

Mechanism Insight into the direct N-C coupling in Selective Catalytic Reduction of NO by CO over Ni(111)-Supported Graphene

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S1. Calculation method tests

Table S1 The convergence tests of 0.02 eV/Å force tolerance, 10^{-4} eV energy tolerance and 0.01 eV/Å force tolerance, 10^{-5} eV energy tolerance for some key intermediates and critical transition state at Grimme-D2 method.

Species	Energy	$\Delta E(\text{eV})$	
		-0.02/ 10^{-4}	-0.01/ 10^{-5}
NO		-0.55	-0.54
CO		-0.34	-0.30
IS (NO + CO)		-0.77	-0.76
TS1 (ON--CO)		-0.66	-0.64
MS1 (ONCO)		-1.23	-1.22
MS2 (ON*CO)		-1.32	-1.31
MS4 (*ONCO)		-1.64	-1.62

Table S2 The testes of Grimme-D2 and Grimme-D3 methods for some key intermediates and critical transition state at 0.02 eV/Å force tolerance, 10^{-4} eV energy tolerance.

Species	Energy	$\Delta E(\text{eV})$	
		Grimme-D2	Grimme-D3
NO		-0.55	-0.55
CO		-0.34	-0.35
IS (NO + CO)		-0.77	-0.79
TS1 (ON--CO)		-0.66	-0.66
MS1 (ONCO)		-1.23	-1.20
MS2 (ON*CO)		-1.32	-1.24
MS4 (*ONCO)		-1.64	-1.53

S2. Thermodynamic feasibility of CO dimerization

Table S3 Calculated Gibbs free energy (ΔG , eV), changes of energy (ΔE , eV), the zero point energy (ΔE_{ZPE} , eV), entropy ($-T\Delta S$, eV) of NO and CO to form ONCO in gas state and on the surfaces of Gr/Ni(111), Gr/Ni(110) and Gr/Ni(100), respectively.

	ΔE	ΔE_{ZPE}	$-T\Delta S$	ΔG
Gaseous	-0.13	0.09	0.41	0.36
*ONCO-Gr/Ni(111)	-1.64	0.17	1.02	-0.45
*ONCO-Gr/Ni(110)	-1.40	0.16	1.07	-0.17
*ONCO-Gr/Ni(100)	-1.89	0.17	1.08	-0.65

The Gibbs free energy ΔG of NO and CO to form C_2O_2 is defined as

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

There, ΔE , ΔE_{ZPE} , ΔS are the energy change, the zero point energy (ZPE) change and entropy change of the reaction, respectively. The ZPE and entropy correction (TS) were obtained from the vibrational frequency calculations at 298.15 K. ZPE and -TS can be calculated by the following formula:

$$E_{ZPE} = \frac{1}{2} \sum_i h\nu_i$$
$$-TS = K_B T \sum_i \left(1 - e^{-\frac{h\nu_i}{K_B T}} \right) - \sum_i h\nu_i \left(\frac{1}{e^{-\frac{h\nu_i}{K_B T}} - 1} \right)$$

where h , ν , K_B are the Planck constant, vibrational frequencies and Boltzmann constant, respectively.

S3. The adsorption of NO, CO and ONCO on Gr/Ni(111)

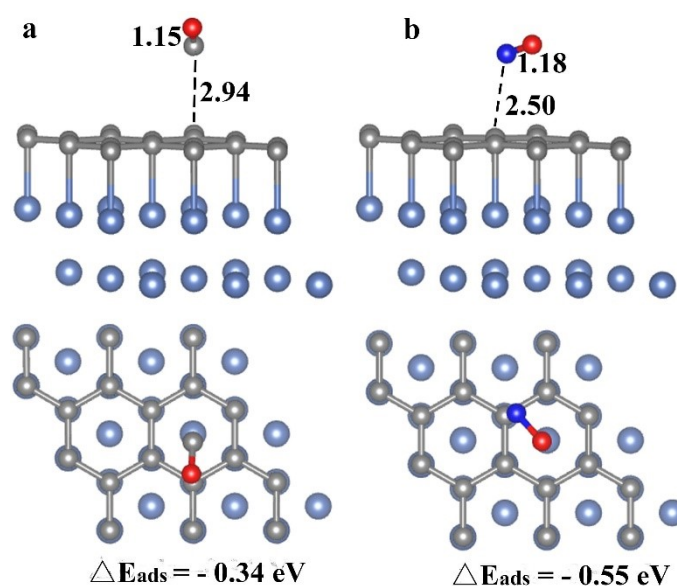


Figure S1. Optimized physisorption configurations of CO and NO monomers on Gr/Ni(111) surface. The atomic distance is presented in Å, and the N, C, O and Ni atoms are represented with dark blue, grey, red and light blue spheres, respectively.

To investigate the interaction between reactants of CO and NO and the surface of Gr/Ni(111) catalyst, the adsorption behaviors of CO and NO on Gr/Ni(111) are calculated firstly, and the adsorption configurations are shown in Figure S1. The adsorption energies of CO and NO on Gr/Ni(111) surface are -0.34 and -0.55 eV, their corresponding adsorption distances of are 2.94 and 2.50 Å, and the bond lengths of C-O and N-O are 1.15 and 1.18 Å, respectively, indicating that CO and NO are physically adsorbed on Gr/Ni(111) surface.

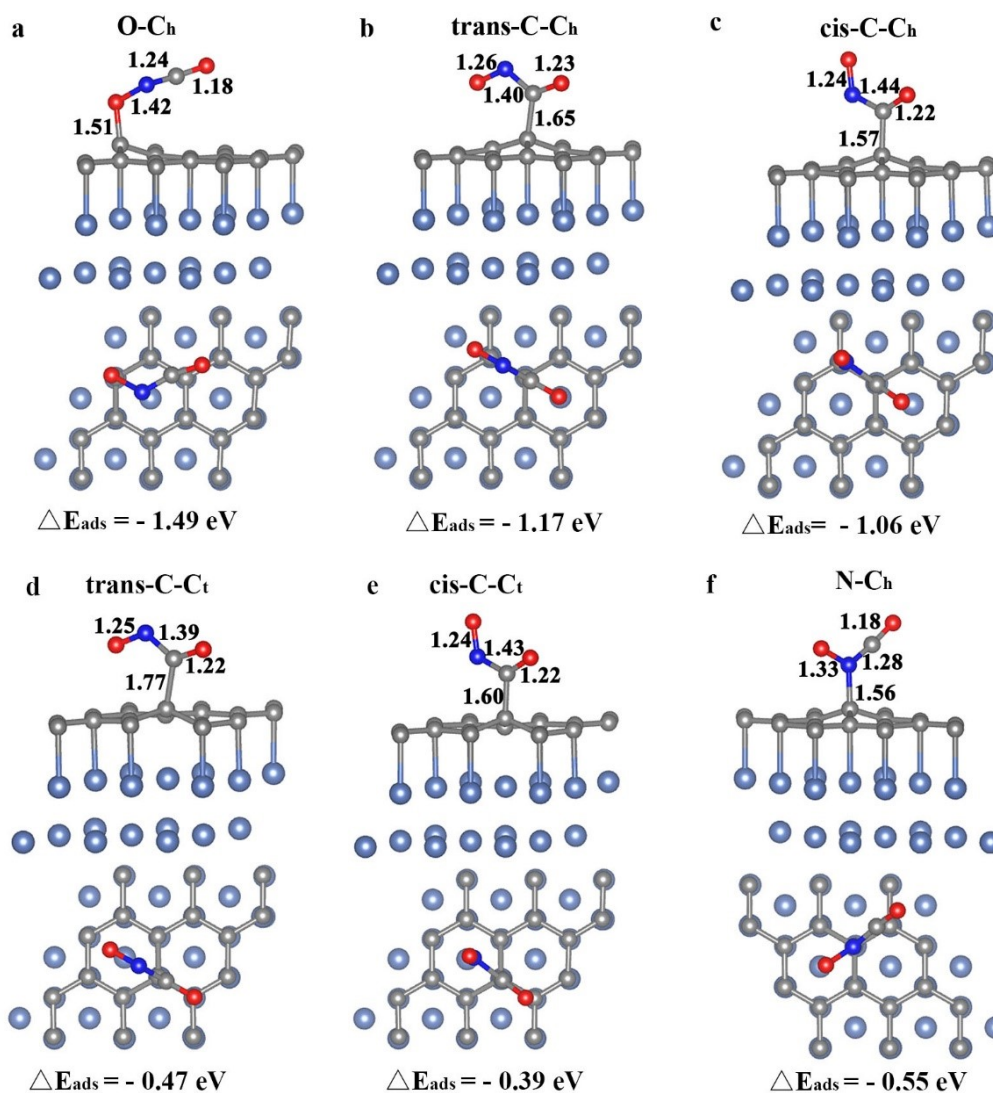


Figure S2. Optimized configurations and adsorption energies (eV) of $*\text{ONCO}$ on $\text{Gr}/\text{Ni}(111)$ surface for monatomic adsorption by single O-atom of (a) $*\text{ONCO}(\text{O-C}_h)$, by single C-atom of (b) $\text{trans-ON}^*\text{CO}(\text{C-C}_h)$, (c) $\text{cis-ON}^*\text{CO}(\text{C-C}_h)$, (d) $\text{trans-ON}^*\text{CO}(\text{C-C}_t)$, (e) $\text{cis-ON}^*\text{CO}(\text{C-C}_t)$, and by single N-atom of (f) $\text{O}^*\text{NCO}(\text{N-C}_h)$ located at the C atoms of $\text{Gr}/\text{Ni}(111)$ surface. There are two types of C atoms of graphene, located at the top (C_t) and hollow (C_h) sites on the surface of $\text{Ni}(111)$. The atomic distance is presented in Å, and the N, C, O and Ni atoms are represented with dark blue, grey, red and light blue spheres, respectively.

ONCO would be further chemically adsorbed on the Gr/Ni(111) surface by two types of mon- and di-atomic adsorption. Optimized configurations and adsorption energies of monatomic adsorption are depicted in Fig. S2. For the monatomic adsorptions, Fig. S2 shows that the configurations of ONCO adsorbed on the C_h hollow site of Gr/Ni(111) surface are energetically favorable than that on the C_t top site of Gr/Ni(111) surface. The *ONCO adsorption in the O- C_h configuration is the most energetically favorable with the adsorption energy of -1.49 eV. The ON*CO with trans- $C-C_h$ and cis- $C-C_h$ configurations has higher adsorption energies of -1.17 and -1.06 eV, while that with trans- $C-C_t$ and cis- $C-C_t$ configurations has lower adsorption energies of -0.47 and -0.39 eV. The adsorption energy of the O*NCO adsorption in N- C_h configuration is only -0.55 eV. It is note that the O- C_t configuration of *ONCO adsorption and N- C_h configuration of O*NCO adsorption are not found.

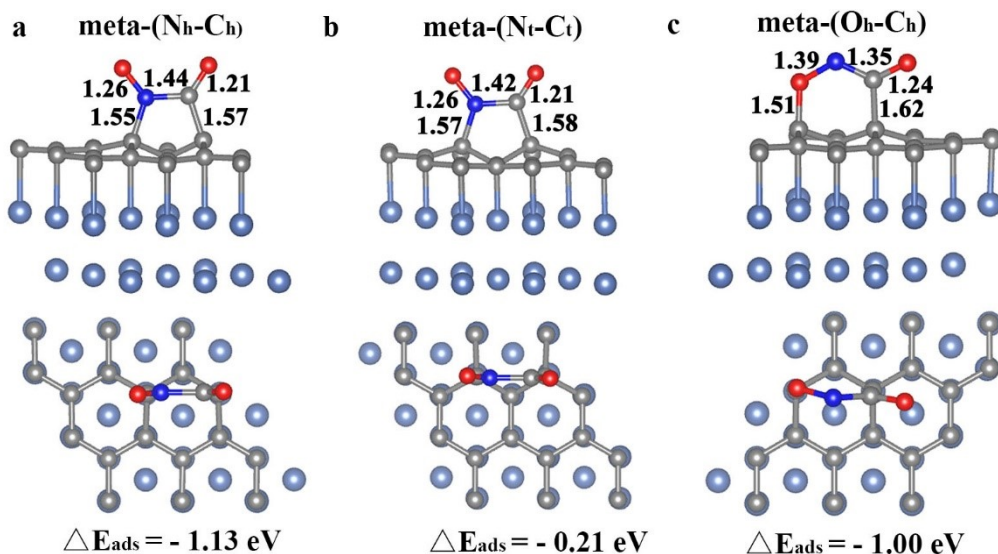


Figure S3. Optimized configurations and adsorption energies (eV) of *ONCO on Gr/Ni(111) surface for diatomic adsorption by N and C, or O and C atoms located at two Meta-C atoms of six-membered rings of Gr/Ni(111). There are two types of C atoms of graphene, located at the top (C_t) and hollow (C_h) sites on the surface of Ni(111). The atomic distance is presented in Å, and the N, C, O and Ni atoms are represented with dark blue, grey, red and light blue spheres, respectively.

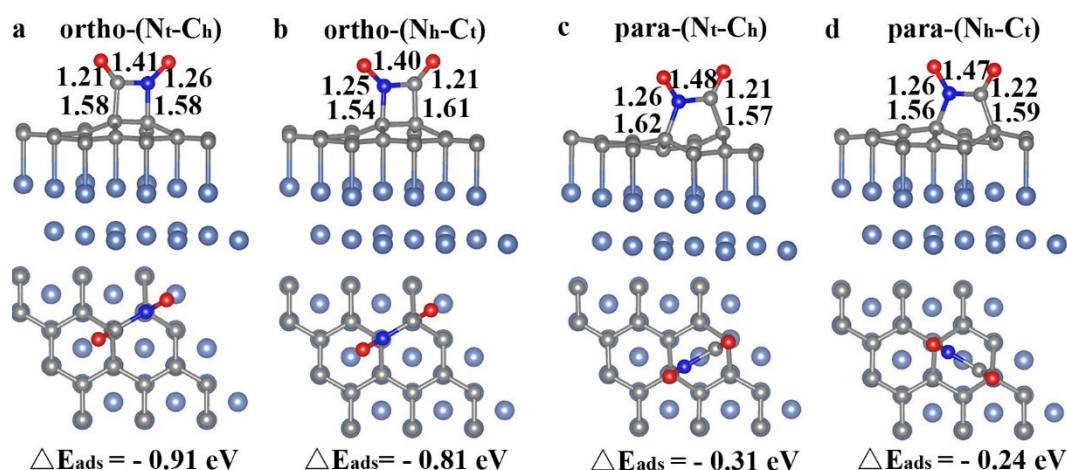


Figure S4. Optimized configurations and adsorption energies (eV) of ONCO on Gr/Ni(111) surface for diatomic adsorption by N and C, or O and C atoms located at two (a, b) ortho-, (c, d) para-C atoms of six-membered rings of Ni(111)-supported

graphene. There are two types of C atoms of graphene, located at the top (C_t) and hollow (C_h) sites on the surface of Ni(111). The atomic distance are presented in Å, and the N, C, O and Ni atoms are represented with dark blue, grey, red and light blue spheres, respectively.

Fig. S3 and S4 illustrate that for the co-adsorption chemical adsorption configurations of ONCO on Gr/Ni(111), meta-C adsorption was preferred over para-C and ortho-C adsorptions. The adsorption energies of ONCO co-adsorption chemical adsorption configurations on Gr/Ni(111) are as follows: (a) meta- (N_h-C_h) adsorption (-1.13 eV) > (c) meta- (O_h-C_h) adsorption (-1.00 eV) > (b) meta- (N_t-C_t) adsorption (-0.21 eV), details on the structure parameters of meta-adsorptions of the ONCO on Gr/Ni(111) are illustrated in Fig. S3.

The N-C, C-C bond lengths between O^*N^*CO and surface are 1.55 and 1.57 Å (meta- (N_h-C_h)), 1.57 and 1.58 Å (meta- (N_t-C_t)), the O- *N and *C -O bond of O^*N^*CO were similar, which are 1.26 and 1.21 Å, respectively. The *N - *C bond lengths of O^*N^*CO are 1.44 and 1.42 Å, respectively. The O-C, C-C bond lengths between $^*ON^*CO$ and surface are 1.51 and 1.62 Å (meta- (O_h-C_h)), the *O -N, *C -N, and *C -O bond lengths of $^*ON^*CO$ on Gr/Ni(111) are 1.39, 1.35, and 1.24 Å, respectively. The adsorption energies of para-C and ortho-C adsorptions co-adsorption chemical adsorption configurations on Gr/Ni(111) are as follows: (a) ortho- (N_t-C_h) adsorption (-0.91 eV) > (b) ortho- (N_h-C_t) adsorption (-0.81 eV) > (c) para- (N_t-C_h) adsorption (-0.31 eV) > (d) para- (N_h-C_t) adsorption (-0.24 eV). Details on the structure parameters are illustrated in Fig. S4. The O- *N and *C -O bonds of para-C and ortho-C adsorptions of

O*N*CO are similar, which are 1.26 and 1.21 Å, respectively. Further, the *N-*C bond of ortho-C and para-C adsorptions of O*N*CO were similar, which are 1.41 and 1.48 Å, respectively. The N-C, C-C bond lengths between O*N*CO and surface are 1.58 (ortho-(N_t-C_h)), 1.54 and 1.61 Å (ortho-(N_h-C_t)), 1.62 and 1.57 Å (para-(N_t-C_h)), 1.56 and 1.59 Å (para-(N_h-C_h)), respectively.

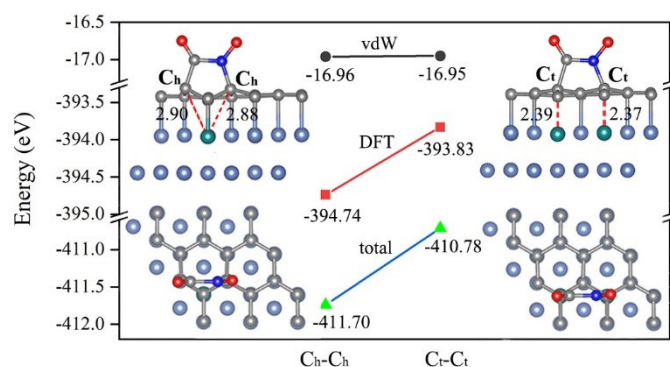


Figure S5 Optimized chemisorption configurations, structure parameters and adsorption energies of O*N*CO on Gr/Ni(111) by two C-atoms located on two hollow-hollow (C_h-C_h) or two top-top (C_t-C_t) sites of Ni(111) surface.

The C and N atoms are adsorbed on the hollow-hollow sites of Ni(111) surface in the C_h-C_h configuration with a total energy of -411.70 eV. The interatomic distances between the C_h and Ni atoms at adjacent hollow site are 2.88 and 2.90 Å in the C_h-C_h configuration. The contributions of vdW and electronic attraction to the total energy are -16.96 and -394.74 eV, respectively. For the C_t-C_t configuration, the C and N atoms are directly adsorbed on the top-top sites of Ni(111) with a total energy of -410.78 eV. The interatomic distances between the C_t and Ni atoms at adjacent top sites were ~2.37 Å in the C_t-C_t configuration. The contributions of vdW and electronic attraction to the total energy are -16.95 and -393.83 eV, respectively. In comparison, the shortening of the interatomic distances between the C_t and adjacent Ni atoms led

directly to the increase of electronic repulsion, eventually resulting in decrease of the contribution of electronic attraction in the C_r-C_t configuration. The difference of vdW attraction is not significant.

S4. The influences of temperature and pressure for direct coupling of NO and CO

In this work, the influences of temperature and pressure were further considered for the key step of the gaseous NO and CO coupling into ONCO and subsequent ONCO hydrogenation on the Gr/Ni(111). For the free energy correction, we use VASPKIT code.[1] The Gibbs free energy *G* of reaction is defined as

$$G = E + (ZPE) + U(T) + (PV) - T\Delta S$$

There, *E* is the energy of DFT calculation.

ZPE is the zero point energy. ZPE can be calculated by the following formula:

$$ZPE = \frac{1}{2} \sum_i hv_i$$

U(T) is the heat capacity correction.

(PV) is the energy generated by the change of molecular volume, which is generally directly based on the ideal gas assumption and can be directly calculated with *nRT*.

-*TS* is the entropy change of the reaction. -*TS* can be calculated by the following formula:

$$-TS = K_B T \sum_I \left(1 - e^{-\frac{hv_i}{K_B T}} \right) - \sum_I hv_i \left(\frac{1}{e^{-\frac{hv_i}{K_B T}} - 1} \right)$$

where h , ν , K_B are the Planck constant, vibrational frequencies and Boltzmann constant, respectively.

Through VASPKIT code, we can directly get these correction values. The influence of pressure on the rate-limiting barriers of the surface adsorption reaction is relatively small, only the influence of temperature on the rate-limiting barriers of the O*CO hydrogenation on the Gr/Ni(111) is considered.

[1] V. Wang, N. Xu, J. Liu, G. Tang, W.J.P.a.h.a.o.a. Geng, VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code, (2019).