalyst, indicating a relatively high consumption rate of C₃H₈ and a relatively high formation rate of olefins (Figure 3E). Additionally, the requirement for high catalytic stability was indispensable. We further applied the optimal h-BON-1 catalyst for ODHP, which showed compelling catalytic activity and stability, as displayed in Figure 3F. After 50 h of operation, propane conversion increased from 34.5% to 50.4%, accompanied by a slight decrease in propylene and olefin selectivity. Moreover, this catalyst demonstrated high activity in ODHP, nearly surpassing other B-based catalysts used in previous studies at the same reaction temperature (500 °C) (Figure S19). The HRTEM images of the spent catalyst suggested that the h-BN nanosheet-like structure remained intact after the reaction, which was consistent with the diffraction peaks in the XRD pattern and FTIR spectra (Figure S4, Figure S20-S22). Additionally, the spectra of the BN_xO_{3-x} species in h-BON-1 before and after ODHP were similar, with a slight increase in intensity at lower δ_{iso} values associated with BO₃ species and the disappearance of BN₃, suggesting further oxidation and the loss of some boron sites after ODHP (Figure S23).

Density functional theory (DFT) calculations were performed to elucidate the active structure and mechanism

of the h-BON catalyst. Based on our characterization analysis, six different types of models were considered, including O-O, BO-ON+B-O, B-O₃, N₂-B-O, N-B₂-O, and B-O edge models (Figure S24). Initially, these models were constructed to identify the one that provides the most stable adsorption configuration for C₃H₈. As displayed in Figure S25, the B-O₃ model was the most stable active site for ODHP, as evidenced by its lowest C₃H₈ adsorption energy for both configurations horizontal and vertical to the surface (E_{ads} of -2.11 eV and -1.98 eV, respectively), which is consistent with the C₃H₈-temperature programmed desorption curves (Figure S26A). Additionally, charge density differences and the relative electron localization function (ELF) contours revealed significant chemisorption between the B atom and C₃H₈ at the B-O₃ site, indicating strong and favorable interactions (Figure 4A). The optimized B-O₃ site was selected for further evaluation of the following C₃H₈ dehydrogenation reaction involving O₂ to produce C₃H₆, while the B-O-edge site was chosen for comparison, as shown in Figure 4B. The ODHP process was initiated with the adsorption of propane, which proceeded as a thermodynamically favorable step for both the B-O₃ and B-O-edge sites, with adsorption energies of -2.117 eV and -

0.795 eV, respectively. Following previous studies, the subsequent step in ODHP was considered to start with H abstraction from the secondary carbon (-CH₂-). Based on the relative free energy diagram, the step with the highest uphill energy is defined as the rate-limiting step. Therefore, the rate-limiting step on the B-O₃ site was the first H abstraction of C₃H₈, with a reaction energy of 1.93 eV. To drive the formation of propylene from propyl on the B-O₃ surface, O₂ was introduced in the following step by first abstracting H from the surface O-H/B-H with a reaction energy of 0.90 eV, which simultaneously reduces O₂ to HO₂; this is followed by H₂O₂ formation by HO₂ abstracting the hydrogen from the propyl. Finally, both propylene and H₂O₂ desorbed readily from the surface, and H₂O₂ decomposed to form water (Figure S26B), thereby closing the cycle and regenerating the active site.⁴⁶ In contrast, even though a series of thermodynamically downhill steps occurred for the ODHP reaction over the B-O-edge site, the rate-limiting step for the B-O-edge site was C₃H₇*+HO₂*→C₃H₆*+H₂O₂*, with a high reaction energy of 3.08 eV. Consequently, the B-O₃ site was more thermodynamically favorable than the B-O-edge site for O₂-assisted C₃H₈ dehydrogenation to propylene.

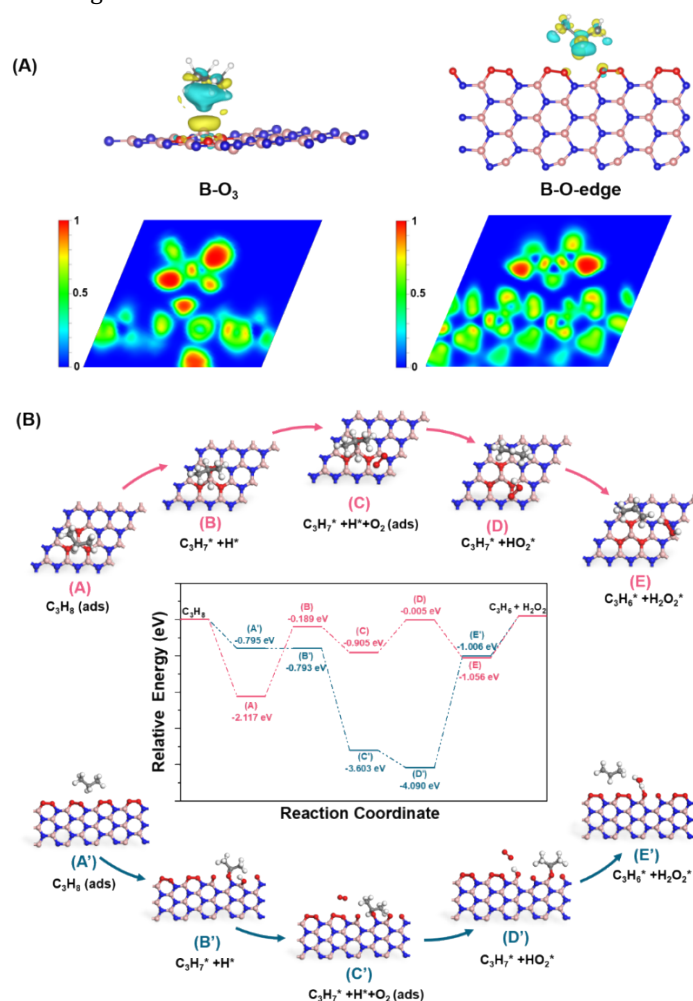


Figure 4. (A) Optimized adsorption model and charge density differences and relative ELF contours of C₃H₈ chemisorbed on the B-O₃ site and B-O-edge site (isosurface level=0.0003). (B) Reaction pathways for the oxidative dehydrogenation of propane to propylene at the B-O₃ site and B-O-edge site and the corresponding atomic configuration (transition states could not be acquired using the current level of theory; thus, quantitative comparisons with experimental data cannot be obtained from our model).

In summary, the successful creation of B–O₃ active sites for ODHP in the h-BN skeleton was achieved through a controllable in situ carbon-to-oxygen switch strategy using molten salts (NaNH₂, NaBH₄ and CaC₂) as precursors. The construction of a high number of B–O₃ species in the h-BN structure resulted in an attractive performance in the ODHP process, achieving a propane conversion of 50.4% and an olefin yield of 32.7% at 500 °C, almost surpassing those of previously reported h-BN materials. Furthermore, the original h-BN skeleton was preserved in the BON, providing structural advantages that ensured long-term stability over 50 h at 500 °C during ODHP on stream. This efficient strategy not only facilitates the engineering of active sites in h-BN, which are conducive to the formation of B–O₃ active centers to increase ODHP but also provides a novel synthesis capable of providing easy access to BCN nanostructures with a controlled composition and good crystallinity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website, including experimental procedures, supplementary contents and figures.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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