Mechanistic Insights into Solvent-Assisted BHMF Hydrogenation: Diatomic Catalysts Beyond Conventional Pathways

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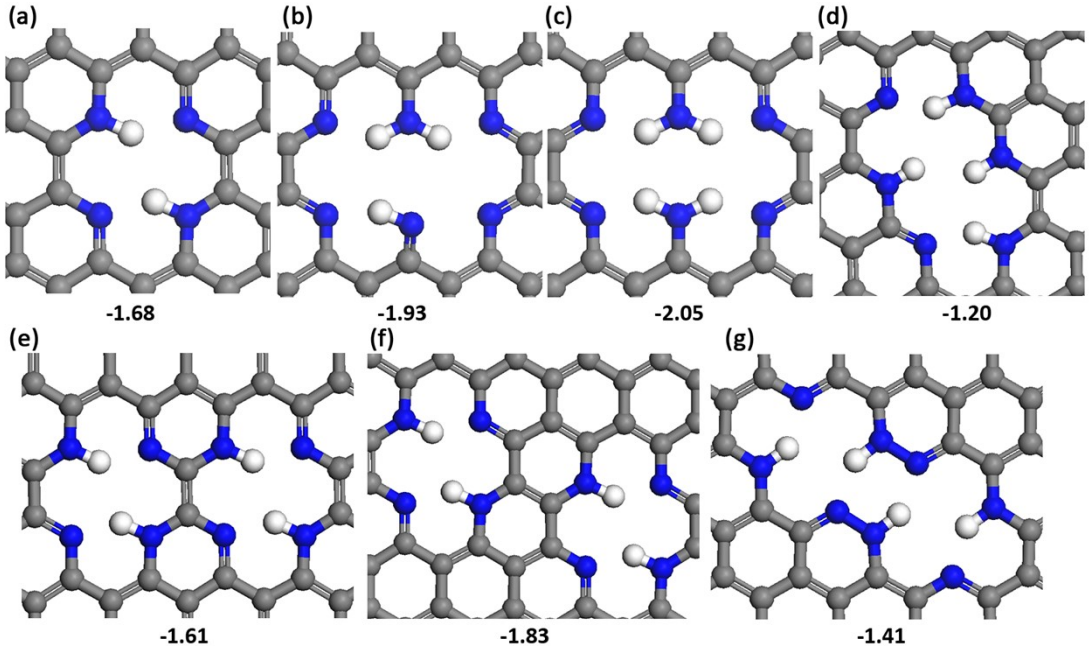

Figure S1. Calculated average H adsorption energies (eV) for various N-doping motifs.

The construction method of N-doped defective graphene.

The defective graphene model was constructed by removing two carbon atoms to create a divacancy defect, followed by substituting the six undercoordinated carbon atoms around the defect with nitrogen atoms, forming the defective configuration. The adsorption of H was calculated to evaluate the structural stability.

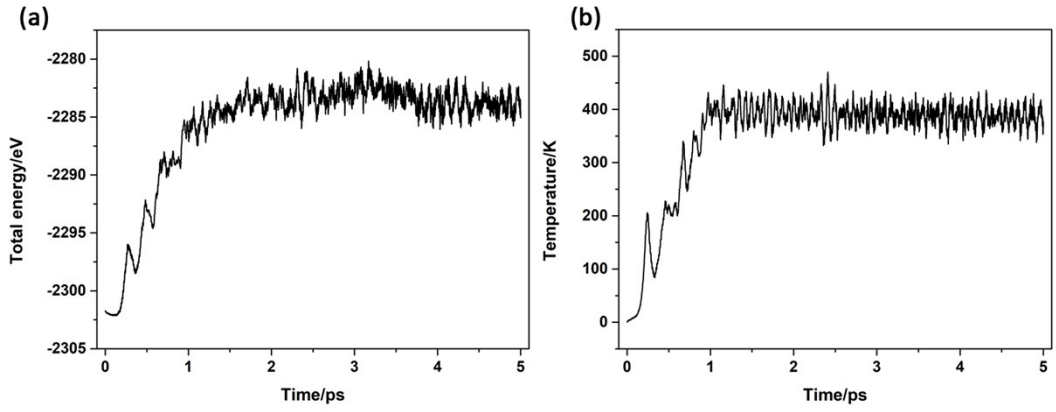

Figure S2. The change of total energy (a) and temperature (b) during the AIMD simulations.

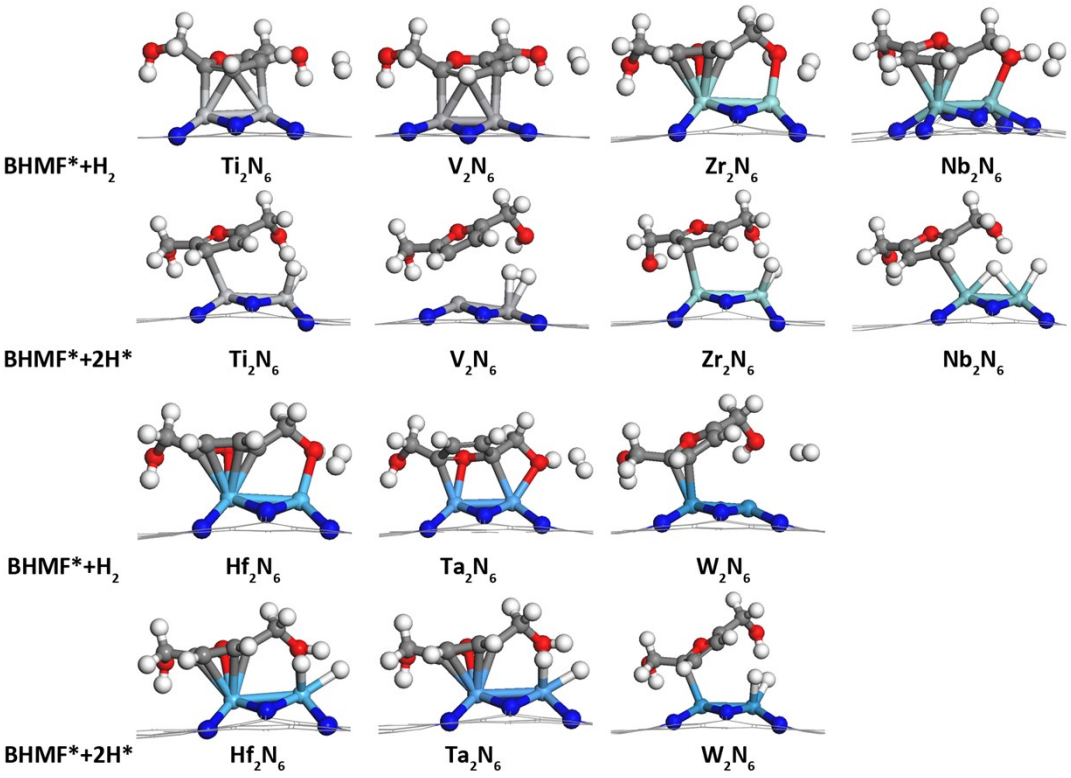

Figure S3. The coadsorption structures of BHMF and H_2, BHMF and 2H on Ti, V, Zr, Nb, Hf, Ta and W DACs surfaces.

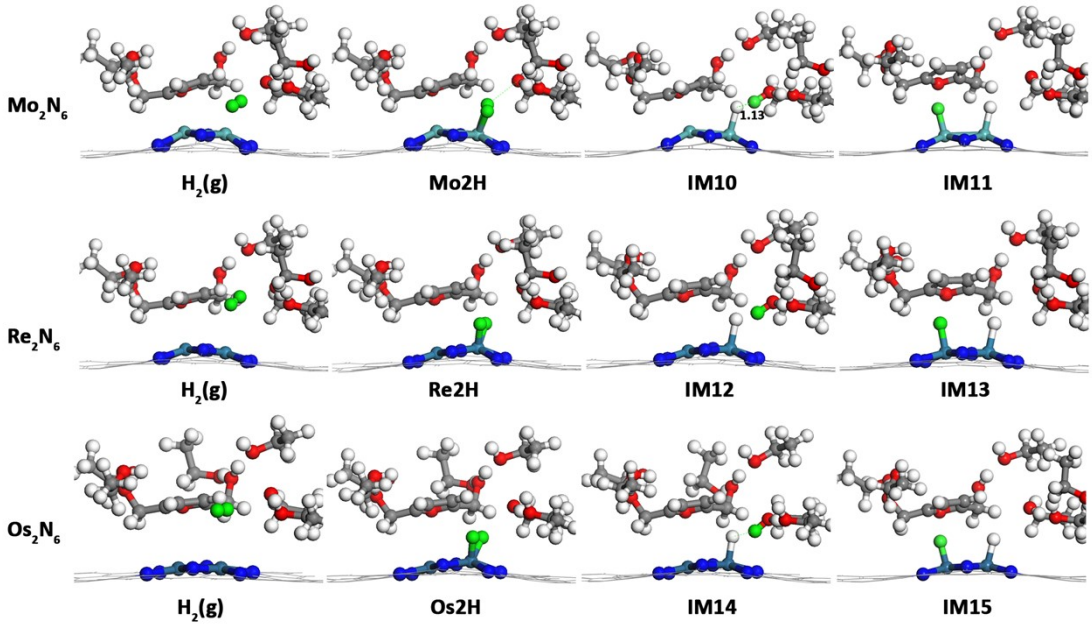

Figure S4. The optimized structures during the H_2 dissociation and the diffusion of H on Mo, Re and Os DACs.

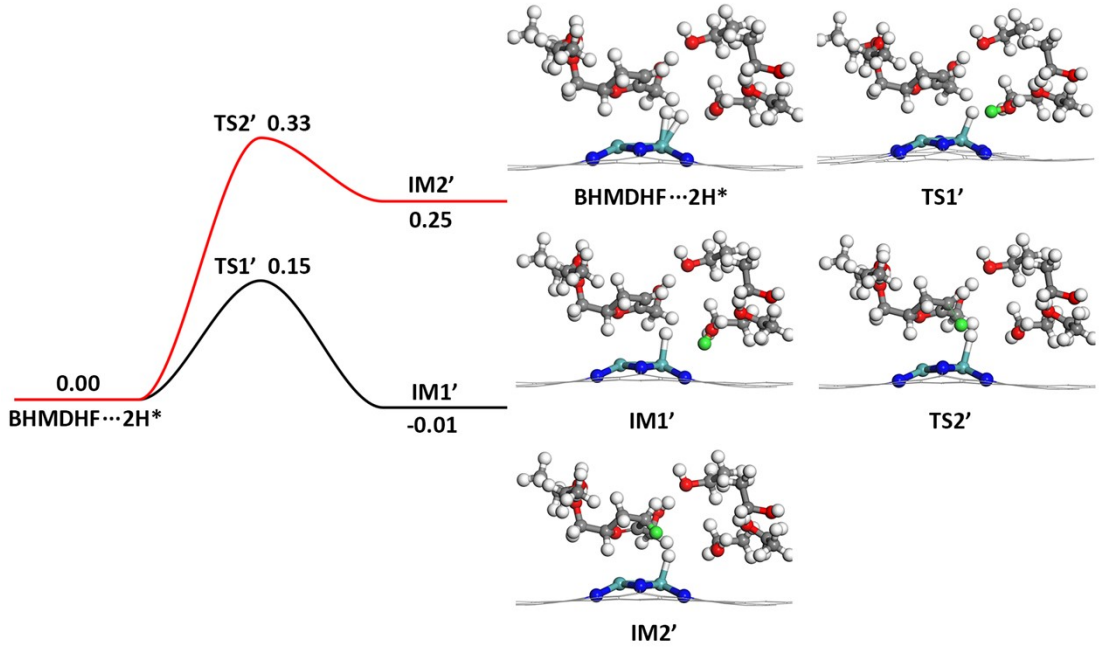

Figure S5. The pathways for hydrogen diffusion to EtOH and direct hydrogenation of BHMDHF via Mo2H on Mo DAC.

Table S1. Calculated interaction energies (E_{int}, eV) of typical intermediates with ethanol solvent during ring hydrogenation and hydrodeoxygenation on Ru DACs.

	Intermediates	E_{int} (eV)
1	BHMF (Ring hydrogenation)	-3.33
2	BHMDHF (Ring hydrogenation)	-1.22
3	BHMF (Side chain hydrodeoxygenation)	-4.47

Table S2. Calculated the reaction energies (E_r, eV) for H_2 dissociative adsorption on two separate metal sites as well as the dissociation barrier (E_a, eV) on Fe DAC.

	Catalysts	E_r (eV)	E_a (eV)
1	Fe DAC	0.26	1.49
2	Co DAC	1.03	/
3	Ni DAC	2.32	/
4	Ir DAC	0.89	/
5	Rh DAC	1.06	/

Microkinetic Model on Ru and Mo DACs.

1. Site balance equation

The total coverage of surface active sites is conserved:

$\theta_{BHMF} + \theta_H + \theta_{BHMFH} + \theta_{BHMDHF} + \theta_{BHMDHFH} + \theta_{BHMTHF} + \theta_{BHMF\text{-}OH} + \theta_{5\text{-}MFA} + \theta_* = 1$ (1)

Where θ_i denotes the surface coverage of intermediate i, and θ_* is the coverage of free active sites.

2. Steady-state approximation (SSA) for surface intermediates

Under steady-state conditions, the net formation rate of each surface intermediate is zero ($d\theta_i/dt = 0$):

$$\frac{d\theta_{BHMFH}}{dt} = k_3\theta_{BHMF}\theta_H - k_4\theta_{BHMFH}\theta_H = 0 \quad (2)$$

$$\frac{d\theta_{BHMDHF}}{dt} = k_4\theta_{BHMFH}\theta_H - k_5\theta_{BHMDHF}\theta_H = 0 \quad (3)$$

$$\frac{d\theta_{BHMDHFH}}{dt} = k_5\theta_{BHMDHF}\theta_H - k_6\theta_{BHMDHFH}\theta_H = 0 \quad (4)$$

$$\frac{d\theta_{BHMTHF}}{dt} = k_6\theta_{BHMDHFH}\theta_H - k_7\theta_{BHMTHF} = 0 \quad (5)$$

$$\frac{d\theta_{BHMF-OH}}{dt} = k_8\theta_{BHMF}\theta_H - k_9\theta_{BHMF\text{-}OH}\theta_H = 0 \quad (6)$$

$$\frac{d\theta_{MFA}}{dt} = k_9\theta_{BHMF\text{-}OH}\theta_H - k_{10}\theta_{5\text{-}MFA} = 0 \quad (7)$$

Where k_i (i = 3,⋯,10) denote the rate constants of the elementary steps.

3. Coverage of reactants

BHMF and H adsorption is treated as a quasi-equilibrium step:

$\theta_{BHMF} = P_{BHMF}K_{BHMF}\theta_* = c_{BHMF}RTK_{BHMF}\theta_*$; $\theta_H = \sqrt{P_{H_2}K_{H_2}}\theta_*$

Where

P_{BHMF} : partial pressure of BHMF;

c_{BHMF} : concentration of BHMF in solution;

K_{BHMF} : adsorption equilibrium constant of BHMF;

P_{H_2} : partial pressure of H_2;

K_{H_2} : adsorption equilibrium constant of H_2;

R: ideal gas constant;

T: reaction temperature.

For calculating the adsorption equilibrium constant (K), we used: $K = \exp[-(\Delta E_{ads} - T\Delta S)/k_B T]$, where ΔE_{ads} is the adsorption energy that incorporates vibrational corrections, and ΔS is the entropy change associated with the adsorption process. The rate constant k for each reaction step is derived from the Eyring equation,

$$k = (\frac{k_B T}{h}) e^{(\frac{\Delta S}{k_B})} e^{(\frac{-\Delta H}{k_B T})}$$

where, k_B is the Boltzmann constant, T is the temperature, and h represents Planck's constant. ΔS denotes the entropy change, while ΔH corresponds to the enthalpy change during the reaction at temperature T. The enthalpy changes (ΔH) were directly obtained from DFT calculations, while the entropy changes (ΔS) were determined by vibrational frequency analysis. Both ΔH and ΔS were calculated as the differences between the transition state and the reactants, with the corresponding data generated via VASPkit.[1]

4. Analytical coverage expressions of intermediates

From the steady-state equations (2)–(7), the coverage of each intermediate can be analytically derived:

$\theta_{BHMFH} = k_3\theta_{BHMF}/k_4$

$\theta_{BHMDHF} = k_3\theta_{BHMF}/k_5$

$\theta_{BHMDHFH} = k_3\theta_{BHMF}/k_6$

$\theta_{BHMTHF} = k_3\theta_{BHMF}\theta_H/k_7$

$\theta_{BHMF\text{-}OH} = k_8\theta_{BHMF}/k_9$

$\theta_{5\text{-}MFA} = k_8\theta_{BHMF}\theta_H/k_{10}$

5. Formation rates and selectivity of main products

The formation rates of the two dominant products are written as:

$r_{BHMTHF} = k_7\theta_{BHMTHF}$, $r_{5\text{-}MFA} = k_{10}\theta_{5\text{-}MFA}$, respectively.

The product selectivity can be further calculated from the ratio of formation rates:

$S_{BHMTHF} = r_{BHMTHF}/(r_{5\text{-}MFA} + r_{BHMTHF})$, $S_{5\text{-}MFA} = r_{5\text{-}MFA}/(r_{5\text{-}MFA} + r_{BHMTHF})$

References

1. V. WANG, N. XU, J.-C. LIU, G. TANG, W.-T. GENG, VASPKIT: A User-Friendly Interface Facilitating High-Throughput Computing and Analysis Using VASP Code, *Computer Physics Communications*. **2021,** 267, 108033, DOI: 10.1016/j.cpc.2021.108033