Supporting Information

Phosphorus-doped h-Boron Nitride as an Efficient Metal-free Catalyst for Direct Dehydrogenation of Ethylbenzene

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Table

Table S1 Specific activity per surface area of h-BN and PBN-*x* catalysts.

Sample	Specific surface area (S_{BET}, $m^2 \cdot g^{-1}$)	Styrene rate ($\mu mol_{ST} \cdot m^{-2} \cdot h^{-1}$)
h-BN	219.4	9.57
PBN-0.2	240.7	11.67
PBN-1.0	288.3	28.75
PBN-1.2	312.3	55.87
PBN-1.4	317.8	25.05

Figures

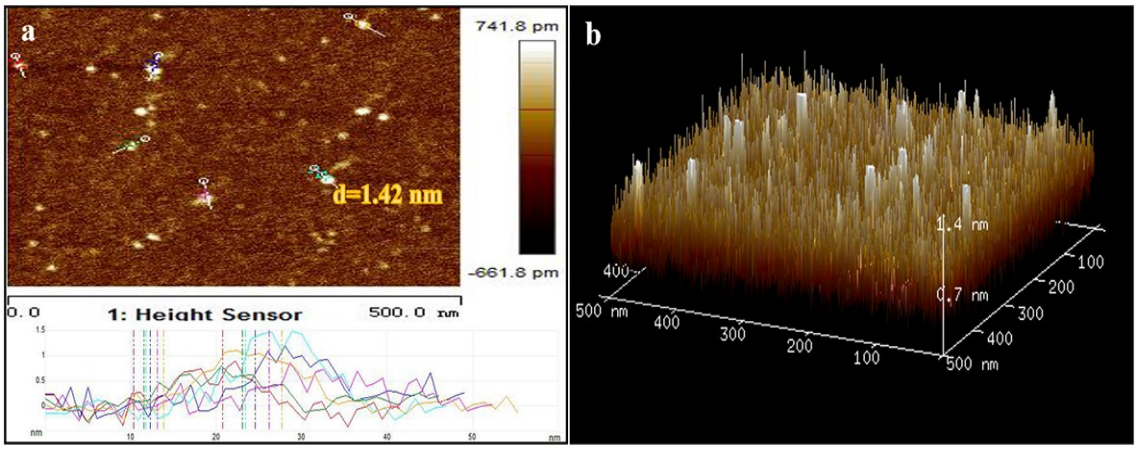

Fig. S1 AFM images of the PBN-1.2 sample.

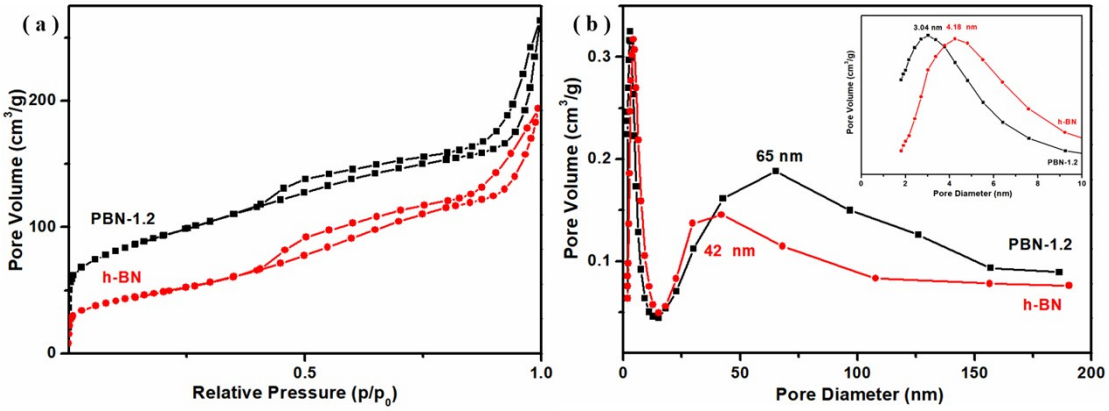

Fig. S2 Adsorption-desorption isotherm and BJH pore-size distribution curve of the PBN-1.2 and h-BN sample.

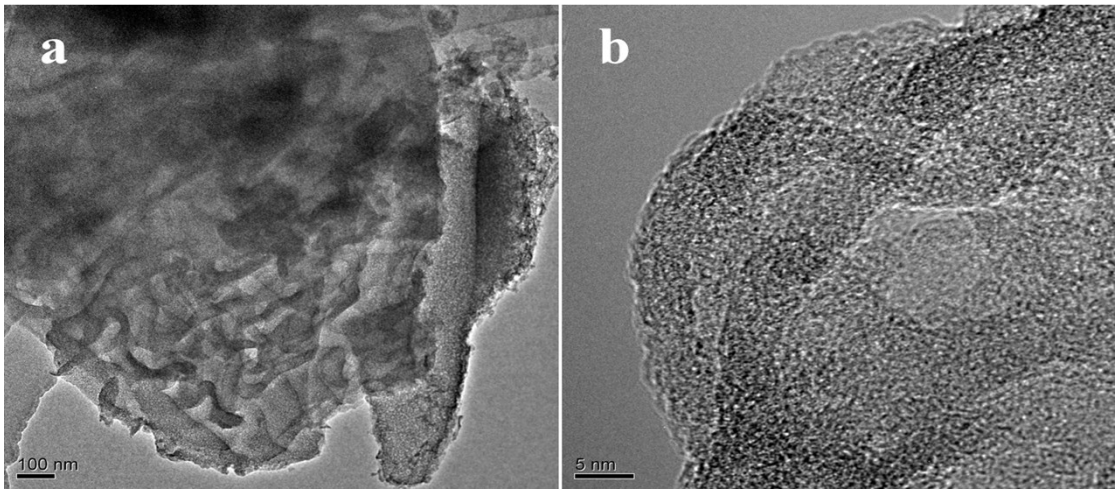

Fig. S3 HRTEM images of the h-BN sample.

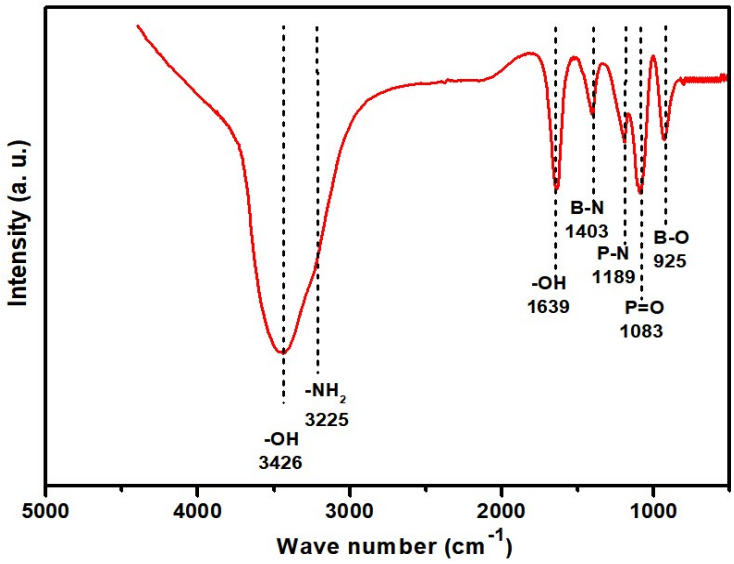

Fig. S4 FT-IR spectrum of PBN-1.2 sample.

According to reference,[1] in Fig. S4, the broad peak at 3225 cm^{-1} is ascribed to the stretching vibration of the -NH_2 group. Two bands at 1403 and 799 cm^{-1} correspond to the in plane B-N transverse stretching vibration and the out-of plane B-N-B bending vibration, respectively. The peak at 925 cm^{-1} is ascribed to the B-O vibration. The peaks at 1639 and 3426 cm^{-1} are attributed to the bending and stretching vibrations of the -OH group, respectively. After phosphor doping, the B-N, B-N-B, and B-O vibration modes are still dominant, indicating a backbone role of the B-N networks for the PBN samples. Moreover, new peaks at 1083 and 1189 cm^{-1} attributed to the P=O and P-N stretching vibrations appear for PBN. In addition, due to the stronger electronegativity of phosphor than boron, the in-plane B-N transverse stretching vibration shifts from 1380 cm^{-1} to a higher value of 1400 cm^{-1}.

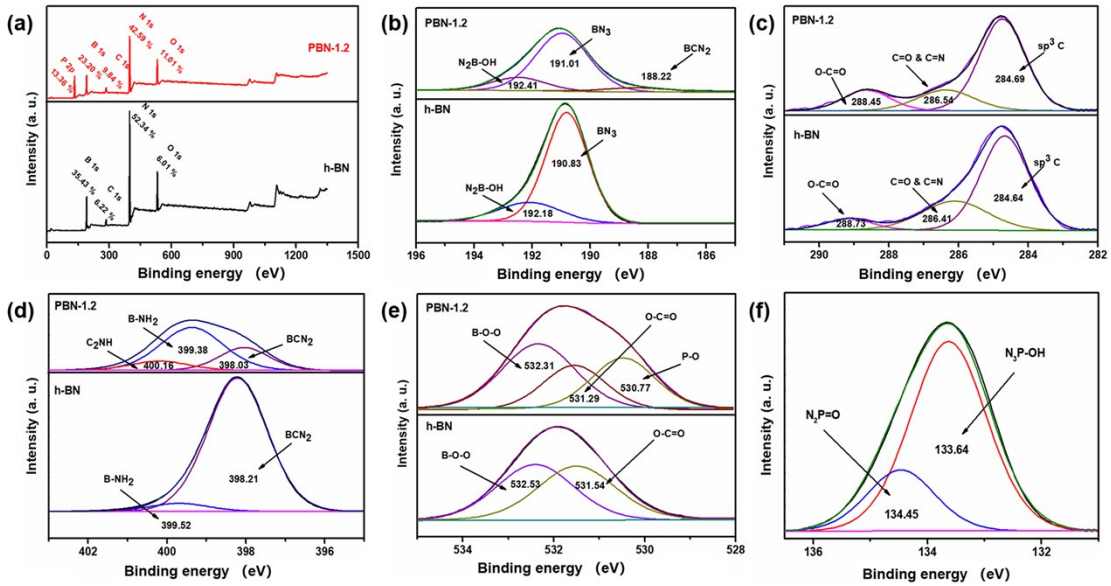

Fig. S5 (a) The survey, (b) deconvolution of B 1s, (c) C 1s, (d) N 1s, (e) O 1s spectra of PBN-1.2 and BN samples, and deconvolution of (f) P 2p spectrum of the PBN-1.2 sample.

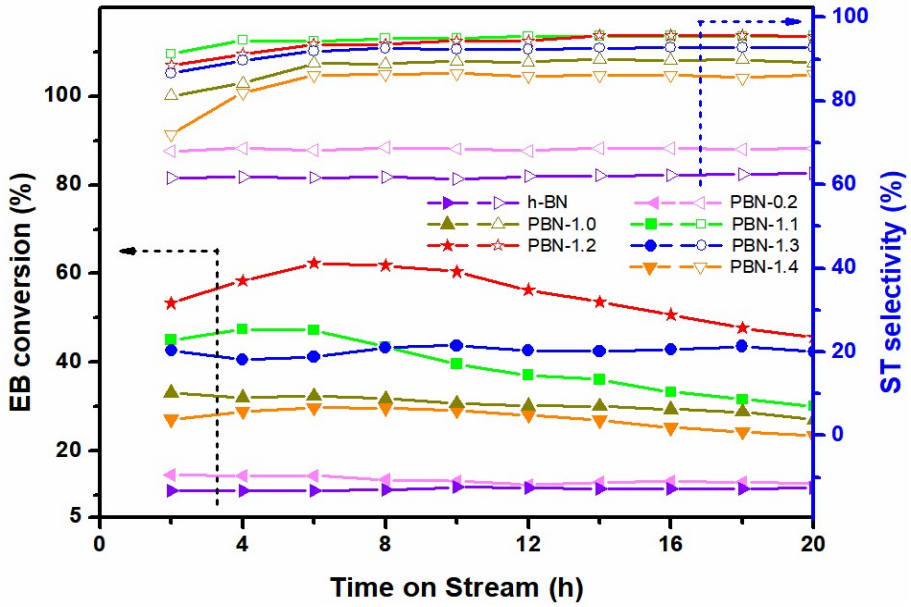

Fig. S6 The catalytic performance of PBN-*x* samples for DDH of ethylbenzene to styrene. Reaction conditions: 50mg catalyst diluted with 2mL arenaceous quartz, 600 °C, 2.8% ethylbenzene in N_2, 20 mL·min^{-1}.

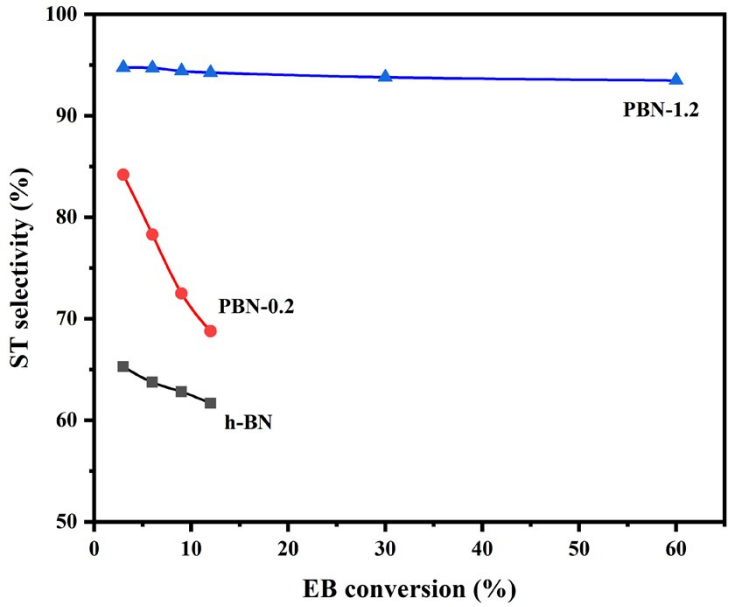

Fig. S7 Styrene selectivity versus ethylbenzene conversion obtained by variation of reaction temperature. Reaction conditions: 50mg catalyst diluted with 2mL arenaceous quartz, 500-600 °C, 2.8% ethylbenzene in N_2, 20 mL·min^{-1}.

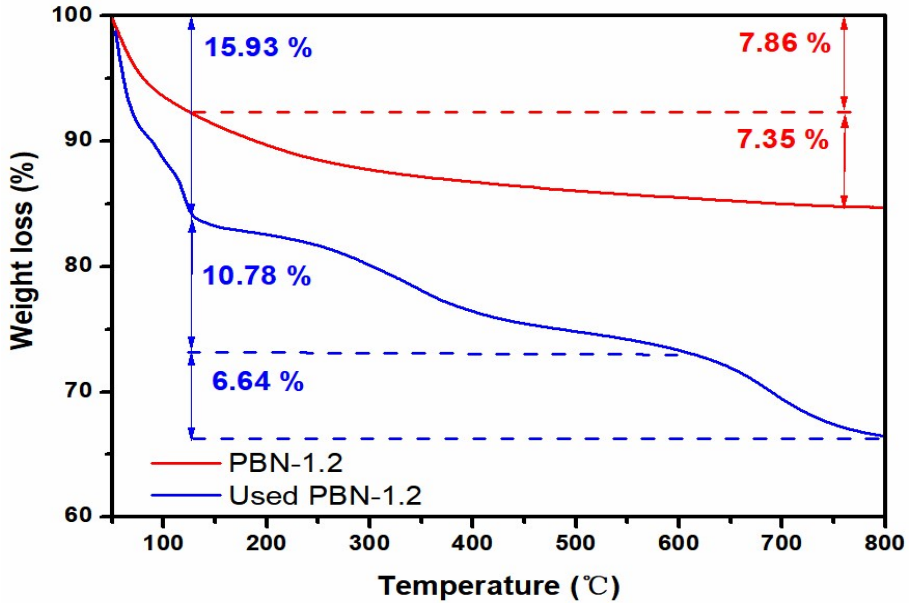

Fig. S8 TGA curves of the PBN-1.2 catalyst before and after reaction.

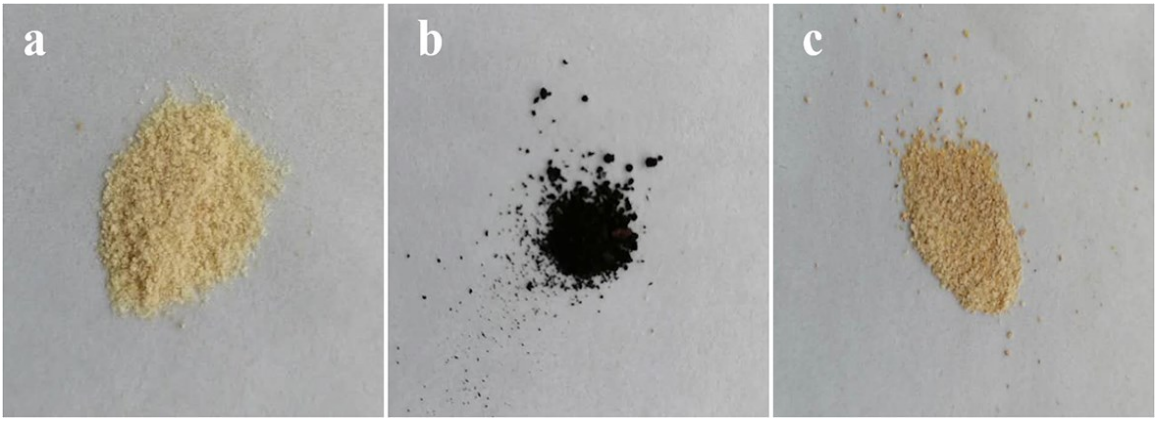

Fig. S9 Photo images of (a) fresh and (b) used PBN-1.2 catalyst, and (c) Reg-PBN-1.2 catalyst.

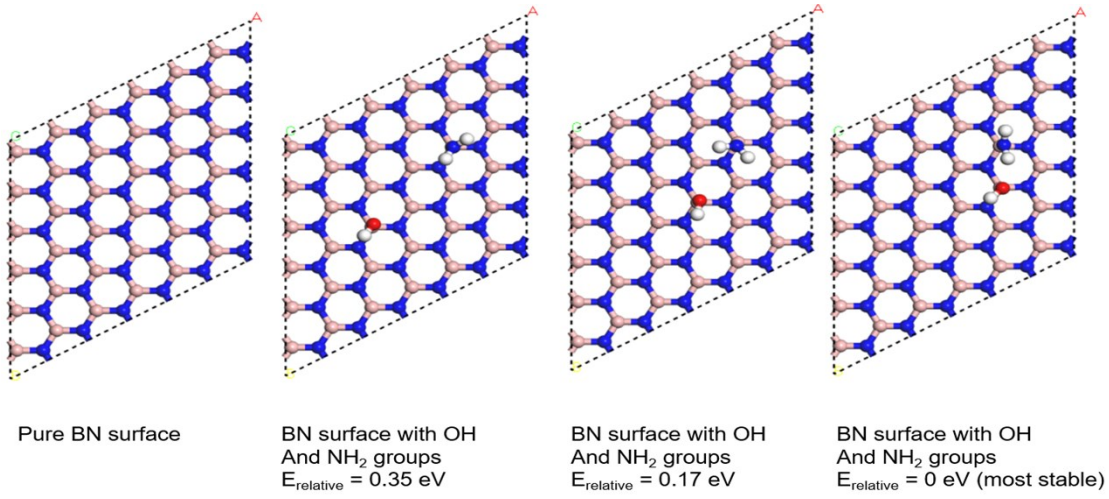

Fig. S10 The structure of the pure h-BN surface and h-BN surfaces with OH and NH_2 groups. The one with the lowest relative energy is chosen for further investigation. The white, blue, pink and red balls represent H, N, B and O atoms, respectively.

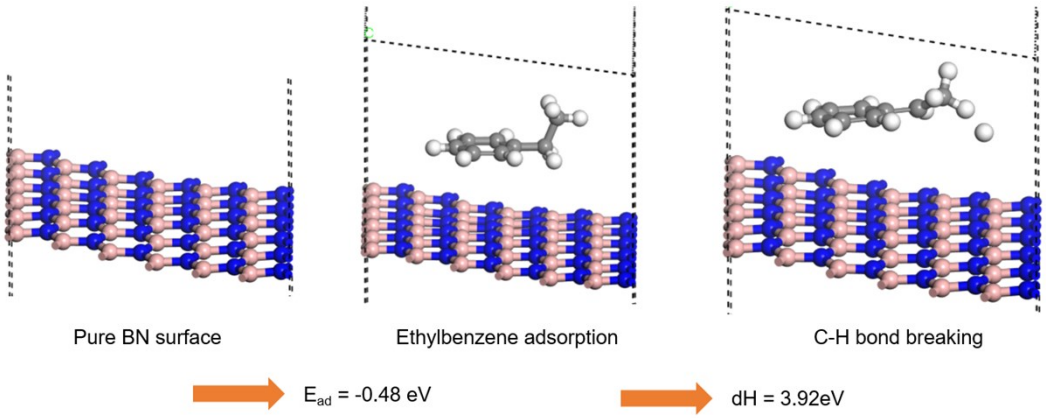

Fig. S11 Ethylbenzene adsorption and following C-H bond breaking over pure h-BN surface. The white, blue, pink and gray balls represent H, N, B and C atoms, respectively.

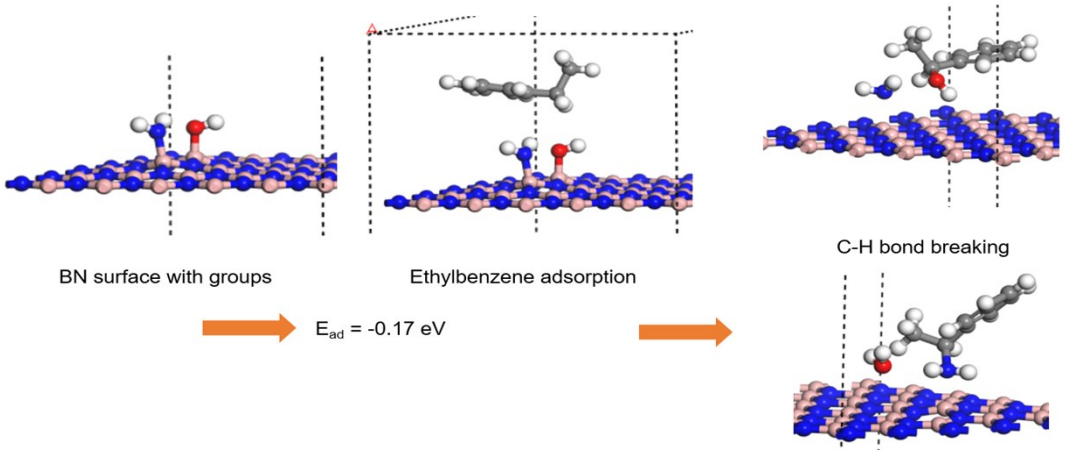

Fig. S12 Ethylbenzene adsorption and following C-H bond breaking over h-BN surface with OH and NH_2 groups. The white, blue, pink, red and gray balls represent H, N, B, O and C atoms, respectively.

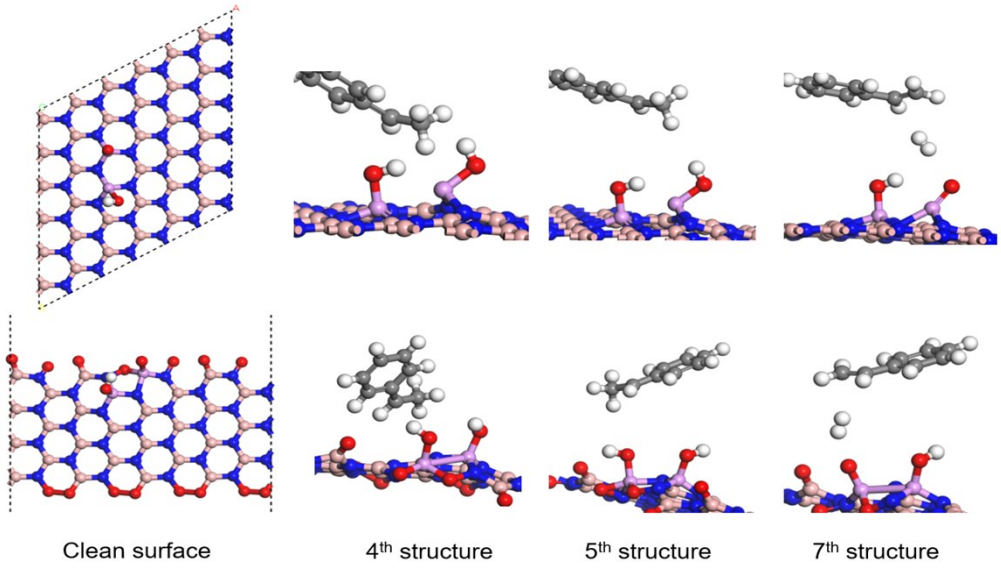

Fig. S13 Remaining structures in Fig. 6 of the main text. Upper half for basal PBN plane while lower half for PBN armchair band. The white, blue, pink, purple, red and gray balls represent H, N, B, P, O and C atoms, respectively.

References

1 J. Zhao, B. Lin, Y. Zhu, Y. Zhou, H. Liu, *Catal. Sci. Technol.*, 2018, **8**, 5900-5905.