Electronic Supplementary Information for

Syngas Molecules as Probes for Defects in 2D Hexagonal Boron Nitride: their Adsorption and Vibrations

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To ensure that sampling of the total energy of the system at a single k-point (Γ point of the two-dimensional Brillouin zone) does not lead to systematic errors in the calculated energetics, as a test case, we have carried out calculations of the total energy of the system with the N vacancy, V_N, with and without adsorbed CO, for three additional sets of k-point sampling: 2×2×1, 3×3×1, 4×4×1. The results summarized below in Table S1 show the binding energy of CO calculated from the ionically relaxed structures differ by about 0.007 eV (7 meV). In fact, the Γ point results for total energy of *dh*-BN with V_N, without CO, is also within 0.007 eV, as compared to that obtained with higher number of k-points. The difference is even smaller for system with adsorbed CO. We thus find the computationally efficient Γ point sampling to be reasonable for obtaining binding energies and other energetics, within two decimal point accuracy.

Table S1. K-points Sampling Test based on $\mathbf{V_N}$ and **CO on $\mathbf{V_N}$**

K-point sampling	**Total energy of $\mathbf{V_N}$** (eV)	**Total energy of CO on $\mathbf{V_N}$** (eV)	**Binding Energy** (eV)
1×1×1 (Γ)	-19725.44890	-20566.21585	-3.451
2×2×1	-19725.44196	-20566.21506	-3.457
3×3×1	-19725.44217	-20566.21538	-3.457
4×4×1	-19725.44219	-20566.21536	-3.457

Additionally, the calculated reaction pathways for both CO and CO_2 to transit from their physisorbed to chemisorbed states on SW type defect in *dh*-BN are plotted in Figure S1. The reaction barriers of 0.57 eV for CO (Figure S1a) and 1.71 eV for CO_2 should be gauged with the reverse barriers in mind (0.01 eV for CO and 1.08 eV for CO_2).

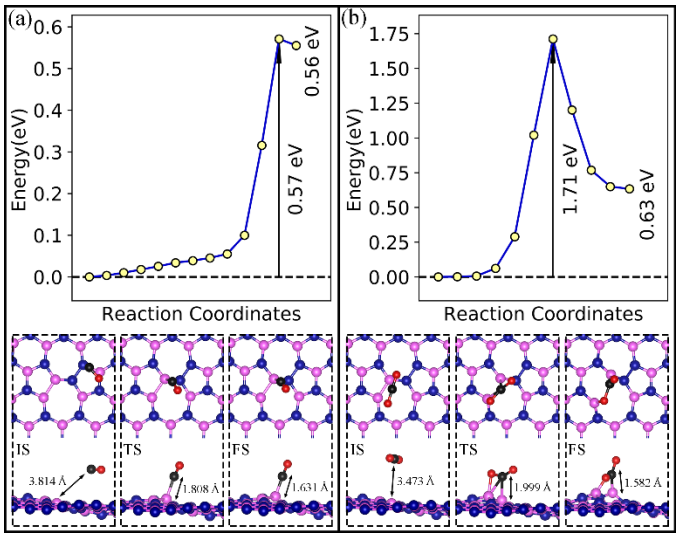

Figure S1 Reaction pathways from physisorbed to chemisorbed state on SW defect in *dh*-BN: (a) CO (b) CO_2. In the bottom panel, IS, TS, and FS represent initial, transition and final states, respectively. Blue, pink, black, and red balls represent N, B, C, and O atoms, respectively.