Supporting Information for:

Promoting the Conversion of CO₂ to CH₄ via Synergistic Dual active sites

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1. Calculation method of CO₂RR activity

The change in free energy is calculated by the following formula: ¹

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{pH}$$
(1)

 ΔE refers to the energy obtained by DFT calculation, $\Delta G_U = -eU$, where U is the electrode potential, e is the number of transferred electrons; $\Delta G_{pH} = k_B T ln 10 \times pH$, in this work, pH = 0 was employed.

2. Calculation method of HER activity

$$H^+ + e^- + * \xrightarrow{\Delta G_H} H^*$$

(2)

* represents the active site and H* represents the adsorbed intermediate. According to the computational hydrogen electrode model, $^{2} \Delta G_{H}$ can be calculated according to the following relationship:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H \tag{3}$$

 $\Delta E_{\rm H}$ is the adsorption energy of hydrogen calculated by DFT, $\Delta E_{\rm ZPE}$ is the difference between the zero point energy of adsorbed hydrogen and gas phase hydrogen, T is the temperature (298.15 K), and $\Delta S_{\rm H}$ is the change of entropy between the adsorption state and the gas phase. The entropy of the gas phase molecule is obtained by the NIST database, and the entropy and zero-point energy of the adsorbate can be obtained by calculating the vibration frequency where the entropy value is calculated by the following formula: ³

$$S(T) = \sum_{i=1}^{3N} \left[-Rln \left(1 - e^{-\frac{hv_i}{k_B T}} \right) + \frac{N_A hv_i e^{-\frac{hv_i}{k_B T}}}{T 1 - e^{-\frac{hv_i}{k_B T}}} \right]$$
(4)

Where R stands for the ideal gas constant, k_B is Boltzmann constant, h is Planck constant, N_A is Avogadro constant, v_i represents the vibration of the normal mode, and N represents the number of adsorbed atoms.

3. Calculation method of selectivity between different products

For two different products, the selectivity between them can be calculated by the following formula:

$$K = exp^{[i0]}(\frac{-\Delta G}{RT})$$

$$K_{1} = exp^{[i0]}(\frac{-\Delta G_{1}}{RT}), \quad K_{2} = exp^{[i0]}(\frac{-\Delta G_{2}}{RT})$$

$$k = \frac{K_{1}}{K_{2}} = exp^{[i0]}(\frac{\Delta G_{2} - \Delta G_{1}}{RT})$$

$$(7)$$

$$(5)$$

Where K, ΔG , R and T represent the chemical equilibrium constant, reaction free energy, ideal gas constant and temperature, respectively. According to this definition, the larger the k value, the higher the selectivity between the two products.

4. Calculation method of ΔE_b

The ΔE_b is defined as the energy difference between binding energy and cohesive energy of TM atoms in their metal crystal: ^{s4}

$$\Delta E_b = E_b - E_{coh} \tag{8}$$

Among them, the E_b is calculated by:

$$E_b = E_{NiNxBy} - E_{Ni} - E_{NxBy}$$
⁽⁹⁾

Where E_{NiNxBy} , E_{Ni} and E_{NxBy} are the energies of NiN_xB_y complex, Ni atom and NxBy substrate, respectively.

The E_{coh} is calculated by:

$$E_{coh} = (E_{Ni(bulk)} - E_{Ni})/n \tag{10}$$

Where the $E_{Ni(bulk)}$ is the energy of Ni metal crystal and n is the number of Ni atoms in the crystal. According to this definition, the negative ΔE_b means that the Ni atom on the B doping NC substrate is energetically more favorable than in the bulk form.

5. Calculation method of dissolution potential

The dissolution potential (U_{diss}) is defined as: ^{s5}

$$U_{diss} = U_{Ni}^{0} + \left[E_{Ni,bulk} - (E_{NiNxBy} - E_{NxBy}) \right] / ne$$
(11)

Where U_{Ni}^{0} is the standard dissolution potentials of Ni in the bulk form, and n is the coefficient for aqueous dissolution reaction:

$$M + nH^+ \leftrightarrow M^{n+} + n/2H_2 \tag{12}$$

6. Calculation method of cohesive energy

The cohesive energy of B doping NiN₄ single atom catalyst was calculated by following formula: ^{s6}

$$E_{coh} = \left[E_{B-NiNC} - (\mathbf{n}^{E_{C}} + \mathbf{m}^{E_{N}} + \mathbf{x}^{E_{Ni}} + \mathbf{y}^{E_{B}}) \right] / (\mathbf{n} + \mathbf{m} + \mathbf{x} + \mathbf{y})$$
(13)

Where E_{B-NiNC} represent the total energy of E_{B-NiNC} , while E_{C} , E_{N} , E_{Ni} and E_{B} are the total energies of an isolated C atom, N atom, Ni atom and B atom in vacuum, and n, m, x, y are the number of atoms of C, N, Ni, B in B doping NiNC, respectively. According to this definition, materials with more negative E_{coh} suggest a higher thermodynamic stability.

7. Calculation method of formation energy

The formation energy of B doping NiN_4 single atom catalyst was calculated by following formula: $^{\rm s7}$

$$E_{f} = E_{B-NiNC} E_{NC+n} \mu_{C+m} \mu_{N-x} \mu_{Ni-y} \mu_{B}$$
(14)

Where E_{B-NiNC} , E_{NC} , are the total energy of B doping NiNC and N doping grephen without Ni adsorption, μ_C , μ_N , μ_{Ni} and μ_B are the chemical potential of C, N, Ni and B atom in bulk crystal, and n, m are the number of replaced C, N atoms while x, y are the number of introduced Ni, B atoms in B doping NiNC, respectively. According to this definition, materials with more negative E_f suggest a higher thermodynamic stability. 8. Figures and Tables Figures:



Figure S1. Top view and Side view figures of charge density difference of (a_1) NiN₃O, (a_2) CO adsorbed NiN₃B, (a_3) NiN₂B₂-2, (a_4) CO adsorbed NiN₂B₂-2, where the isosurface value is set to be 0.005 eÅ⁻³ and yellow represents electron accumulation and cyan denotes electron depletion.



Figure S2. Projected crystal orbital Hamilton population (–pCOHP) and its integrated value (ICOHP) of CO adsorption on NiN₄, NiN₃B and NiN₂B₂-2, respectively.



Figure S3. The top view and side view of two CO adsorbed on (a_1) NiN₃B and (a_2) NiN₂B₂-2, where navy blue, gray, green, pink and red balls represent the N, C, Ni, B and O atoms, respectively.



Figure S4. Minimum-energy pathways of C–C coupling of two *CO species to form *OC–CO* on NiN₂B₂-2. The inserts are the corresponding initial state (IS), transition state (TS), and final state (FS).



Figure S5. Structure of CO adsorbed NiN_2B_2 -2 and the corresponding electron loss function (ELF) spectrum.



Figure S6. The PDOS of CO adsorbed NiN_2B_2 -2, and the Vacuum level is set to zero.

Tables:

Table S1. Calculated free energy (ΔG) of different intermediates catalyzed by NiN₃B.

Reaction intermediates	ΔG (eV)
*СООН	0.13
*ОСНО	0.99

* + HCOOH	-0.64
*CO + H ₂ O	-0.45
*СОН	1.78
*CHO	0.34
*CH ₂ O	0.69
*СНОН	-0.16
*CH ₂ OH	0.42
*CH + H ₂ O	1.32
* + CH ₃ OH	-0.68
*CH ₂ + H ₂ O	-1.05
*CH3	-0.31
* + CH ₄	-0.48

Table S2. Calculated free energy (ΔG) of different intermediates catalyzed by NiN₂B₂-2.

Reaction intermediates	ΔG (eV)
*СООН	-0.20
*ОСНО	0.31

* + HCOOH	-0.10
*CO + H ₂ O	-0.51
*COH	1.41
*CHO	0.20
*CH ₂ O	0.27
*СНОН	-0.04
*CH ₂ OH	0.29
*CH + H ₂ O	-0.63
* + CH3OH	-0.30
*CH ₂	-0.14
*CH3	0.04
* + CH ₄	-0.44

Table S3. Calculated energy difference $(^{\Delta E_b})$ between binding energy $(^{E_b})$ of Ni atom in N_xB_y matrix and cohesive energy $(^{E_{coh}})$ of Ni atom in the bulk crystal and dissolution potential $(^{U_{diss}})$ of NiN₃B and NiN₂B₂-2.

Species	NiN ₃ B	NiN_2B_2-2
^E _b (eV)	-6.86	-6.70

E_{coh} (eV)	-5.93	-5.93
ΔE_b (eV)	-0.93	-0.77
U _{diss} (V)	0.36	0.28

 $\label{eq:calculated} \textbf{Table S4.} Calculated cohesive and formation energy of NiN_3B, NiN_3S, NiN_2B_2-2 \text{ and } ZnN_2B_2.$

Species	NiN ₃ B	NiN ₃ S	NiN_2B_2-2	ZnN ₂ B ₂
Ecoh (eV)	-7.74	-7.67	-7.72	-7.67

E_{for} (eV)	-4.68	-4.56	-3.00	-4.08
JU: ()				

References

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