

## Supplementary Materials

### Engineering boron-terminated defects in carbon-doped boron nitride catalysts for enhanced activity in oxidative dehydrogenation of propane

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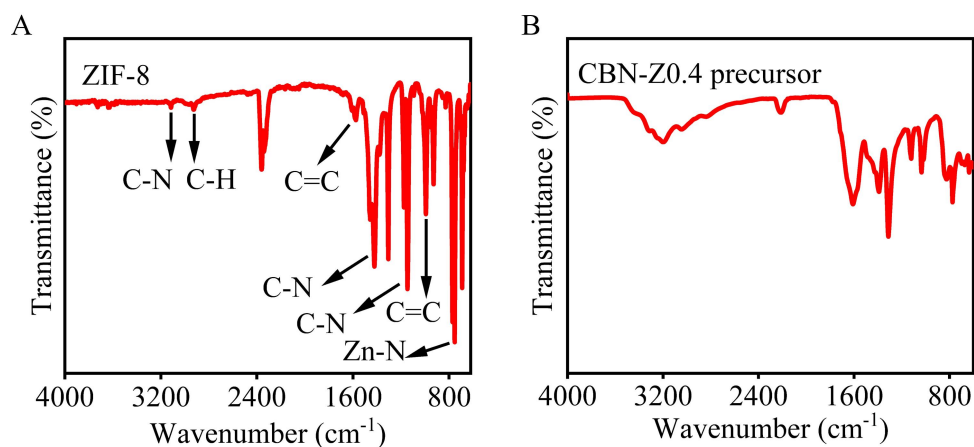
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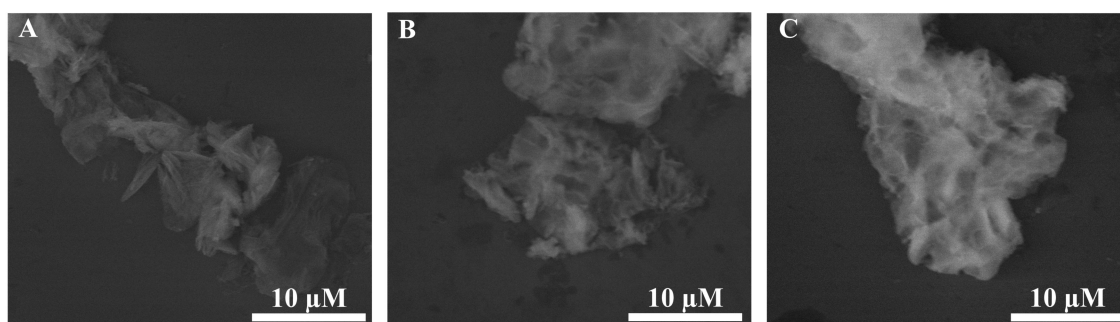
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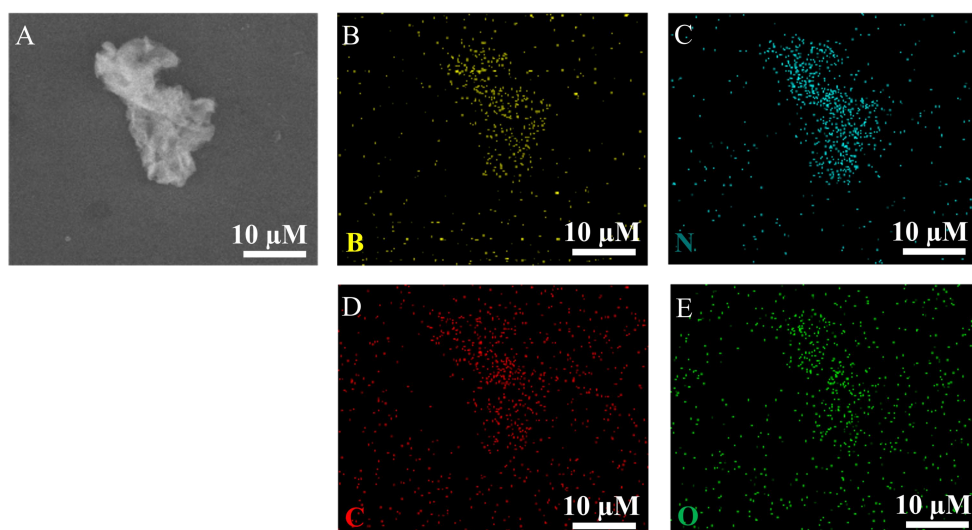
**Supplementary Figure 1.** FTIR spectra of (A) ZIF-8 and (B) CBN-Z0.4 precursor.

FTIR: Fourier transform infrared; CBN-Zx: ZIF-8 derived carbon-doped boron nitride.

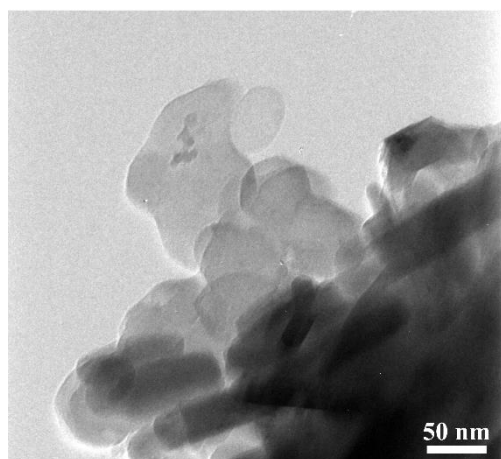


**Supplementary Figure 2.** SEM images of (A) CBN, (B) CBN-Z0.2 and (C) CBN-Z0.4.

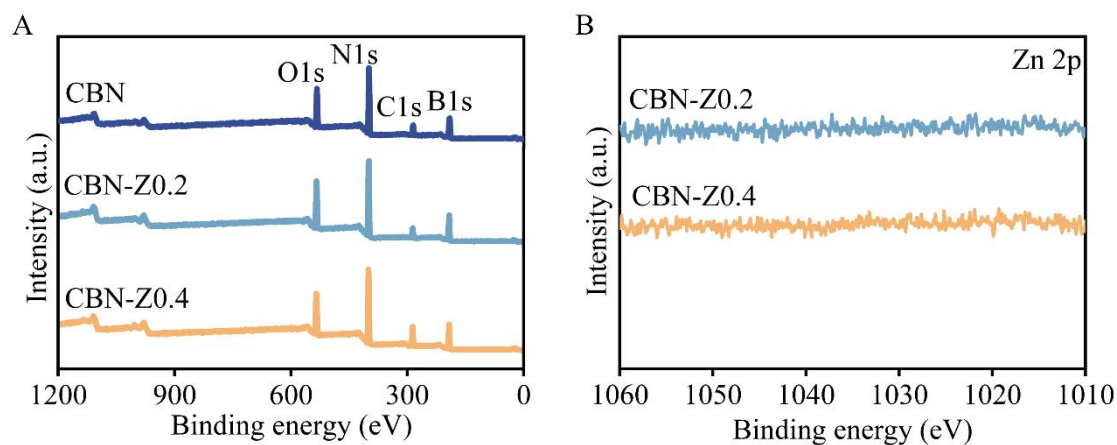
SEM: Scanning electron microscope; CBN: carbon-doped boron nitride; CBN-Zx: ZIF-8 derived carbon-doped boron nitride.



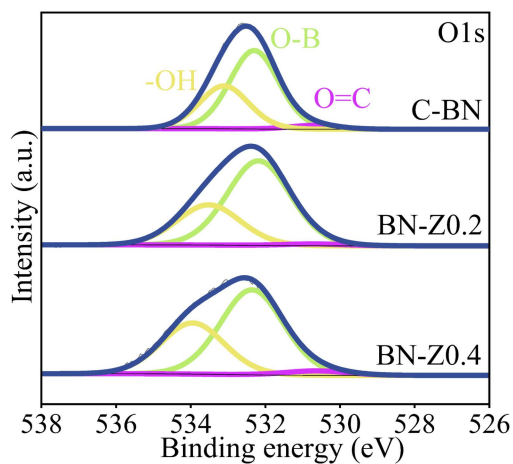
**Supplementary Figure 3.** (A) SEM images of CBN-Z0.4 and EDS elemental mapping of (B) B, (C) N, (D) C and (E) O elemental. EDS: Energy dispersive X-ray spectroscopy; CBN-Zx: ZIF-8 derived carbon-doped boron nitride.



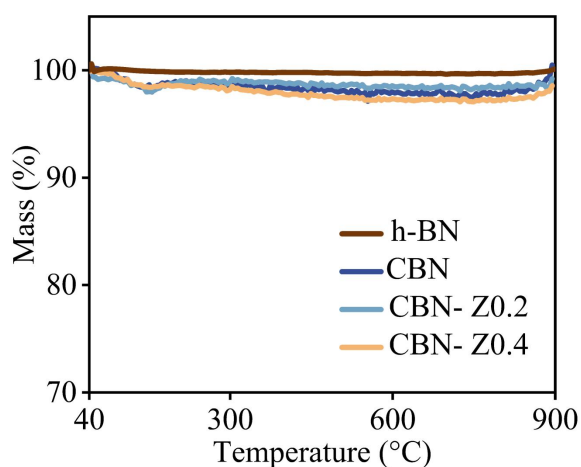
**Supplementary Figure 4.** TEM images of commercial h-BN. TEM: Transmission electron microscope; h-BN: hexagonal boron nitride.



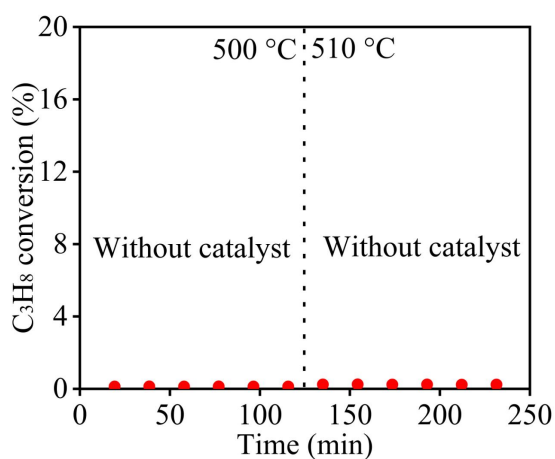
**Supplementary Figure 5.** (A) XPS survey and (B) Zn 2p XPS spectra of CBN, CBN-Z0.2 and CBN-Z0.4 catalysts. XPS: X-ray photoelectron spectra; CBN: carbon-doped boron nitride; CBN-Zx: ZIF-8 derived carbon-doped boron nitride.



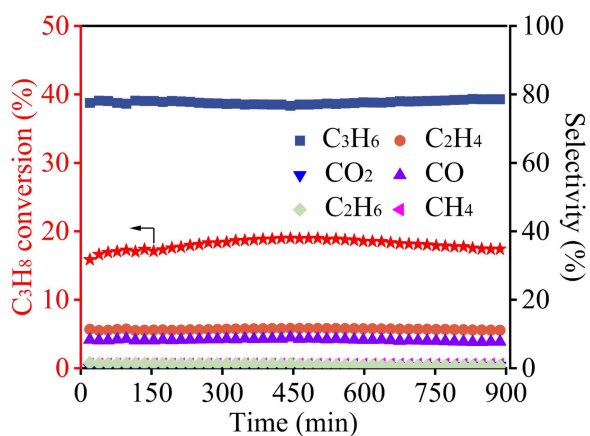
**Supplementary Figure 6.** Deconvolution of O 1s XPS spectra of CBN, CBN-Z0.2 and CBN-Z0.4 catalysts. XPS: X-ray photoelectron spectra; CBN: carbon-doped boron nitride; CBN-Zx: ZIF-8 derived carbon-doped boron nitride.



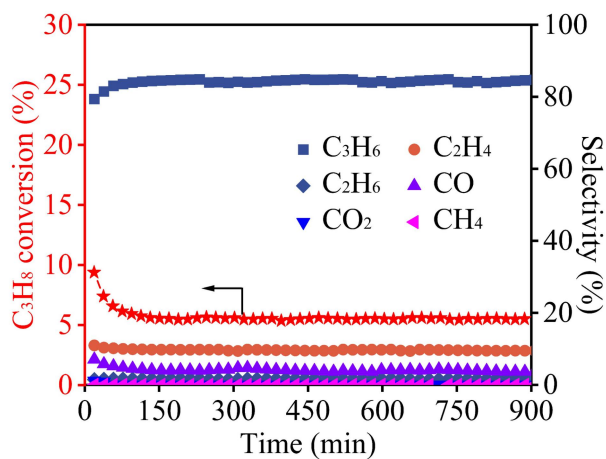
**Supplementary Figure 7.** TGA profiles for h-BN, CBN, CBN-Z0.2 and CBN-Z0.4 in air. TGA: Thermogravimetric analysis; CBN: carbon-doped boron nitride; CBN-Zx: ZIF-8 derived carbon-doped boron nitride.



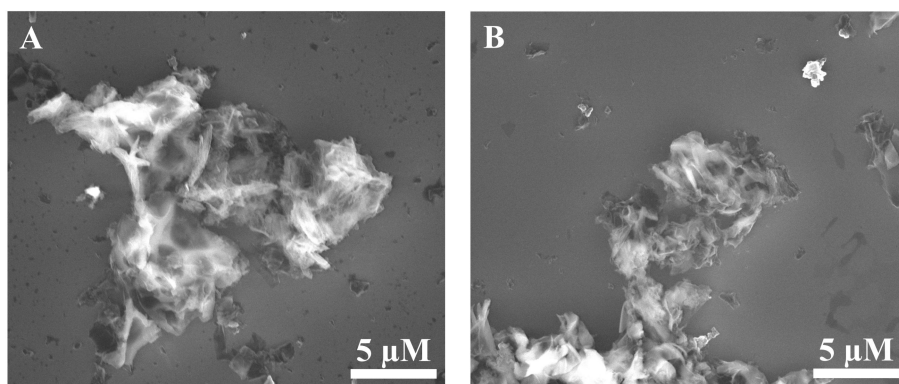
**Supplementary Figure 8.** ODHP reaction performance without catalysts. Reaction conditions: 500 °C or 510 °C, 10 kPa C<sub>3</sub>H<sub>8</sub>, 15 kPa O<sub>2</sub>, He balance total 25 mL min<sup>-1</sup>. ODHP: Oxidative dehydrogenation of propane.



**Supplementary Figure 9.** Catalytic performance of CBN-Z0.2 as a function of time on stream. Reaction conditions: 100 mg catalyst, 500 °C, 10 kPa C<sub>3</sub>H<sub>8</sub>, 15 kPa O<sub>2</sub>, He balance total 25 mL min<sup>-1</sup>. CBN-Zx: ZIF-8 derived carbon-doped boron nitride.



**Supplementary Figure 10.** Catalytic performance of h-BN as a function of time on stream. Reaction conditions: 100 mg catalyst, 500 °C, 10 kPa C<sub>3</sub>H<sub>8</sub>, 15 kPa O<sub>2</sub>, He balance total 25 mL min<sup>-1</sup>.



**Supplementary Figure 11.** SEM images of the used (A) CBN-Z0.2 and (B) CBN-Z0.4 catalysts. SEM: Scanning electron microscope; CBN: carbon-doped boron nitride; CBN-Zx: ZIF-8 derived carbon-doped boron nitride.

**Supplementary Table 1. Catalytic activities of commercial h-BN, CBN, CBN-Z0.2 and CBN-Z0.4 catalysts for ODHP**

| Catalysts | T <sup>1</sup><br>(°C) | C <sup>2</sup><br>(%) | Mass-specific<br>rate<br>(g <sub>C<sub>3</sub>H<sub>8</sub></sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> ) | Productivity<br>(g <sub>C<sub>3</sub>H<sub>6</sub></sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> ) | Selectivity (%)               |                               |
|-----------|------------------------|-----------------------|--------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|-------------------------------|-------------------------------|
|           |                        |                       |                                                                                                                    |                                                                                                           | C <sub>3</sub> H <sub>6</sub> | C <sub>2</sub> H <sub>4</sub> |
| h-BN      | 500                    | 6.5                   | 0.19                                                                                                               | 0.16                                                                                                      | 82.9                          | 8.3                           |
|           | 510                    | 7.9                   | 0.23                                                                                                               | 0.19                                                                                                      | 81.7                          | 9.3                           |
| CBN       | 500                    | 9.4                   | 0.28                                                                                                               | 0.23                                                                                                      | 83.4                          | 9.6                           |
|           | 510                    | 15.5                  | 0.46                                                                                                               | 0.36                                                                                                      | 78.9                          | 12.1                          |
| CBN-Z0.2  | 500                    | 18.9                  | 0.58                                                                                                               | 0.43                                                                                                      | 77.4                          | 11.7                          |
|           | 510                    | 29.9                  | 0.88                                                                                                               | 0.61                                                                                                      | 69.3                          | 14.9                          |
| CBN-Z0.4  | 500                    | 23.9                  | 0.71                                                                                                               | 0.52                                                                                                      | 73.8                          | 12.9                          |
|           | 510                    | 33.9                  | 1.01                                                                                                               | 0.66                                                                                                      | 66.1                          | 15.5                          |

<sup>1</sup>Reaction temperature; <sup>2</sup>Propane conversion. h-BN: Hexagonal boron nitride; CBN: carbon-doped boron nitride; CBN-Zx: ZIF-8 derived carbon-doped boron nitride.



**Supplementary Table 2. Comparison of the catalytic performance of B-based catalysts reported in the literature**

| Catalysts                   | T <sup>1</sup><br>(°C) | WHSV<br>(mLg <sup>-1</sup> h <sup>-1</sup> ) | C <sup>2</sup><br>(%) | Propylene<br>selectivity<br>(%) | Olefin<br>selectivity<br>(%) | Y <sup>3</sup><br>(%) | Reference |
|-----------------------------|------------------------|----------------------------------------------|-----------------------|---------------------------------|------------------------------|-----------------------|-----------|
| CBN-Z0.4                    | 500                    | 15000                                        | 23.9                  | 73.5                            | 86.4                         | 17.6                  | This work |
|                             | 510                    |                                              | 33.9                  | 66.1                            | 81.6                         | 22.5                  |           |
| DFNS/BN                     | 490                    | 3600                                         | 25.5                  | 60                              | 75.8                         | 15.3                  | 1         |
| 3D-porous-BN-fibers         | 520                    | 9000                                         | 16.4                  | 76.3                            | 90.4                         | 12.5                  | 2         |
| BN@BPO <sub>4</sub> @BN     | 550                    | 24000                                        | 13.6                  | 75.2                            | 84.0                         | 10.2                  | 3         |
| BN/Cordierite               | 495                    | 28800                                        | 16                    | 84.5                            | 91.0                         | 13.5                  | 4         |
| BN-950                      | 530                    | 3900                                         | 24.3                  | 75.2                            | 85.2                         | 18.3                  | 5         |
| BCN0.3                      | 500                    | 48000                                        | 18.5                  | 86.5                            | 95.6                         | 16                    | 6         |
| boron-hyperdoped<br>silicon | 450                    | 86400                                        | 10.6                  | 64.1                            | 72.5                         | 6.8                   | 7         |
| h-BN bowl foam              | 550                    | 24000                                        | 20.0                  | 70.0                            | N/A                          | 14.0                  | 8         |
| BONNTs                      | 475                    | 12000                                        | 29.0                  | 64.0                            | 80.0                         | 18.6                  | 9         |
| N <sub>2</sub> -Plasma-BN   | 520                    | 28800                                        | 26.0                  | 76.7                            | 89.4                         | 19.9                  | 10        |
| BOS-10                      | 450                    | 28800                                        | 14.8                  | 73.3                            | 87.4                         | 10.8                  | 11        |
| P-CBN-23                    | 500                    | 10800                                        | 23.1                  | 75.2                            | 89.6                         | 17.4                  | 12        |
| h-BN/SiO <sub>2</sub>       | 500                    | 48000                                        | 12.2                  | 84.0                            | 91.0                         | 10.3                  | 13        |
| BM-1.0                      | 550                    | 28800                                        | 15.0                  | 50.0                            | 80.0                         | 7.5                   | 14        |

<sup>1</sup>Reaction temperature; <sup>2</sup>Propane conversion; <sup>3</sup>Propylene yield.

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