

## Supporting Information

# H<sub>2</sub> Purification by Functionalized Graphdiyne – Role of Nitrogen Doping

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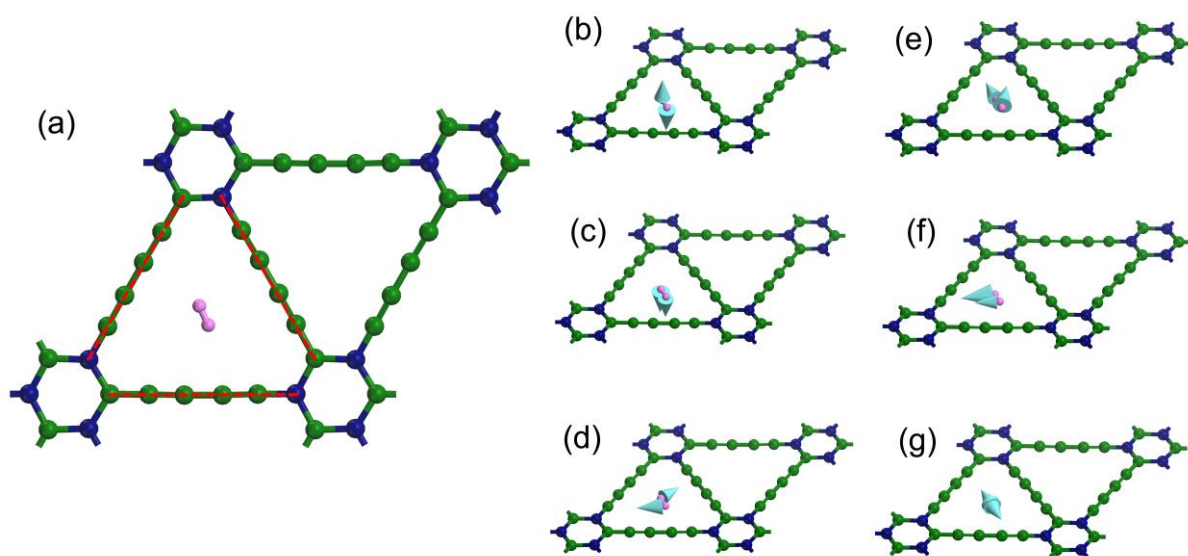
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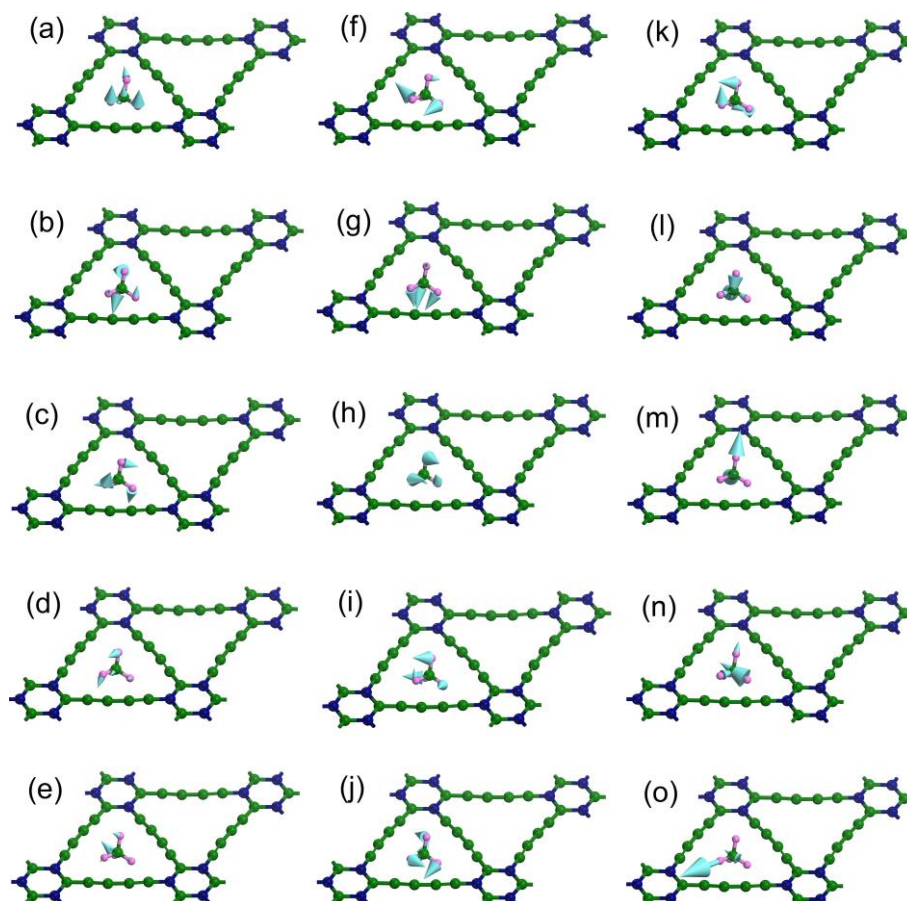
**Table S1** Adsorption energy  $E_{ad}$  and frequencies of H<sub>2</sub>, CH<sub>4</sub> and CO at React and TS.

Gas	Position	$E_{ad}$ (eV)	Frequencies ( $cm^{-1}$ ) <sup>a</sup>					
H <sub>2</sub>	React	-0.07	107.58	130.06	156.10	158.77	166.63	4325.41
	TS	+0.01	155.84 <i>i</i>	319.15	324.05	380.15	380.58	4309.26
			80.59	90.79	91.35	227.89	273.28	300.47
CH <sub>4</sub>	React	-0.14	1298.25	1316.72	1330.47	1524.86	1528.87	2997.17
			3108.92	3121.85	3131.99	–	–	–
	TS	+0.59	157.85 <i>i</i>	183.33	226.42	315.23	317.08	412.44
			1296.96	1317.63	1327.26	1531.66	1541.91	3040.70
			3137.67	3223.15	3264.82	–	–	–
CO	React	-0.12	39.12	55.09	56.99	105.60	211.91	2090.75
	TS	+0.26	66.43 <i>i</i>	157.60	170.81	189.95	198.19	2082.30

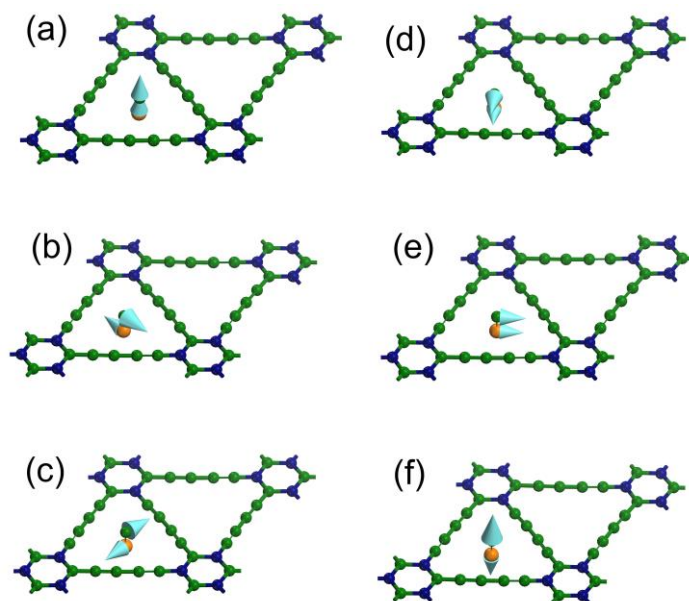
<sup>a</sup> The imaginary frequencies are denoted by *i* after values.



**Figure S1** (a) Top view and framework distortion of  $H_2$  flat at the pore centre of N-graphdiyne (not the genuine transition state) and (b) to (g) vibration modes of such state. (b)  $170.15i$  and (c)  $181.89i$  are the imaginary frequencies, which means this is not the transition state. Other frequencies, (d)  $184.18$ , (e)  $399.43$ , (f)  $411.21$ , (g)  $4367.38$  are real which means this structure is on the local minimum of these directions. Blue is nitrogen, green is carbon, pink is hydrogen. Red dashes in (a) is a guideline for lattice distortion. Cyan arrows in (b) to (g) are the vibration directions. Units of the frequencies are  $cm^{-1}$ .



**Figure S2** Vibration modes of  $\text{CH}_4$  at the transition state. (a) is the imaginary frequency identified with trans-membrane direction which means this is the transition state on this direction. Other frequencies ascending from (b) to (o) are real which means this structure is on the local minimum of these vibrational directions. Blue is nitrogen, grey is carbon, pink is hydrogen. Cyan arrows are the vibration directions.



**Figure S3** Vibration modes of CO at the transition state of diffusion through N-graphdiyne. One imaginary frequency (a) is identified with trans-membrane direction which means this is the transition state on this direction. Other frequencies (b) to (f) are real which means this structure is on the local minimum of these directions. Blue is nitrogen, grey is carbon, orange is oxygen. Cyan arrows are the vibration directions.

#### Rate coefficient calculation by transition state theory.

The rate coefficient of a reaction is given by the ratio of the flux of species through the transition state to the relative population of reactants:

$$k = \frac{k_B T}{h} \cdot \frac{Q^{TS}}{Q^{React}} \cdot e^{-E_0/k_B T} \quad (S1)$$

in which  $Q^{TS}$  and  $Q^{React}$  are partition functions for the transition state (TS, gas in the pore centre of N-graphdiyne) and reactant state (React, gas molecule at the most stable position above pores on N-graphdiyne),  $h$  is the plank constant,  $E_0$  is the energy barrier value,  $T$  is the separation temperature, and  $k_B$  is the Boltzmann constant.

To calculate the partition functions, energy levels need to be obtained first. All the translational, rotational and vibrational motions of the investigated states were treated as harmonic oscillations because their frequency could be derived by calculating the hessian matrix of the appropriate

stationary states. The energy levels corresponding to the frequencies  $\nu_i$  ( $i=1-6$  for  $H_2$  and  $CO$ , and  $i=1-15$  for  $CH_4$ ) are calculated as:

$$E_j(\nu_i) = (j + 1/2)h\nu_i, (j=0, 1, 2 \dots) \quad (S2)$$

And the partition functions are calculated as:

$$Q = \prod_{i=1}^n Q_i = \prod_{i=1}^n \frac{1}{1 - e^{-h\nu_i/k_B T}}, (n=6 \text{ for } H_2 \text{ and } CO, n=15 \text{ for } CH_4) \quad (S3)$$

with Eq.4 as defined,  $E_0$  in Eq.S1 becomes more specifically the zero-point energy difference between reactant and transition states. The selectivities of  $H_2$  over  $CH_4/CO$  were derived by dividing the corresponding rate coefficients.