Supporting Information for:

Promoting the Conversion of CO\textsubscript{2} to CH\textsubscript{4} via
Synergistic Dual active sites

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1. Calculation method of CO\textsubscript{2}RR activity

The change in free energy is calculated by the following formula: \( \Delta G = \Delta E + \Delta E_{ZPE} - T \Delta S + \Delta G_U + \Delta G_{pH} \)

\( \Delta E \) 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

\[ H^+ + e^- + \ast \rightarrow H^* \]

\( \ast \) represents the active site and \( H^* \) represents the adsorbed intermediate. According to the computational hydrogen electrode model, \( \Delta G_H \) can be calculated according to the following relationship:

\[ \Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H \]

\( \Delta E_H \) is the adsorption energy of hydrogen calculated by DFT, \( \Delta E_{ZPE} \) is the difference between the zero point energy of adsorbed hydrogen and gas phase hydrogen, \( T \) is the temperature (298.15 K), and \( \Delta S_H \) 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: \( \Delta G_{pH} = k_B T \ln 10 \times pH \).
\[ S(T) = \sum_{i=1}^{3N} \left[ - R \ln \left( 1 - e^{-\frac{h\nu_i}{k_B T}} \right) + \frac{N_A h\nu_i e^{-\frac{h\nu_i}{k_B T}}}{T} \right] \]

Where \( R \) stands for the ideal gas constant, \( k_B \) is Boltzmann constant, \( h \) is Planck constant, \( N_A \) is Avogadro constant, \( \nu_i \) 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:

\[ K = \exp\left( -\frac{\Delta G}{R T} \right) \]

(5)

\[ K_1 = \exp\left( -\frac{\Delta G_1}{R T} \right), \quad K_2 = \exp\left( -\frac{\Delta G_2}{R T} \right) \]

(6)

\[ k = \frac{K_1}{K_2} = \exp\left( \frac{\Delta G_2 - \Delta G_1}{R T} \right) \]

(7)

Where \( K, \Delta G, R \) 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 \( \Delta E_b \)

The \( \Delta E_b \) is defined as the energy difference between binding energy and cohesive energy of TM atoms in their metal crystal: \(^{34}\)

\[ \Delta E_b = E_b - E_{coh} \]

(8)

Among them, the \( E_b \) is calculated by:

\[ E_b = E_{NiNxB_y} - E_{Ni} - E_{NxBy} \]

(9)

Where \( E_{NiNxB_y}, E_{Ni} \) and \( E_{NxBy} \) are the energies of NiN\textsubscript{xB}\textsubscript{y} complex, Ni atom and NxBy substrate, respectively.

The \( E_{coh} \) is calculated by:

\[ E_{coh} = \frac{(E_{Ni(bulk)} - E_{Ni})}{n} \]

(10)
Where the \( E_{\text{Ni(bulk)}} \) is the energy of Ni metal crystal and \( n \) is the number of Ni atoms in the crystal. According to this definition, the negative \( \Delta E_b \) 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 \( (U_{\text{diss}}) \) is defined as: \(^5\)
\[
U_{\text{diss}} = U_{\text{Ni}}^0 + \left[ E_{\text{Ni,bulk}} - (E_{\text{NiNxB}} - E_{\text{NxBy}}) \right]/ne
\]
(11)
Where \( U_{\text{Ni}}^0 \) is the standard dissolution potentials of Ni in the bulk form, and \( n \) is the coefficient for aqueous dissolution reaction:
\[
M + nH^+ \leftrightarrow M^{n+} + n/2H_2
\]
(12)

6. Calculation method of cohesive energy

The cohesive energy of B doping NiN\(_4\) single atom catalyst was calculated by following formula: \(^6\)
\[
E_{\text{coh}} = \left[ E_{B-\text{NiNC}}(nE_{\text{C}}+mE_{\text{N}}+xE_{\text{Ni}}+yE_{\text{B}}) \right]/(n+m+x+y)
\]
(13)
Where \( E_{B-\text{NiNC}} \) represent the total energy of \( E_{B-\text{NiNC}} \), while \( E_{\text{C}}, E_{\text{Ni}}, E_{\text{B}} \) 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 \( E_{\text{coh}} \) 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: \(^7\)
\[
E_f = E_{B-\text{NiNC}} + E_{\text{NC}} + n\mu_{\text{C}} + m\mu_{\text{N}} - x\mu_{\text{Ni}} - y\mu_{\text{B}}
\]
(14)
Where \( E_{B-\text{NiNC}}, E_{\text{NC}} \) are the total energy of B doping NiNC and N doping graphene without Ni adsorption, \( \mu_{\text{C}}, \mu_{\text{N}}, \mu_{\text{Ni}} \) and \( \mu_{\text{B}} \) 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 (a₁) NiN₃O, (a₂) CO adsorbed NiN₃B, (a₃) NiN₂B₂-2, (a₄) 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 (a₁) NiN₃B and (a₂) 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$_2$B$_2$-2 and the corresponding electron loss function (ELF) spectrum.
Figure S6. The PDOS of CO adsorbed NiN\textsubscript{2}B\textsubscript{2}-2, and the Vacuum level is set to zero.

Tables:

Table S1. Calculated free energy (\(\Delta G\)) of different intermediates catalyzed by NiN\textsubscript{2}B.

<table>
<thead>
<tr>
<th>Reaction intermediates</th>
<th>(\Delta G) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*COOH</td>
<td>0.13</td>
</tr>
<tr>
<td>*OCHO</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Table S2. Calculated free energy ($\Delta G$) of different intermediates catalyzed by NiN$_2$B$_2$-2.

<table>
<thead>
<tr>
<th>Reaction intermediates</th>
<th>$\Delta G$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*COOH</td>
<td>-0.20</td>
</tr>
<tr>
<td>*OCHO</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table: Calculated free energy ($\Delta G$) of different intermediates catalyzed by NiN$_2$B$_2$-2.
Table S3. Calculated energy difference (Δ$E_b$) between binding energy ($E_b$) of Ni atom in Ni$_3$B$_y$ matrix and cohesive energy ($E_{coh}$) of Ni atom in the bulk crystal and dissolution potential ($U_{diss}$) of NiN$_3$B and NiN$_2$B$_2$-2.

<table>
<thead>
<tr>
<th>Species</th>
<th>NiN$_3$B</th>
<th>NiN$_2$B$_2$-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_b$ (eV)</td>
<td>-6.86</td>
<td>-6.70</td>
</tr>
</tbody>
</table>
### Table S4. Calculated cohesive and formation energy of NiN$_3$B, NiN$_3$S, NiN$_2$B$_2$-2 and ZnN$_2$B$_2$.

<table>
<thead>
<tr>
<th>Species</th>
<th>NiN$_3$B</th>
<th>NiN$_3$S</th>
<th>NiN$_2$B$_2$-2</th>
<th>ZnN$_2$B$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{coh}$ (eV)</td>
<td>-7.74</td>
<td>-7.67</td>
<td>-7.72</td>
<td>-7.67</td>
</tr>
<tr>
<td>$\Delta E_b$ (eV)</td>
<td>-0.93</td>
<td>-0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U_{diss}$ (V)</td>
<td>0.36</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{fo}$ (eV)</td>
<td>-4.68</td>
<td>-4.56</td>
<td>-3.00</td>
<td>-4.08</td>
</tr>
</tbody>
</table>

**References**