Supporting Information

Metal-Free Boron Nanosheet as "Buffer Electron Pool" for Urea and Ethanol Synthesis via C−N and C−C Coupling

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Computational Details

1 The adsorption energy and reaction Gibbs Free Energy Calculations

The adsorption energy (E_{ads}) of all intermediates was defined as:

$$E_{ads} = E_{adsorbates+cat} - E_{adsorbates} - E_{cat} \quad (1)$$

where $E_{adsorbates+cat}$, $E_{adsorbates}$, and E_{cat} correspond to the energies of adsorbates on the surface of β_{12}-BM, the free adsorbates, and the β_{12}-BM catalyst using DFT calculations, respectively.

The change in Gibbs free energy (ΔG) for the adsorbed species is calculated from the following equation:

$$\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S \quad (2)$$

Where ΔE_{DFT} is the reaction energy calculated based on DFT calculations, ΔE_{ZPE} and $T\Delta S$ are the zero−point energy correction and entropy contributions, T is the temperature. Entropy values of gaseous molecules, such as H_2, NO, CO_2, CO, and NH_3, are taken from the standard tables in *Physical Chemistry*.

In the computational hydrogen electrode (CHE) model,[1,2] the chemical potential of proton-electron pair (H^+/e^-) is equal to half of a hydrogen molecule at standard hydrogen electrode (SHE) conditions:

$$\Delta G(H^+/e^-) = 1/2\,\Delta G_{H2} - eU \quad (3)$$

The bias effect on the free energy is taken into account by shifting the energy of the state by:

$$\Delta G_U = -neU \quad (4)$$

where n is the number of H^+/e^- pairs transferred in the reaction.

U_L is the highest potential where all of the steps are downhill in free energy.[3] It is calculated as:

$$U_L = -\Delta G/e \quad (5)$$

where ΔG is the free energy of the potential–limiting step.

2. Selectivity Calculations

Since only two competitive reactions are considered according to the Boltzmann distribution in the formulation, it only can simply estimate the selectivity of reaction. However, the urea and the ethanol formation are complex reactions that involve multiple competitive hydrogen evolution reaction (HER), NO reduction reaction (NORR), and CO_2 reduction reaction (CO_2RR) in this study. To solve this problem, the urea and ethanol formation main reaction, side reactions and ΔG value of potential-determining step (PDS) of corresponding reactions are all listed in the Table S3. For urea formation, there are five competitive reactions, including H_2, NH_3, CO, CH_4 and CH_3OH formation. The NH_3 formation is considered to be the dominant competitive reaction among above five reactions based on ΔG value of PDS. Similarly, the selectivity of ethanol formation also is simply estimated by only considering CH_4 formation. Therefore, the selectively of urea and ethanol according to Boltzmann distribution[4] can be defined as:

$$f = 1/(1 + exp\ \{-\delta G/k_B T\}) \qquad (6)$$

Where δG is the Gibbs free energy difference between two competitive reactions, k_B is the Boltzmann constant, and T is the temperature. Considering the competitive formation of H_2 and NH_2CONH_2 as an example, for instance, if the possibility of the formation of NH_2CONH_2 is set as 1, the possibility of the formation of NH_2CONH_2 would be $exp\ \{-\delta G/k_B T\}$, where $\delta G = \Delta G_{H2} - \Delta G_{NH2CONH2}$. If δG is positive, the possibility of the formation of NH_2CONH_2 is less than 1, and its selectivity will be larger than 50%.

3. Slow-growth approach Calculations

The slow growth method is based on thermodynamic integration to compute the free energy profile along the reaction coordinates. Therefore, the constrained AIMD and the "slow-growth" approach were employed to evaluate the kinetic barriers to obtain the free-energy profile of C–N and C–C coupling along the collective variable (CV).[5,6] The free energy difference between two states (initial state (IS) and final state (FS)) can be calculated by thermodynamic integration as:

$$W_{FS}—W_{IS} = \int_{\xi(I)}^{\xi(F)} \frac{dF}{d\xi} d\xi \qquad (7)$$

where F is the free energy; $\frac{dF}{d\xi}$ is the potential of mean force, which is calculated along a constrained MD sampling; The CV value is used to limit the degree of freedom ξ in the phase space as the reaction coordinate. The work $W_{FS}—W_{IS}$ corresponds to the free energy difference between the final and initial state. For the C-N coupling formation step, the CV is chosen as the reaction coordinate. The free energy samplings were performed with the CV value of the C−N bond distance ($d_{C–N}$). A dξ value of 0.0005 Å is used for each MD step after testing a shorter step size for the "slow-growth" along the reaction coordinate.

4. Constant-potential Models

In this study, the electrode potential versus SHE was determined by referencing the work function of electrochemical interface to an experimental value of 4.44 eV for the SHE[7]. Then the electrode potentials of the β_{12}-BM surface were determined by:

$$U_{SHE} = (\phi - \phi_{SHE}) / e = (\phi - 4.44) / e \qquad (8)$$

where ϕ is the work function, which can be computed from DFT calculations. The work function values for β_{12}-BM with various C-N and C-C intermediates are summarized in Table S4. We considered the average value of the potential at the initial state (U_{IS}) and transition state (U_{TS}) as the potential (Ur) of the reaction (i.e., Ur = (U_{IS} + U_{TS})/2). As shown in the Table S4, these data show that although the adsorbed intermediates are different, the computed electrode potentials of C-N and C-C intermediates are about 0.65 V vs SHE and 0.68 V vs SHE, respectively.

The constant potential correction method was used to get C-N and C-C electrochemical coupling barrier at constant potential developed by Chan and Nørskov[8].

$$\Delta E = (\Delta q \cdot \Delta \phi) / 2 \qquad (9)$$

where ΔE , Δq , and $\Delta \phi$ corresponds to the energy correction due to change of electrode

potential, charges and workfunctions

Supplementary Results

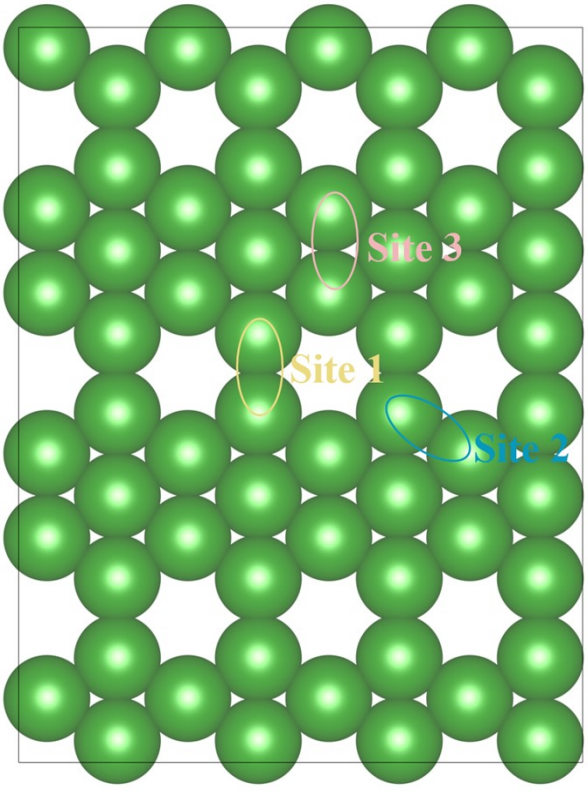

Fig. S1 Top views of the atomic configurations of β_{12}-BM with three different active site for CO_2 and NO molecule adsorption.

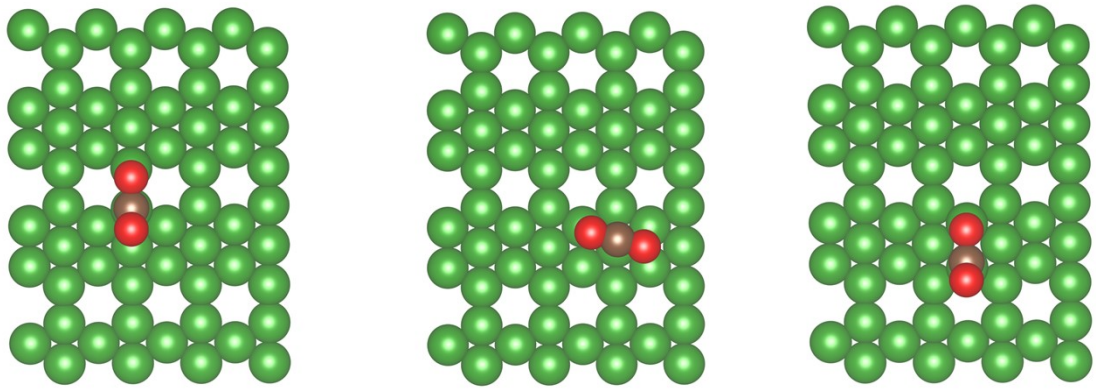

Fig. S2 Top views of the atomic configurations of CO_2 adsorption on (a) site 1 (b) site 2 and (c) site 3 in β_{12}-BM.

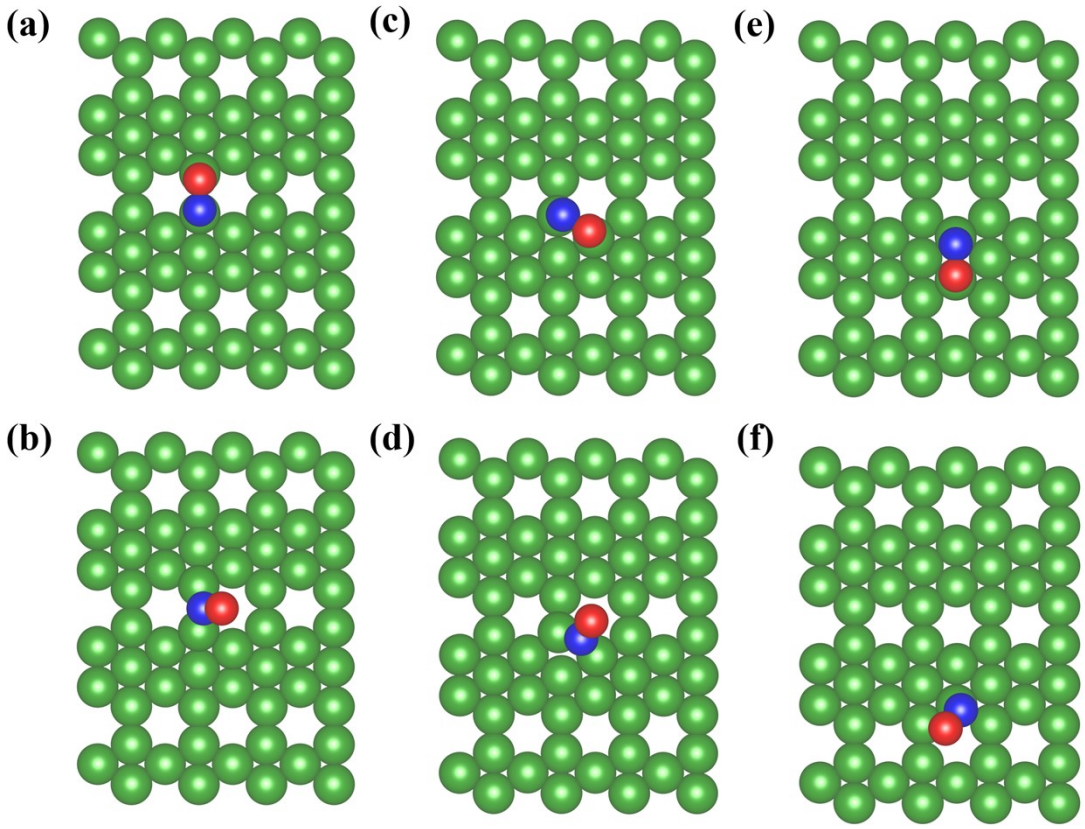

Fig. S3 Top views of the atomic configurations of NO adsorption on (a) − (b) site 1, (c) − (d) site 2, and (e)-(f) site 3 in β_{12}-BM via side-on and end-on pattern, respectively.

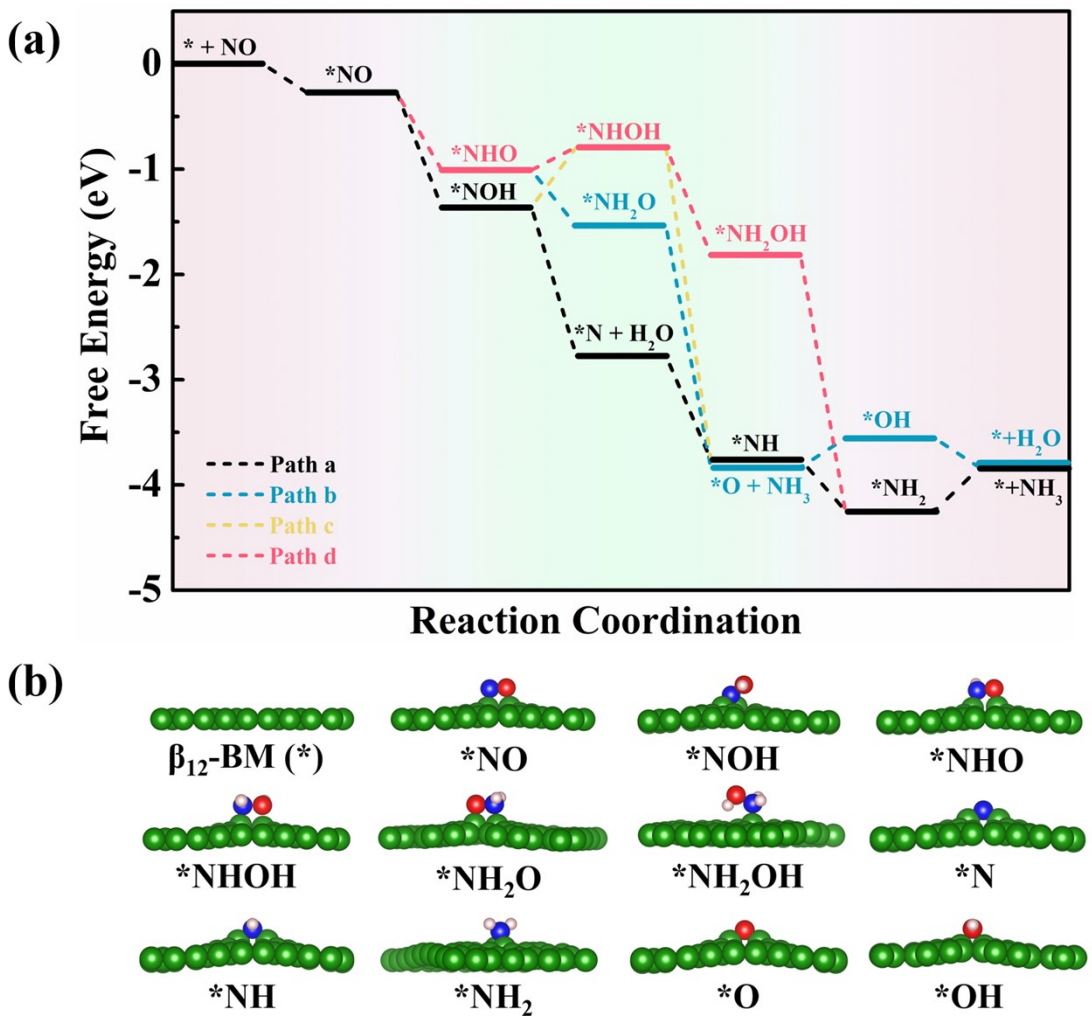

Fig. S4 (a) Free energy profiles for the NORR on β_{12}-BM and (b) the corresponding configurations of all the possible intermediates

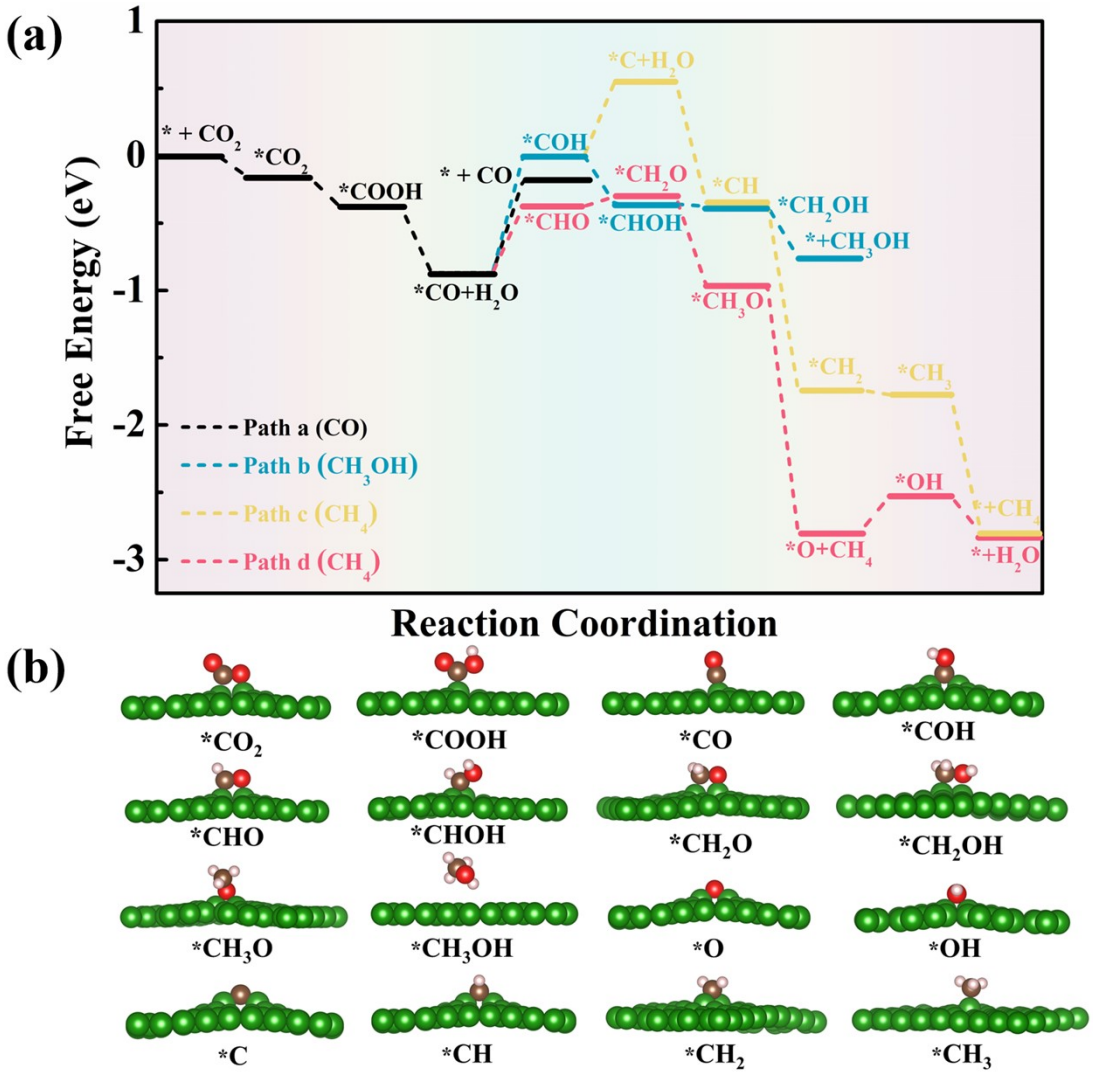

Fig. S5 (a) Free energy profiles of the CO_2RR for producing the C1 products on β_{12}-BM and (b) the corresponding configurations of all the possible intermediates

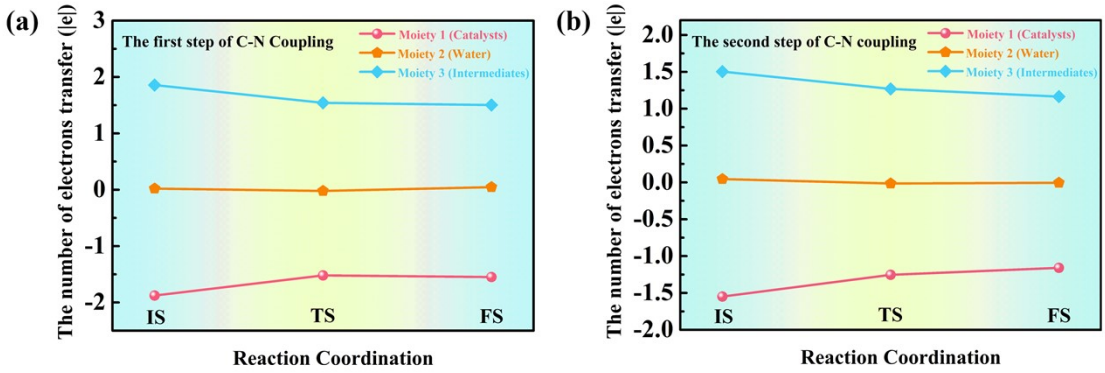

Fig. S6 (a), (b) Charge variation of the three moieties along two steps of C-N coupling reactions. Moieties 1, 2, and 3 represent the β_{12}-BM surface, the water molecules, and the adsorbed species, respectively. The positive values represent the electron obtained; negative values represent the loss of electrons.

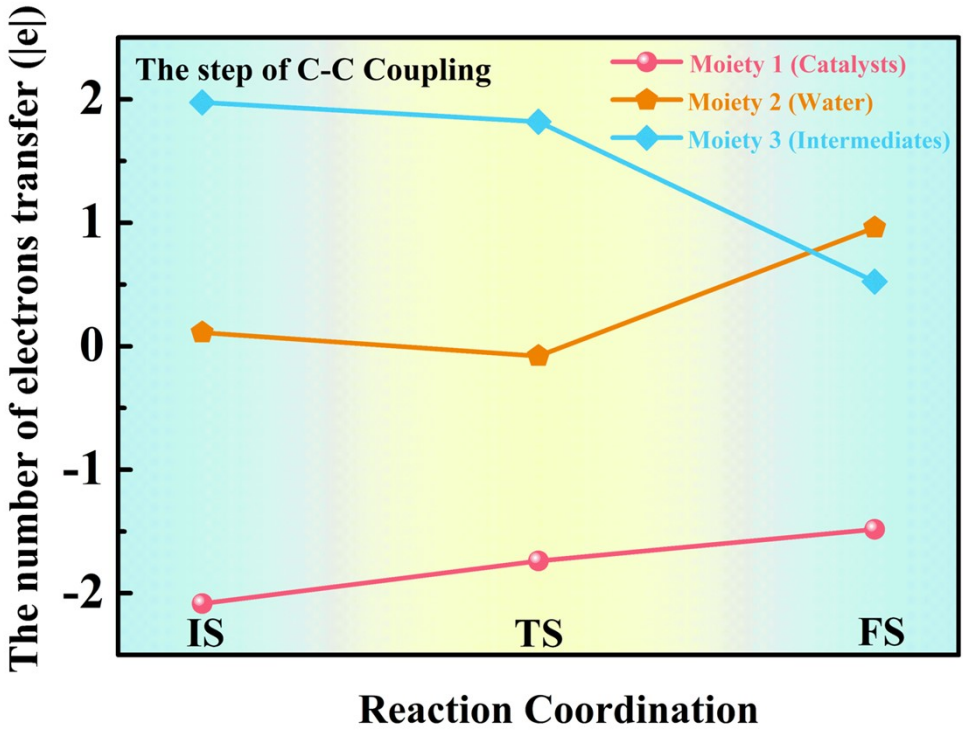

Fig. S7 Charge variation of the three moieties along C-C coupling reactions. Moieties 1, 2, and 3 represent the β_{12}-BM surface, the water molecules, and the adsorbed species, respectively. The positive values represent the electron obtained; negative values represent the loss of electrons.

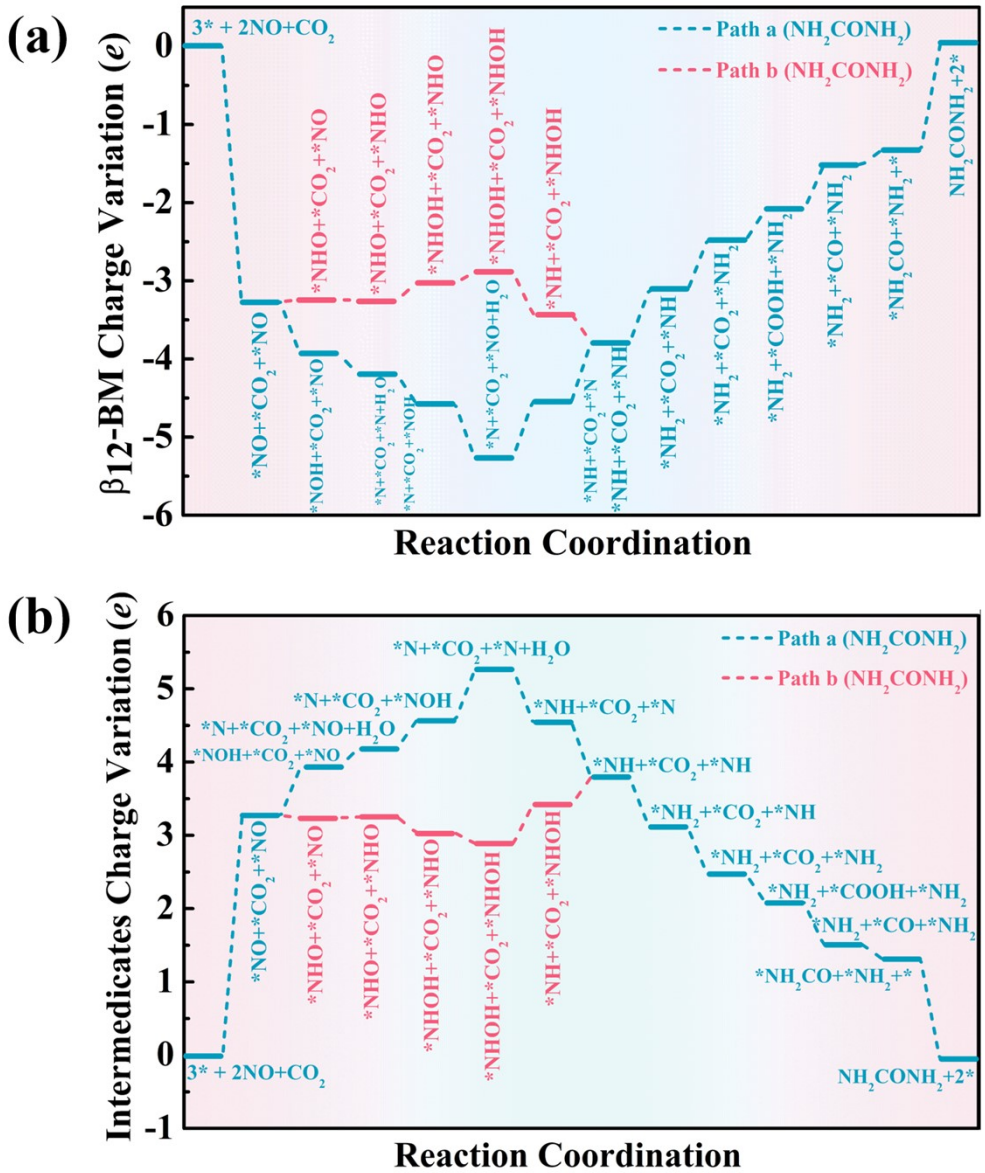

Fig. S8 Charge variation of the (a) β_{12}-BM and (b) intermediates during the urea formation. The positive values represent that the intermediates gain electrons from β_{12}-

BM; the negative values represent the loss of electrons.

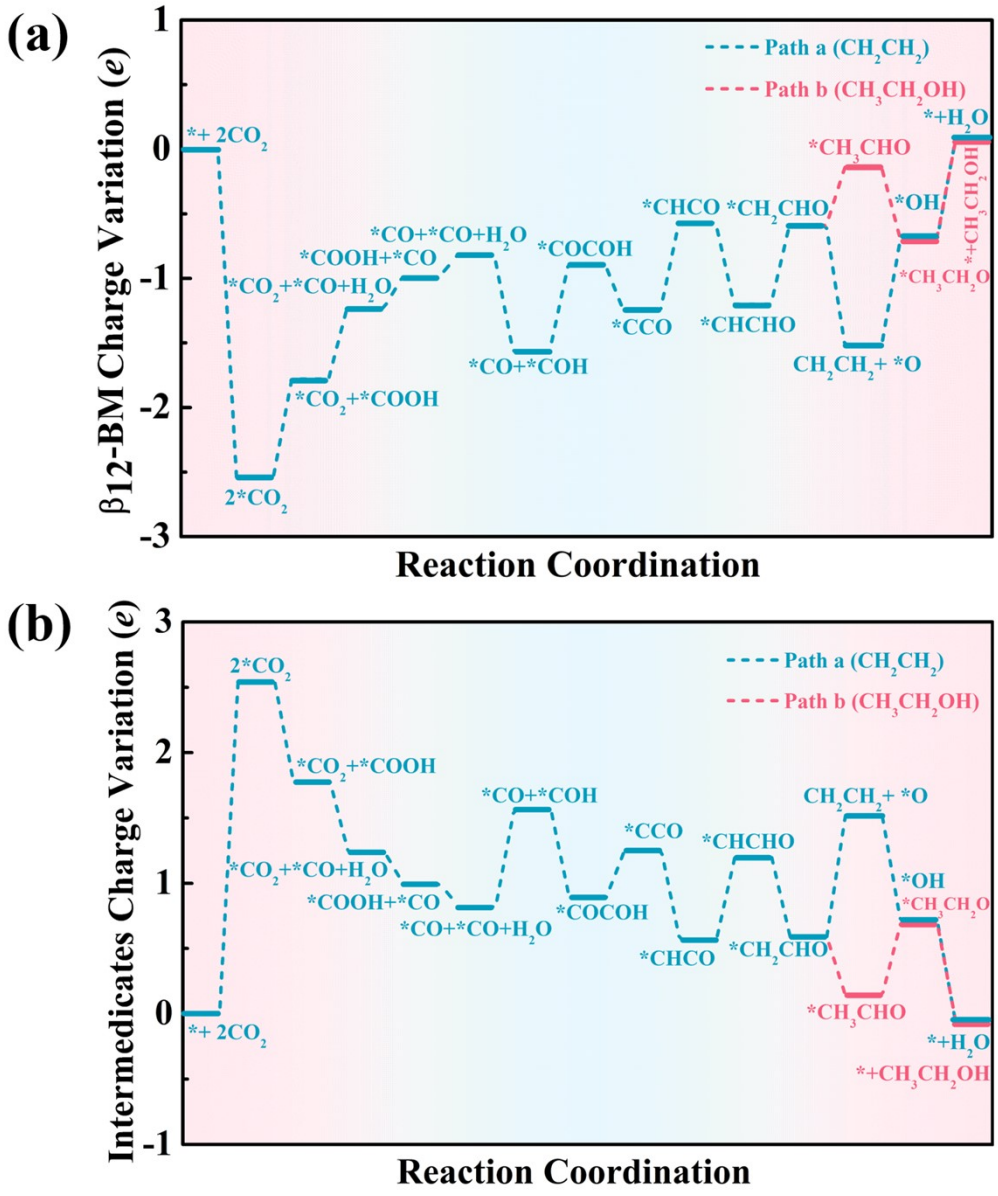

Fig. S9 Charge variation of (a) β_{12}-BM and (b) intermediates during the ethanol formation. The positive values represent that the intermediates gain electrons from β_{12}-BM; the negative values represent the loss of electrons.

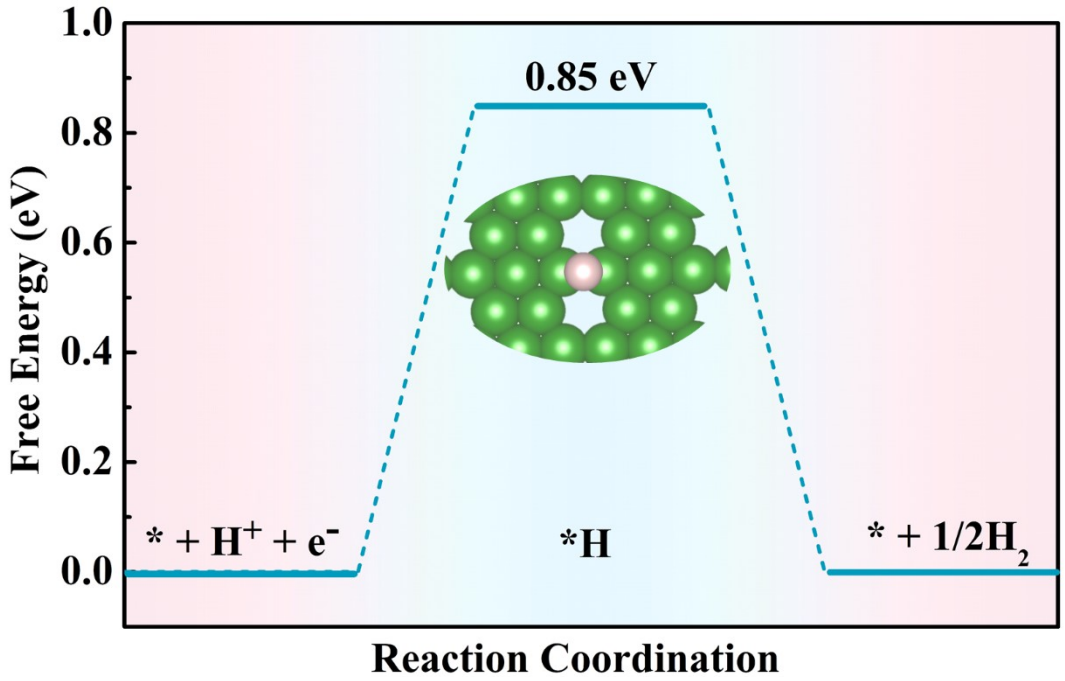

Fig. S10 Free energy profiles and the corresponding configuration for the HER on β_{12}-BM.

Table S1. Workfunctions (ϕ) of initial state and transition state, average value of the potential and Energy correction for C-N and C-C coupling reaction

	Reaction Equation	ϕ values of IS (eV)	ϕ values of TS (eV)	Potential of reaction (V)	Energy correction (eV)
C-N Coupling	$*CO+*NH_2 \rightarrow *CONH_2$	5.16	5.03	0.66	0.04
	$*CONH_2+*NH_2 \rightarrow *NH_2CONH_2$	5.12	5.02	0.63	0.03
C-C coupling	$*CO+*COH \rightarrow *COCOH$	5.10	5.13	0.68	0.01

Table S2. The adsorption energy of the adsorbed CO_2 and NO molecules (E_{ads}), the angle of adsorbed CO_2 (degree) and the bond length of adsorbed NO (Å) in the gas phase and liquid phase for β_{12}-BM.

	Gas phase			Liquid phase		
	E_{asd} (eV)	Angle of CO_2 (degree)	Bond length of N-O (Å)	E_{asd} (eV)	Angle of CO_2 (degree)	Bond length of N-O (Å)
$*CO_2$	-0.54	127.23	---	-4.47	124.72	--
*NO	-0.87	---	1.31	-5.93	---	1.45/1.41
$*CO_2$_$*CO_2$	-0.53/ -0.54	125.04/121.54	---	-5.34/ -5.42	122.11/118.32	---
$*CO_2$_2*NO	-0.54/	126.11	1.32/1.31	-4.47/	120.82	1.46

-0.47/	-3.12/
-0.47	-3.12

Table S3. The urea and ethanol formation main reaction, side reaction and the change of the free energy values of potential-determining step

Main Reaction product	ΔG_{PDS} (eV)	Side reaction	ΔG_{PDS} (eV)
$2NO+CO_2+11(H^++e^-)\rightarrow CO(NH_2)_2+3H_2O$	0.09	$2H^++2e^-\rightarrow H_2$	0.85
		$NO+5(H^++e^-)\rightarrow NH_3+H_2O$	0.27
		$CO_2+2(H^++e^-)\rightarrow CO+H_2O$	0.69
		$CO_2+8(H^++e^-)\rightarrow CH_4+2H_2O$	0.50
		$CO_2+6(H^++e^-)\rightarrow CH_3OH+H_2O$	0.86
$2CO_2+12(H^++e^-)\rightarrow CH_3CH_2OH+3H_2O$	0.75	$2H^++2e^-\rightarrow H_2$	0.85
		$2CO_2+12(H^++e^-)\rightarrow C_2H_4+4H_2O$	0.75
		$CO_2+2(H^++e^-)\rightarrow CO+H_2O$	0.69
		$CO_2+8(H^++e^-)\rightarrow CH_4+2H_2O$	0.50
		$CO_2+6(H^++e^-)\rightarrow CH_3OH+H_2O$	0.86

References

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