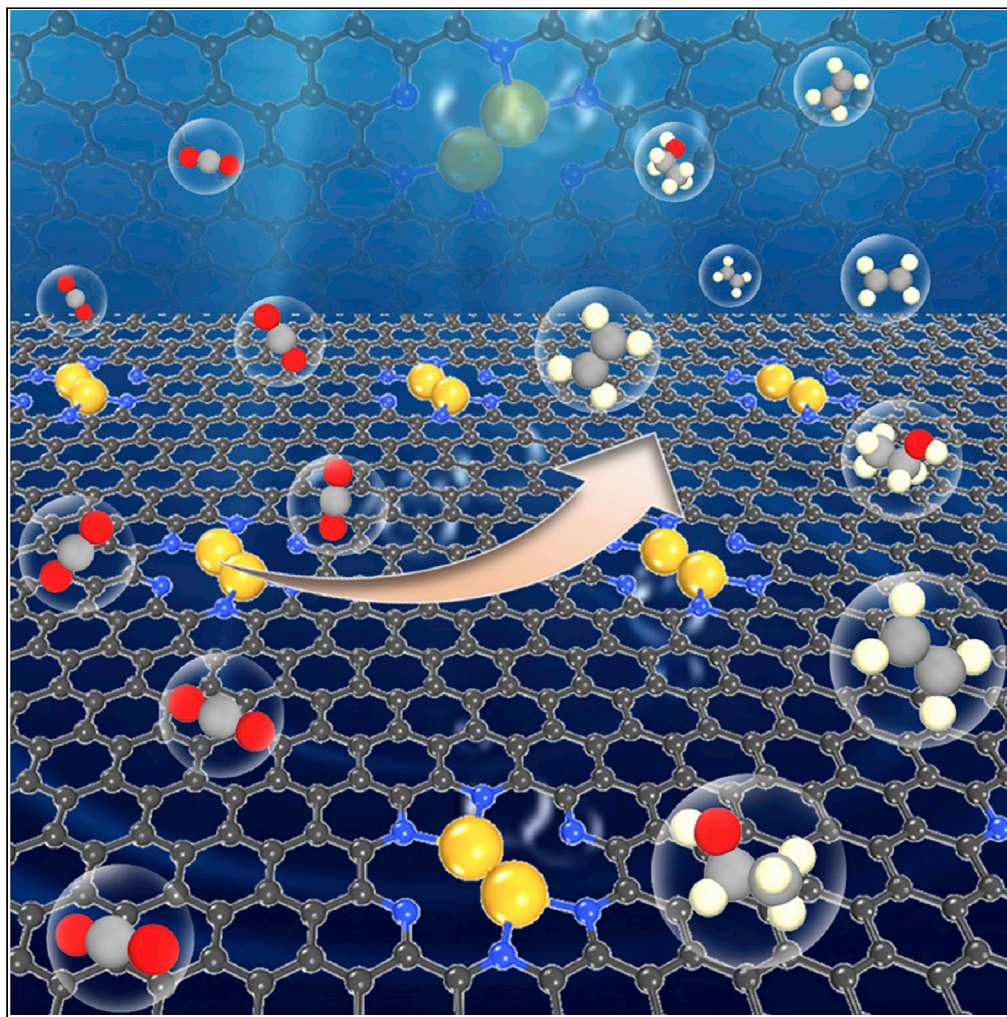


## Article

Selective C–C Coupling by Spatially Confined  
Dimeric Metal Centers

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**HIGHLIGHTS**

Dual metal centers  
provide an exclusive  
pathway for CO<sub>2</sub>  
reduction to C<sub>2</sub> products

Activity and selectivity are  
modulatable by the metal-  
support interaction

Fe<sub>2</sub> dimer anchored on  
C<sub>2</sub>N leads to remarkable  
selectivity for ethanol

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## Article

## Selective C–C Coupling by Spatially Confined Dimeric Metal Centers

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## SUMMARY

Direct conversion of carbon dioxide (CO<sub>2</sub>) to high-energy fuels and high-value chemicals is a fascinating sustainable strategy. For most of the current electrocatalysts for CO<sub>2</sub> reduction, however, multi-carbon products are inhibited by large overpotentials and low selectivity. Herein, we exploit dispersed 3d transition metal dimers as spatially confined dual reaction centers for selective reduction of CO<sub>2</sub> to liquid fuels. Various nitrogenated holey carbon monolayers are shown to be promising templates to stabilize these metal dimers and dictate their electronic structures, allowing precise control of the catalytic activity and product selectivity. By comprehensive first-principles calculations, we screen the suitable transition metal dimers that universally have high activity for ethanol (C<sub>2</sub>H<sub>5</sub>OH). Furthermore, remarkable selectivity for C<sub>2</sub>H<sub>5</sub>OH against other C<sub>1</sub> and C<sub>2</sub> products is found for Fe<sub>2</sub> dimer anchored on C<sub>2</sub>N monolayer. The role of electronic coupling between the metal dimer and the carbon substrates is thoroughly elucidated.

## INTRODUCTION

Production of liquid fuels by catalytic conversion of CO<sub>2</sub>, the main greenhouse gas and meanwhile an abundant carbon feedstock, has been regarded as an appealing strategy to solve both energy and environmental crises, albeit facing great challenges (Birdja et al., 2019; Jia et al., 2019; Amal et al., 2017). Copper-based materials have been widely adopted as catalysts for electro-reduction of CO<sub>2</sub> to multi-carbon (C<sub>2</sub> or C<sub>2+</sub>) products (Zheng et al., 2019). Although fairly good activity can be achieved by modification or morphology engineering of copper, such as sculpturing it into nanoparticles or nanocubes, doping or alloying, and making oxide-derived copper, the selectivity and efficiency of most copper-based electrocatalysts remain unsatisfactory for commercialization of the CO<sub>2</sub> conversion technique to high-energy fuels and high-value chemicals (Gao et al., 2019; Kim et al., 2017; Wang et al., 2018; Zhou et al., 2018).

Recently, transition metal atoms dispersed on nitrogen-doped porous carbon nanomaterials emerge as a promising category of electrocatalysts for CO<sub>2</sub> reduction, which have maximum atomic efficiency, high electrical conductivity and good durability, and can be facilely synthesized in the laboratory (Bayatsarmadi et al., 2017; Chen et al., 2019; Cheng et al., 2018; Wang et al., 2019). The transition metal atoms are usually anchored in the pores of the carbon matrix and coordinated with the nitrogen atoms, exhibiting unique electronic states and acting as isolated reaction centers for CO<sub>2</sub> reduction. Remarkable activity and selectivity toward carbon monoxide (CO) has been observed for various dispersed transition metal atoms (Fe, Co, Ni, Mn, and Cu) on N-doped graphene, carbon nanosheets or nanospheres, with selectivity up to 97% and Faradaic efficiency above 80% (Jiang et al., 2018; Ren and Zhao, 2020; Wang et al., 2019; Yang et al., 2018; Zhang et al., 2018). First-principle calculations show that the activity highly depends on the type of metal atoms, which provide different binding strengths with the reaction intermediates (Ju et al., 2017). The single metal sites also have an advantage of suppressing the competing hydrogen evolution reaction (HER), due to the unique adsorption configuration of H\* species compared with those on the transition metal surfaces (Bagger et al., 2017).

Furthermore, homonuclear and heteronuclear dimers of transition metal immobilized in carbon-based nanostructures, such as Fe<sub>2</sub> and Fe-Co on nitrogenated graphitic carbon materials, Fe-Ni on N-doped graphene, and Pt-Ru on g-C<sub>3</sub>N<sub>4</sub>, have been synthesized in the laboratory (Wang et al., 2017, 2018; Ye et al., 2019; Zhou et al., 2019). This opens up the windows for a broader range of chemical processes that require dual reaction centers either with enhanced activity or carrying different functionalities simultaneously. For

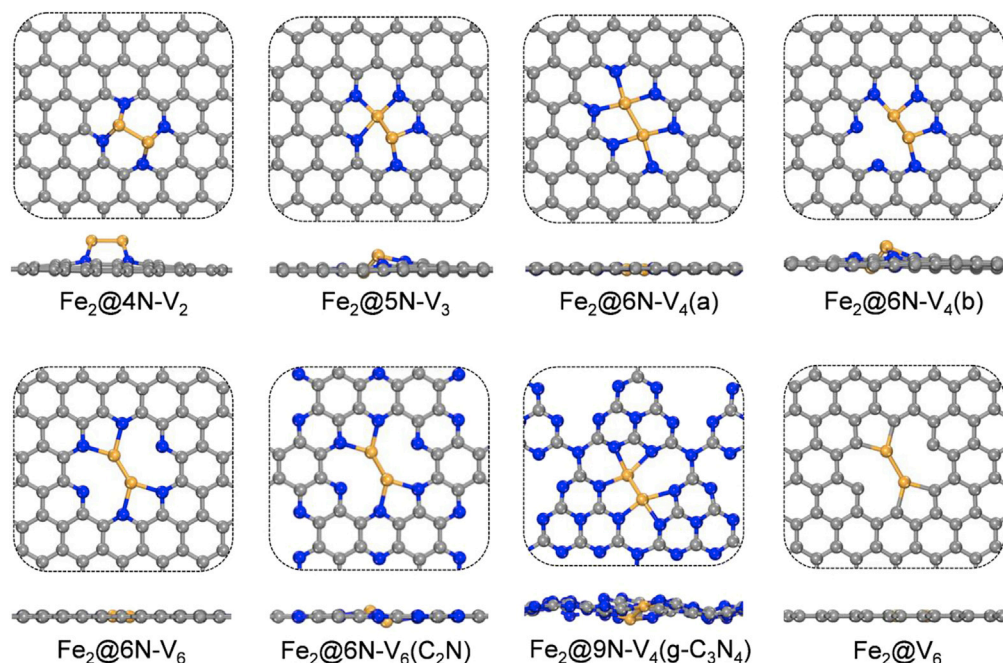
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**Figure 1. Atomic Structures of a Fe<sub>2</sub> Dimer Anchored on Various Nitrogenated Holey Carbon Monolayers (Top Panel: Top View; Bottom Panel: Side View)**

The C, N, and Fe atoms are shown in gray, blue, and orange colors, respectively.

instance, Ren et al. fabricated diatomic Fe-Ni sites embedded in nitrogenated carbon (Ren et al., 2019). By taking advantage of the strong binding capability of Fe with CO<sub>2</sub> molecule and the weak adsorption of CO on Ni, they achieved impressively high selectivity of 99% for CO and Faradaic efficiency above 90% over a wide potential range from  $-0.5$  to  $-0.9$  V, reaching 98% at  $-0.7$  V versus reversible hydrogen electrode (RHE). On the theoretical side, a Cu<sub>2</sub> dimer supported on the C<sub>2</sub>N monolayer was predicted to have high selectivity for methane (CH<sub>4</sub>), whereas dimerization of two CO species leading to the formation of ethene (C<sub>2</sub>H<sub>4</sub>) is possible with an energy cost of 0.76 eV (Zhao et al., 2018). Heteronuclear dimers such as V-Mo on 2D C<sub>2</sub>N and Cu-B on g-C<sub>3</sub>N<sub>4</sub> have been shown to effectively reduce CO<sub>2</sub> to ethanol (C<sub>2</sub>H<sub>5</sub>OH) and C<sub>2</sub>H<sub>4</sub>, owing to the synergistic interaction and asymmetric coupling between two reaction centers yielding favorable binding strength for the formation of C<sub>2</sub> intermediates (Li et al., 2019; He et al., 2020).

Two adjacent metal atoms that are spatially confined in a hole of N-doped carbon materials as unique active sites not only enable the simultaneous fixation of two CO<sub>2</sub> molecules but also sterically limit the reaction pathways that may be beneficial for C–C coupling toward C<sub>2</sub> or C<sub>2+</sub> products. Moreover, various combinations of metal dimers and carbon substrates give high degrees of freedom for modulating the catalytic performance. However, the atomistic mechanism and composition recipe of such heterogeneous catalysts remain largely unknown, which impede their rational design and experimental synthesis for practical uses.

Here we exploit 3d transition metal dimers immobilized on various nitrogenated holey carbon sheets for selective reduction of CO<sub>2</sub> to C<sub>2</sub> products. By systematic first-principle calculations, the detailed C–C coupling mechanism on the spatially confined dual metal centers has been elucidated for the first time. The suitable transition metal elements and carbon substrates that lead to high activity and selectivity for C<sub>2</sub>H<sub>5</sub>OH and C<sub>2</sub>H<sub>4</sub> are screened, and the underlying electronic structure-activity relationship is unveiled. These theoretical explorations illuminate important clues for precisely engineering the dispersed metal catalysts on porous carbon nanomaterials for direct conversion of greenhouse gas to multi-carbon hydrocarbons and oxygenates.

Substrate	$E_{\text{form}}$ (eV/Å)	$E_b$ (eV)	$d$ (Å)		CT (e)	$\Delta E_{\text{CO}_2^*}$ (eV)
			Fe–Fe	N–Fe		
4N- $V_2$	0.17	−5.01	2.09	1.98	0.71	−1.02
5N- $V_3$	0.19	−7.33	1.91	1.87	0.97	−1.15
6N- $V_4$ (a)	0.20	−9.47	2.21	1.94	0.96	−0.11
6N- $V_4$ (b)	0.21	−7.48	2.14	1.98	0.81	−1.15
6N- $V_6$	0.16	−6.02	1.96	2.00	0.76	−1.12
$C_2N$	–	−5.80	2.01	1.97	0.74	−0.64
g- $C_3N_4$	–	−5.09	1.98	1.99	0.72	−1.58
$V_6$	0.67	−12.03	2.21	1.94	0.87	−0.30

**Table 1. Structural and Energetic Properties of Supported Fe<sub>2</sub> Dimer**

Formation energy ( $E_{\text{form}}$ ) of various nitrogenated 2D holey carbon materials, binding energy ( $E_b$ ) of a Fe<sub>2</sub> dimer on the carbon sheet, bond length ( $d$ ) of Fe–Fe and N–Fe/C–Fe bonds, Mulliken charge transfer (CT) from Fe<sub>2</sub> to the carbon sheet, and adsorption energy of a CO<sub>2</sub> molecule ( $\Delta E_{\text{CO}_2^*}$ ) on the supported Fe<sub>2</sub> dimer.

## RESULTS AND DISCUSSION

In the laboratory, N-doped graphitic carbon materials with controllable doping contents (up to 16.7% of N content) and atomic geometries can be achieved via either direct synthesis or posttreatment (Xue et al., 2012; Xu et al., 2018; Qu et al., 2010). Here we focused on pyridine N dopants in graphene, which are the main doping species at high N contents and are usually associated with the vacancies or pores of the carbon basal plane (Sheng et al., 2011; Sarau et al., 2017). As displayed in Figure 1, we considered a series of N-doped holey graphene monolayers, comprising C vacancies of various sizes (denoted as  $V_n$ ,  $n = 2, 3, 4, 6$ ) with the edges coordinated with different numbers of N atoms (denoted as  $mN$ ,  $m = 4, 5, 6$ ). Specifically, 4N- $V_2$ , 5N- $V_3$ , and 6N- $V_4$  systems can be viewed as four, five, and six N atoms decorating the edges of di-vacancy, tri-vacancy, and tetra-vacancy in graphene, respectively, all of which have been commonly observed in experiment (He et al., 2014; Lin et al., 2015; Wang et al., 2018). Note that the  $V_6$  pore in graphene is a favorable defect according to transmission electron microscopy experiment (Robertson et al., 2015), and our previous calculation showed that N-doped  $V_6$  (namely 6N- $V_6$ ) has extraordinary thermodynamic stability (Luo et al., 2013). We further created a number of randomly N-doped graphene lattices, which shows that the 6N- $V_6$  configuration would emerge as N doping content reaches 10% (see Figure S1 for details). Besides the N-doped graphitic sheets, we also considered the synthetic carbon nitride monolayers, including g- $C_3N_4$  and  $C_2N$  (Zhao et al., 2014; Mahmood et al., 2015). All these porous N-coordinated carbon sheets have formation energies (defined by Equation S1 in Supplemental Information) in the range of 0.16–0.21 eV/Å, whereas the N-free  $V_6$  is higher in energy by over 0.46 eV/Å than the others (Table 1). These nitrogenated 2D holey carbon materials are ideal templates to stabilize and disperse metal atoms or small clusters. Indeed, isolated Fe<sub>2</sub>, Fe-Ni, and Fe-Co dimers embedded in 6N- $V_4$ (a), as well as Fe<sub>2</sub> and Pt-Ru dimers anchored on g- $C_3N_4$  have already been realized in experiment (Ye et al., 2019; Wang et al., 2017; Zhou et al., 2019; Ren et al., 2019; Tian et al., 2018).

To evaluate the capability of various supported metal dimers for CO<sub>2</sub> reduction toward C<sub>2</sub> products, we first explored the atomic structures, electronic and adsorption properties of dimeric 3d transition metal clusters on the 6N- $V_6$  monolayer (as will be shown later, this substrate gives metal dimers the highest activity for CO<sub>2</sub> reduction). As presented in Figures 1 and S2, all metal dimers are embedded in the hole of the graphitic sheet, except that Sc<sub>2</sub> with a larger atomic size induces a noticeable buckling of 0.94 Å in the out-of-plane direction. Four N–metal bonds are formed with bond length of 1.95–2.09 Å, and the metal–metal bond length ranges from 1.96 Å to 2.79 Å (Table 2). The binding energy (defined by Equation S2 in Supplemental Information) between the metal dimer and the graphitic sheet is −4.29 to −10.28 eV, excluding the possibility of dissociation or aggregation of the metal dimer. The thermal stability of these carbon-substrate-anchored metal dimers was further assessed by *ab initio* molecular dynamics (AIMD) simulations, which manifest that they can sustain at least 800 K for 10 ps with small vertical displacement of metal atoms (<0.2 Å) (see Figure S3 for details), suggesting superior thermal stability for practical uses.

Metal Dimer	$E_b$ (eV)	$d$ (Å)		$\Delta E$ (eV)		$\epsilon_d$ (eV)
		M–M	N–M	CO <sub>2</sub>	2CO <sub>2</sub>	
Sc <sub>2</sub>	–10.28	2.79	2.09	–3.40	–3.71	1.16
Ti <sub>2</sub>	–8.50	2.17	1.99	–2.85	–3.31	0.62
V <sub>2</sub>	–8.80	2.14	1.96	–2.26	–	0.41
Cr <sub>2</sub>	–4.99	2.16	1.97	–1.44	–0.76	0.07
Mn <sub>2</sub>	–6.52	2.04	2.01	–1.05	–0.48	–0.42
Fe <sub>2</sub>	–6.02	1.96	2.00	–1.12	–0.50	–1.00
Co <sub>2</sub>	–5.71	2.10	1.95	–1.20	–	–1.09
Ni <sub>2</sub>	–5.93	2.17	2.00	–0.82	–	–1.12
Cu <sub>2</sub>	–4.29	2.35	1.96	–0.35	–	–2.08

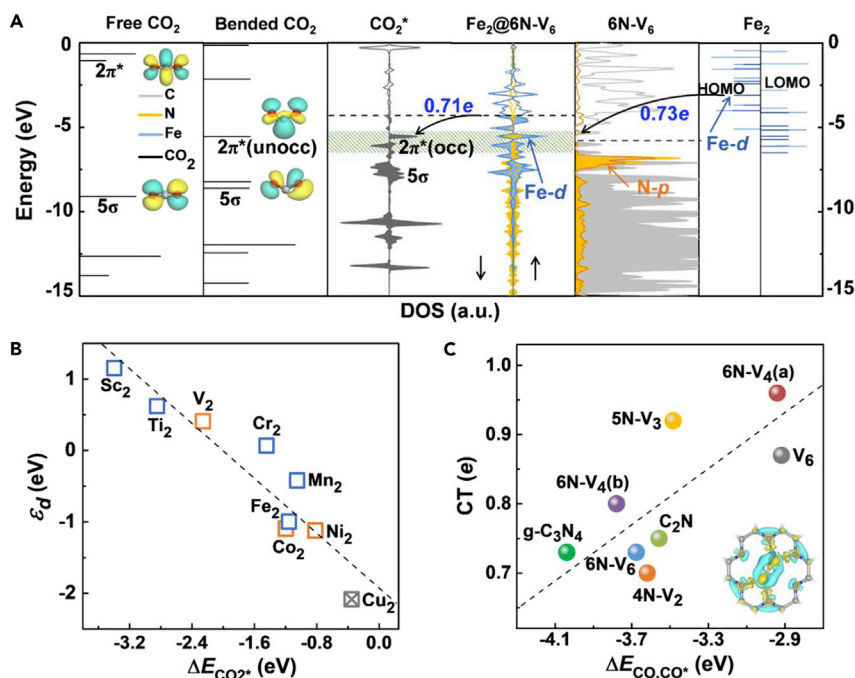
**Table 2. Structural and Energetic Properties of Various Supported 3d Transition Metal Dimers**

Binding energy ( $E_b$ ) of various 3d transition metal dimers anchored on the  $\delta$ N-V<sub>6</sub> monolayer, bond lengths ( $d$ ) of metal dimer (M–M) and N–metal (N–M), adsorption energy of single and dual CO<sub>2</sub> molecules on the supported metal dimers ( $\Delta E$ ), and the  $d$  band center ( $\epsilon_d$ ) of the supported metal dimers (Hammer and Nørskov, 2000).

A CO<sub>2</sub> molecule can favorably chemisorb on these dispersed metal dimers except Cu<sub>2</sub>. The molecule is bended in the bidentate configuration with O–C–O angle of 124.90–141.96°. The C atom and one of the O atoms of CO<sub>2</sub> form two bonds with the underlying metal atoms; the C–O bond length is elongated to 1.21–1.36 Å, compared with 1.16 Å for a free CO<sub>2</sub> molecule. The dynamic process of CO<sub>2</sub> adsorption was also examined by AIMD simulations at 100 K and 300 K, respectively, both showing that the molecule can quickly chemisorb on the dimeric metal centers within a simulation time of 1 ps (see Videos S1 and S2 for the dynamic movies). The adsorption energy (defined by Equation S3 in Supplemental Information) of CO<sub>2</sub> ranges from –0.82 eV to –3.40 eV. Overall speaking, stronger binding is provided by the metal element with fewer  $d$  electrons. The trend of activity can be understood by the electronic density of states (DOS) shown in Figure 2A. Taking Fe<sub>2</sub>@ $\delta$ N-V<sub>6</sub> as an example, hybridization between the  $d$  orbitals of Fe<sub>2</sub> dimer and the  $p$  orbitals of  $\delta$ N-V<sub>6</sub> monolayer substrate is evident, with prominent electronic states close to the Fermi level mainly contributed by the Fe atoms (see Figure S4 for projected DOS). Electron transfer of 0.73  $e$  occurs from Fe<sub>2</sub> to  $\delta$ N-V<sub>6</sub> monolayer, which lifts the Fermi level of the hybrid system above the  $2\pi^*$  state of CO<sub>2</sub>. As a result, Fe<sub>2</sub>@ $\delta$ N-V<sub>6</sub> can favorably donate about 0.71 electrons to the antibonding orbital of CO<sub>2</sub>, as manifested by the differential charge densities in Figure 3A, which is a general mechanism for activation of reactant molecules on metal active centers (Liu et al., 2018). As depicted in Figure 2B, CO<sub>2</sub> adsorption energy generally follows a linear relationship with the  $d$  band center of the supported metal dimers (relative to the Fermi level), as the metal dimer with a higher  $d$  band center would provide stronger binding with CO<sub>2</sub> (Hammer and Nørskov, 2000).

In addition, we examined the capability of various dispersed 3d transition metal dimers for activating two CO<sub>2</sub> molecules simultaneously, which is a prerequisite for C–C coupling to yield C<sub>2</sub> products. Several candidate systems including Sc<sub>2</sub>, Ti<sub>2</sub>, Cr<sub>2</sub>, Mn<sub>2</sub>, and Fe<sub>2</sub> dimers on the  $\delta$ N-V<sub>6</sub> monolayer have adsorption energies of –3.71 to –0.48 eV for fixation of two CO<sub>2</sub> molecules (Figures 3 and S5), whereas the other metal dimers are only able to bind one CO<sub>2</sub> molecule. Considering that Fe is an earth-abundant element and dispersed Fe atoms and dimers can be readily obtained in the experiment (Ye et al., 2019; Tian et al., 2018), thereafter we explored Fe<sub>2</sub> dimer on various nitrogenated 2D holey carbon materials as a representative of dual metal centers.

Figure 1 presents the structures of a Fe<sub>2</sub> dimer immobilized on several 2D carbon substrates. The dimer forms 4–6 bonds with the neighboring N or C atoms, having bond lengths of 1.91–2.21 Å for Fe–Fe and 1.87–2.00 Å for N–Fe (C–Fe) bonds, respectively, and the binding energies are –5.01 to –12.03 eV (Table 1). The Fe<sub>2</sub> dimer exhibits different buckling height in the out-of-plane direction (0.01–2.06 Å) and meanwhile induces some local vertical distortions on the carbon basal plane (0.09–0.35 Å). The dimer-substrate coupling strength depends on the size of the hole as well as the saturation degree of the edge atoms. For



**Figure 2. Electronic Structure-Activity Relationship**

(A) From left to right: molecular orbital levels or local density of states (DOS) of a free and a bended (with C–O–C angle of 130°) CO<sub>2</sub> molecule in vacuum, an adsorbed CO<sub>2</sub> molecule on Fe<sub>2</sub>@6N-V<sub>6</sub>, an individual 6N-V<sub>6</sub> monolayer, and a Fe<sub>2</sub> dimer. The insets display the HOMO and LUMO charge densities of CO<sub>2</sub>. The energy is relative to the vacuum. The dashed line shows the Fermi level, with the occupied states shadowed. The hybridization region between *d* orbital of Fe atoms and 2π\* state of CO<sub>2</sub> is shadowed in green. The dark blue and orange colors represent the *d* orbital of Fe atoms and *p* orbital of N atoms, respectively.

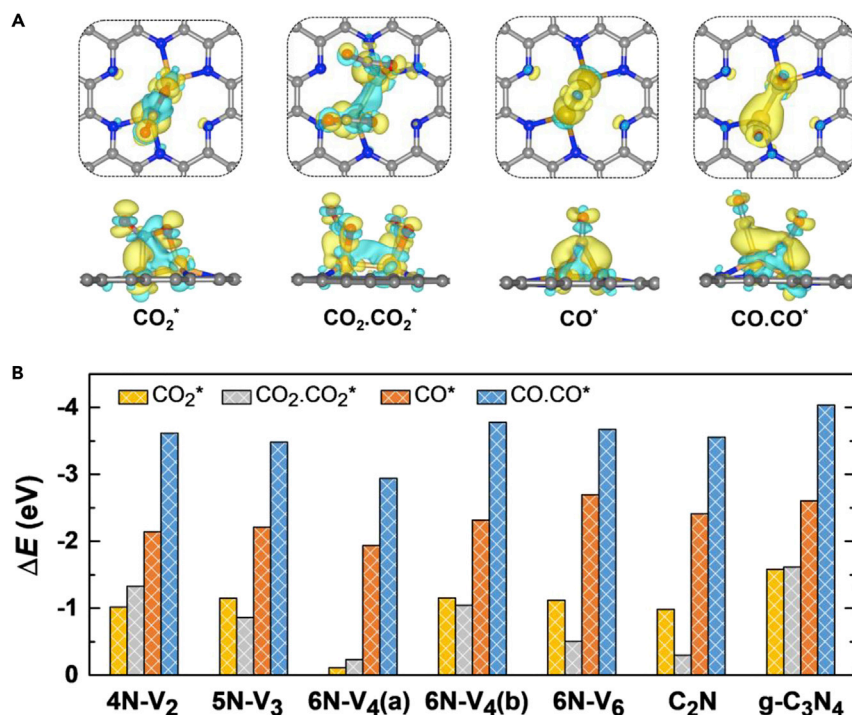
(B) The *d* band center (ε<sub>d</sub>) of various supported 3*d* transition metal dimers as a function of the adsorption energy of single CO<sub>2</sub> molecule. The blue/orange/gray symbols denote that two/one/none CO<sub>2</sub> molecule can be chemisorbed on the metal dimer. The dashed line is a linear fit of the data points.

(C) Charge transfer (CT) from the Fe<sub>2</sub> dimer to various nitrogenated carbon hole monolayer as a function of the adsorption energy of dual CO molecules. The dashed line is a linear fit of the data points. The insert shows the differential charge density of Fe<sub>2</sub>@6N-V<sub>6</sub>. The yellow and cyan colors represent the electron accumulation and depletion regions, respectively, with an isosurface value of 0.005 e/Å<sup>3</sup>.

instance, binding strength between Fe<sub>2</sub> and 4N-V<sub>2</sub>, 5N-V<sub>3</sub>, and 6N-V<sub>4</sub>(a) increases with both N content and hole size. The bonding interaction between Fe<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> or C<sub>2</sub>N is relatively weak, due to the electronic saturation of these two semiconducting carbon nitride monolayers (as manifested by their large band gaps). In sharp contrast, Fe<sub>2</sub> is strongly anchored on the nitrogen-free V<sub>6</sub> defect that has six unsaturated carbon atoms on the hole edge, thereby leading to the largest binding energy of −12.03 eV.

All the supported Fe<sub>2</sub> dimers are able to chemisorb two CO<sub>2</sub> molecules with total adsorption energies of −0.23 to −1.62 eV (compared with −0.11 to −1.58 eV for adsorption of single CO<sub>2</sub> molecule), as revealed by Figure 3B. Our nudged elastic band (NEB) calculations show that adsorption of the second CO<sub>2</sub> molecule involves kinetic barriers of 0.29–1.04 eV. Both CO<sub>2</sub> molecules are bended with O–C–O angle of 141.00–152.13° and elongated C–O bond lengths of 1.17–1.29 Å. The C atom in each CO<sub>2</sub> is bonded to the underlying Fe atom with Fe–C bond length of 1.93–2.12 Å. Furthermore, we investigated the interaction between the dispersed Fe<sub>2</sub> dimers and the CO molecule, which is an important reaction intermediate in the CO<sub>2</sub> reduction process. Our calculations indicate strong binding of CO on the anchored Fe<sub>2</sub> dimers, with adsorption energies of −2.94 to −4.04 eV (−1.94 to −2.70 eV) for two (one) CO molecules. Consequently, desorption of CO from dual metal centers would be rather difficult, which allows further protonation of CO and thus provides the opportunity for successive C–C coupling.

The distinct binding capability of various supported Fe<sub>2</sub> dimers with gas molecules can be related to the electronic coupling between Fe<sub>2</sub> and the carbon substrate. As displayed in Figure 2C, the amount of charge



**Figure 3. Structures and Energies of Molecular Adsorption**

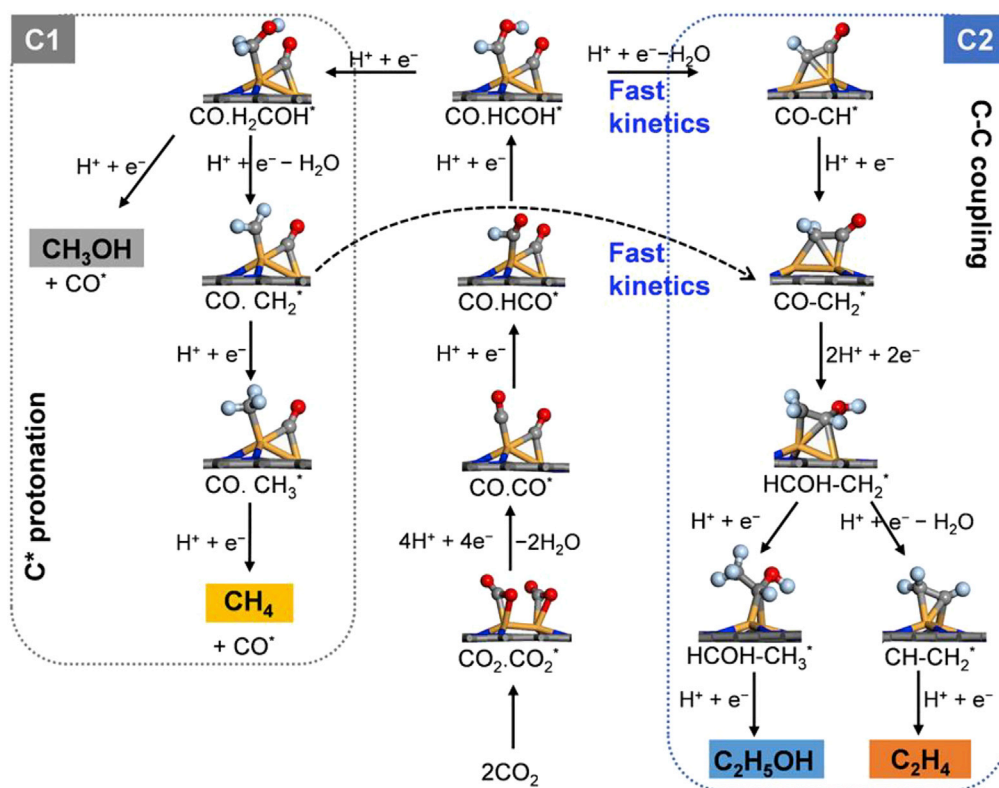
(A) From left to right: differential charge densities of single and dual CO<sub>2</sub> molecules, single and dual CO molecules adsorbed on Fe<sub>2</sub>@6N-V<sub>6</sub>. The yellow and cyan colors represent the electron accumulation and depletion regions, respectively, with an isosurface value of 0.005 e/Å<sup>3</sup>.

(B) Adsorption energies of single and dual CO<sub>2</sub> and CO molecules on the Fe<sub>2</sub> dimer anchored on various nitrogenated holey carbon monolayers. The C, N, O, and Fe atoms are shown in gray, blue, red, and orange colors, respectively.

transfer from Fe<sub>2</sub> to the substrate varies from 0.71 e to 0.97 e. Generally speaking, less electron transfer leads to higher activity of the Fe<sub>2</sub> dimer for CO<sub>2</sub> and CO chemisorption, which is consistent with the trend of binding energies between Fe<sub>2</sub> and the carbon templates discussed before (Table 1). It is the N content, the degree of electronic saturation of the hole edge, and the bond configuration of Fe<sub>2</sub> in the hole that jointly determine the coupling strength between the metal dimer and the carbon sheets. Therefore, the nitrogenated 2D holey carbon materials with diverse morphologies and controllable N contents can not only stabilize and disperse metal dimers but also dictate the electronic structures and activity of the anchored metal dimers. By choosing proper metal elements and substrates, it is possible to delicately mediate their coupling strength and charge transfer, endowing large degree of freedom to optimize the activity and selectivity of various supported metal dimers for CO<sub>2</sub> reduction.

Note that graphitic N species are inevitably present in the experimentally synthesized N-doped carbon materials (Lin et al., 2014). To clarify their effect on the activity of the dispersed Fe<sub>2</sub> dimer, we investigated the CO<sub>2</sub> adsorption on Fe<sub>2</sub>@6N-V<sub>6</sub> containing various numbers of graphitic N atoms at different distances from the 6N-V<sub>6</sub> hole (Figure S6). For all the considered systems, the CO<sub>2</sub> adsorption energies on the catalysts with and without substitutional N atoms on the graphene lattice differ by less than 0.16 eV, suggesting that existence of the graphitic N species has only minor impact on the catalytic properties of the Fe<sub>2</sub> dimer supported on pyridine holes of 2D carbon substrates.

Figure 4 shows the most efficient pathways for CO<sub>2</sub> reduction toward possible C<sub>1</sub> and C<sub>2</sub> products on the Fe<sub>2</sub> dimer immobilized on various nitrogenated carbon sheets, and the corresponding free-energy diagrams of various model systems calculated by the computational hydrogen electrode (CHE) model (Peterson et al., 2010) are given by Figures 5, S7, and S8. We used point (.) to represent the co-adsorption of two carbon intermediates on the catalyst and strigula (–) to indicate the coupling between two carbon intermediates. The maximum Gibbs free energy of formation ΔG among all the reaction steps defines the



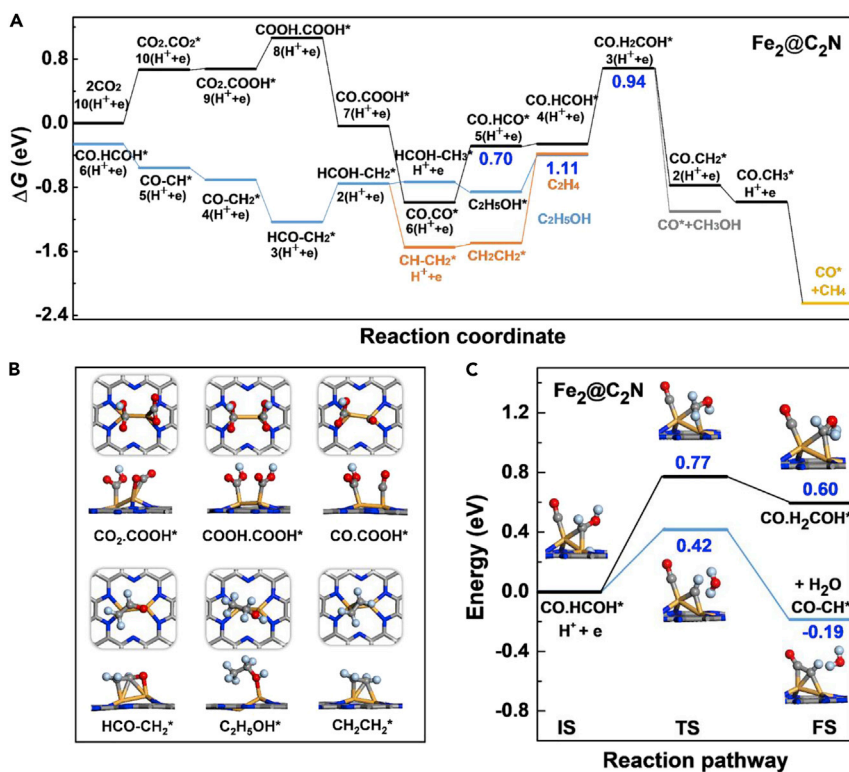
**Figure 4. The CO<sub>2</sub> reduction pathways to various C<sub>1</sub> and C<sub>2</sub> products on the supported Fe<sub>2</sub> dimer**  
The H, C, N, O, and Fe atoms are shown in light blue, gray, blue, red, and orange colors, respectively.

rate-determining step (RDS) and is thus denoted as  $\Delta G_{\text{RDS}}$ . Overall speaking, formation of C<sub>2</sub> products first requires the activation of dual CO<sub>2</sub> molecules on the catalyst. By going through the carboxyl (COOH\*) pathway, two CO\* intermediates can be generated; then protonation of CO\* leads to C<sub>1</sub> products such as methanol (CH<sub>3</sub>OH) and CH<sub>4</sub>. Alternatively, it paves a way to the coupling between two neighboring carbon intermediates, which is energetically favorable and kinetically easy, and finally yields C<sub>2</sub> products (C<sub>2</sub>H<sub>5</sub>OH and C<sub>2</sub>H<sub>4</sub>). A similar path for C–C coupling was also found for the other metal dimers anchored on the nitrogenated carbon sheet, as revealed by Figure S9 for Ni<sub>2</sub>@6N-V<sub>6</sub> as an example.

Specifically, formation of two CO\* species on most of the considered Fe<sub>2</sub> dimers is uphill in the free-energy profile, involving energy steps of 0.24–0.87 eV. Then, reduction of CO\* gives rise to HCO\* species, which is lower in energy by up to 1.13 eV than the other possible intermediates such as COH\* (Figure S10). The CO\* → HCO\* conversion is endothermic with  $\Delta G = 0.49$ –1.01 eV. Further protonation of HCO\* leads to HCOH\* and then produces a CH\* species by release of a H<sub>2</sub>O molecule. The C–C coupling reaction is most likely to occur between a CH\* (or CH<sub>2</sub>\*) species and the neighboring CO\*. Our NEB calculations suggest that the CO–CH\* coupling is exothermic and barrierless on all the considered Fe<sub>2</sub> dimers, except for Fe<sub>2</sub>@C<sub>2</sub>N and Fe<sub>2</sub>@C<sub>3</sub>N<sub>4</sub> that involve a small kinetic barrier of about 0.22 eV (Table S1). According to previous theoretical studies (Goodpaster et al., 2016; Jiang et al., 2018), Cu(211) and (100), as the typical active surfaces for CO<sub>2</sub> reduction, favor dimerization of CO\* or CO–HCO\* coupling involving  $\Delta G = -0.17$ –0.48 eV. For the present Fe<sub>2</sub> dimers on nitrogenated carbon sheets, however, CO–CO\* or CO–HCO\* coupling has higher  $\Delta G$  than the values of CO–CH\* by 0.84–2.42 eV and thus is unlikely to occur.

Following the C–C coupling, successive reduction of CO–CH\* leads to CO–CH<sub>2</sub>\*, HCO–CH<sub>2</sub>\*, HCOH–CH<sub>2</sub>\*, HCOH–CH<sub>3</sub>\*, and finally yields C<sub>2</sub>H<sub>5</sub>OH. Alternatively, reduction of HCOH–CH<sub>2</sub>\* can give rise to CH–CH<sub>2</sub>\* with release of a H<sub>2</sub>O molecule, and further protonation of CH–CH<sub>2</sub>\* eventually produces C<sub>2</sub>H<sub>4</sub>. These elementary reactions involve relatively small steps of 0.15–0.73 eV in free-energy profile and thus would take place readily from the thermodynamic point of view. At the last step, desorption of





**Figure 5. CO<sub>2</sub> Reduction Pathway**

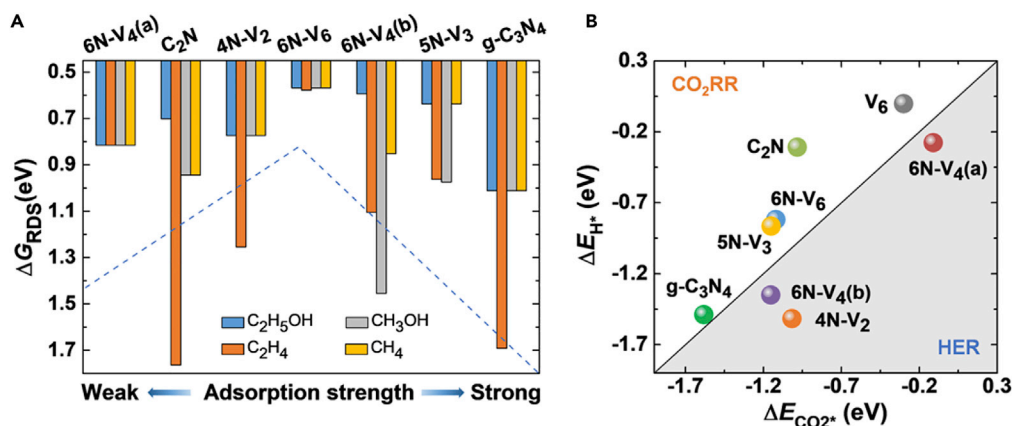
(A and B) (A) Free-energy diagram of CO<sub>2</sub> reduction to various C<sub>1</sub> and C<sub>2</sub> products (indicated by different colors) on Fe<sub>2</sub>@C<sub>2</sub>N. The blue numbers, from left to right, give the Gibbs free energy of formation for the rate determining step of C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>H<sub>4</sub>, and CH<sub>3</sub>OH/CH<sub>4</sub>. The local structures of selected reaction intermediates are presented in (B). The H, C, N, O, and Fe atoms are shown in light blue, gray, blue, red, and orange colors, respectively.

(C) Competing reactions of CO.HCOH\* to form C<sub>1</sub> and C<sub>2</sub> intermediates on Fe<sub>2</sub>@C<sub>2</sub>N. The insets display the structures of initial state (IS), transition state (TS), and final state (FS). The blue numbers give the kinetic barriers (middle) and heat of reaction (right).

C<sub>2</sub>H<sub>5</sub>OH\* and CH<sub>2</sub>CH<sub>2</sub>\* is endothermic by 0.11–0.59 eV and 0.23–1.69 eV, respectively. For most of the considered Fe<sub>2</sub> dimers, the rate-determining step for C<sub>2</sub>H<sub>5</sub>OH production is the CO\* → HCO\* conversion. The release of C<sub>2</sub>H<sub>4</sub> mainly suffers from the strong binding of CH<sub>2</sub>CH<sub>2</sub>\* on the catalyst, which can be overcome by the reaction heat of the corresponding reduction step (0.61–2.07 eV) (Chen et al., 2019b), as well as by adopting some strategies such as the pulse electrolysis mode to accelerate desorption of the final products (Yano et al., 2007; Qiao et al., 2014).

On the other hand, formation of C<sub>1</sub> products is also possible on the dispersed Fe<sub>2</sub> dimers. As discussed earlier, HCOH\* can be reduced to CH\*, followed by the CO–CH\* coupling. Alternatively, HCOH\* may be protonated to H<sub>2</sub>COH\*. Then, reduction of H<sub>2</sub>COH\* yields CH<sub>3</sub>OH or produces CH<sub>2</sub>\* with release of a H<sub>2</sub>O molecule followed by the generation of CH<sub>3</sub>\* and CH<sub>4</sub>. For Fe<sub>2</sub>@4N-V<sub>2</sub>, Fe<sub>2</sub>@6N-V<sub>6</sub>, and Fe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub>, the CO\* → HCO\* conversion is the rate determining step for both C<sub>1</sub> products. For Fe<sub>2</sub>@6N-V<sub>4</sub>(b) and Fe<sub>2</sub>@5N-V<sub>3</sub>, formation of CH<sub>3</sub>OH from H<sub>2</sub>COH\* protonation requires ΔG<sub>RDS</sub> = 1.45 and 0.98 eV, respectively. In particular, Fe<sub>2</sub>@C<sub>2</sub>N encounters ΔG<sub>RDS</sub> = 0.94 eV and a kinetic barrier of 0.77 eV during the reaction of HCOH\* → H<sub>2</sub>COH\* for both C<sub>1</sub> products, whereas the competing step of CO–HCOH\* → CO–CH\* + H<sub>2</sub>O has much reduced ΔG = –0.30 eV and a lower kinetic barrier of 0.42 eV (Figures 5A and 5C). This would lead to high selectivity for C<sub>2</sub> products on Fe<sub>2</sub>@C<sub>2</sub>N.

Figure 6A plots ΔG<sub>RDS</sub> values for various C<sub>1</sub> and C<sub>2</sub> products from CO<sub>2</sub> reduction on the anchored Fe<sub>2</sub> dimers. Among the four products, C<sub>2</sub>H<sub>5</sub>OH exhibits the lowest ΔG<sub>RDS</sub> = 0.57–1.01 eV, and the highest activity is achieved by Fe<sub>2</sub>@6N-V<sub>6</sub> owing to its moderate adsorption strength with the reaction intermediates (indicated by the dashed blue line in Figure 6A). Formation of C<sub>2</sub>H<sub>4</sub> is less favorable with ΔG<sub>RDS</sub> = 0.58–1.76 eV



**Figure 6. Catalytic Performance for CO<sub>2</sub> Reduction**

(A) Gibbs free energy of formation for the rate determining step ( $\Delta G_{RDS}$ ) for various C<sub>1</sub> and C<sub>2</sub> products from CO<sub>2</sub> reduction, and (B) competition between adsorption of a CO<sub>2</sub> molecule and an H<sup>+</sup> species on the Fe<sub>2</sub> dimer anchored on various nitrogenated holey carbon monolayers.

due to the strong binding of CH<sub>2</sub>CH<sub>2</sub>\* on the Fe<sub>2</sub> dimers. Fe<sub>2</sub>@6N-V<sub>4</sub>(a), Fe<sub>2</sub>@4N-V<sub>2</sub>, Fe<sub>2</sub>@6N-V<sub>6</sub>, and Fe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> exhibit similar selectivity for C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>OH, and CH<sub>4</sub>, whereas Fe<sub>2</sub>@5N-V<sub>3</sub> favors both C<sub>2</sub>H<sub>5</sub>OH and CH<sub>4</sub> products. Remarkable selectivity for C<sub>2</sub>H<sub>5</sub>OH is obtained for Fe<sub>2</sub>@C<sub>2</sub>N and Fe<sub>2</sub>@6N-V<sub>4</sub>(b) with  $\Delta G_{RDS} = 0.70$  and  $0.59$  eV, respectively, notably lower than  $\Delta G_{RDS}$  values for the other products (above  $0.94$  and  $0.85$  eV, respectively). Hence, these supported Fe<sub>2</sub> dimers have competitive activity but distinct selectivity with regard to the conventional Cu-based catalysts. It is known that Cu crystals mainly produce CO under low electrode potentials, whereas CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> are the main products at sufficiently high electrode potentials (about  $-1.0$  V versus RHE in experiment) (Dai et al., 2017; Mistry et al., 2016). Previous calculations revealed that Cu(211) surface encounters  $\Delta G_{RDS} = 0.74$  eV for CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, whereas formation of CO is much more favorable with  $\Delta G_{RDS} = 0.41$  eV due to the relatively weak adsorption of CO on the Cu surface (adsorption energy  $\Delta E = -1.01$  eV) (Peterson et al., 2010). Differently, release of CO is prohibited on the present Fe<sub>2</sub> dimers that have strong adsorption energy of  $\Delta E = -2.94$  to  $-4.04$  eV with CO molecule.

As the electroreduction of CO<sub>2</sub> usually take place in the neutral aqueous condition, we further explored the solvent effect on the catalytic behavior of supported Fe<sub>2</sub> dimer. As a representative, we considered an explicit solvent model of Fe<sub>2</sub>@C<sub>2</sub>N. Our calculations show that hydrogen bonds are formed between water molecules and some adsorbed reaction intermediates (such as CO<sub>2</sub>, CO<sub>2</sub>\* and CO-CH\*), which slightly stabilize those species on the catalyst in aqueous environment, consistent with the previous theoretical report (Zhao and Liu, 2020). The variations of CO<sub>2</sub> adsorption energy and Gibbs free energy of formation for elementary steps are below  $0.29$  eV, and the kinetic barriers of rate determining steps for various products increase by less than  $0.35$  eV, with regard to the model in vacuum (see Table 3 and Figure S11 for details). The predicted selectivity is consistent between the model in vacuum and in water. Therefore, free-energy calculations on electrocatalysis of CO<sub>2</sub> reduction using a model of catalyst in vacuum can generally predict reliable results on the trend of activity and product selectivity (De Luna et al., 2018; Zhuang et al., 2018; Li et al., 2018). Besides solvent effect, the surface charge on catalysts during the electrochemical reaction may modify the electronic states and impact the catalytic properties according to a previous theoretical report (Kim et al., 2018). Future studies with sophisticated model theory are necessary to comprehensively evaluate the catalytic performance of the proposed transition metal dimers on the nitrogenated carbon substrates.

The unique geometry and favorable adsorption properties of the Fe<sub>2</sub> dimers immobilized on carbon substrates bring about inimitable advantages for their catalytic behavior. First, CO, as an inevitable and even dominant product of CO<sub>2</sub> reduction on many metal catalysts, severely limits the formation of higher-energy-density products (Zhu et al., 2014; Sarfraz et al., 2016; Peng et al., 2018), but it would be largely suppressed on the anchored Fe<sub>2</sub> dimers. Second, the adjacent dual metal centers and their strong binding with CO pave an efficient pathway for C-C coupling reaction; in contrast, C-C coupling only occurs on metal

	Step	CO <sub>2</sub> → CO <sub>2</sub> <sup>*</sup>	CO <sub>2</sub> <sup>*</sup> + CO <sub>2</sub> → CO <sub>2</sub> .CO <sub>2</sub> <sup>*</sup>	CO.CH <sup>*</sup> → CO-CH <sup>*</sup>	CO.HCOH <sup>*</sup> + H <sup>+</sup> + e <sup>-</sup> →	
					CO.H <sub>2</sub> COH <sup>*</sup>	CO-CH <sup>*</sup> + H <sub>2</sub> O
Vacuum	ΔH	-0.64	0.68	0.11	0.60	-0.19
	E <sub>a</sub>	0	0.70	0.23	0.77	0.42
Aqueous	ΔH	-0.65	0.51	-0.03	0.31	-0.18
	E <sub>a</sub>	0	0.74	0.58	0.93	0.66

**Table 3. Key Reaction Steps in Vacuum and Aqueous Condition**

The reaction energy (ΔH) and kinetic barriers (E<sub>a</sub>) for activating first and second CO<sub>2</sub> molecule, CO-CH<sup>\*</sup> coupling, and protonation of CO.HCOH<sup>\*</sup> to CO.H<sub>2</sub>.COH<sup>\*</sup> species or CO-CH<sup>\*</sup> with H<sub>2</sub>O molecule in vacuum and in the aqueous condition, respectively, given in the unit of eV.

surfaces with homogeneously distributed reaction sites when the coverage of CO is sufficiently high (Moraes-Guio et al., 2018; Huang et al., 2017). Third, the difficult desorption of C<sub>2</sub>H<sub>4</sub> from the Fe<sub>2</sub> dimers may result in superior selectivity for C<sub>2</sub>H<sub>5</sub>OH, which is a clean liquid fuel with high heating value. For most of the Cu based catalysts, however, the yield of C<sub>2</sub>H<sub>5</sub>OH is quite low compared with C<sub>2</sub>H<sub>4</sub> (Liang et al., 2018).

At last, we assess the activity of these supported Fe<sub>2</sub> dimers for HER, which is a competing reaction against CO<sub>2</sub> reduction and highly affects the efficiency of CO<sub>2</sub> conversion (Zhu et al., 2016; Cui et al., 2017). Figure 6B plots the competition between adsorption of H<sup>\*</sup> species and CO<sub>2</sub> molecule on the Fe<sub>2</sub> dimers. The H<sup>\*</sup> adsorption energy ranges from -1.52 eV to -0.28 eV. For Fe<sub>2</sub>@5N-V<sub>3</sub>, Fe<sub>2</sub>@6N-V<sub>6</sub>, Fe<sub>2</sub>@C<sub>2</sub>N, and Fe<sub>2</sub>@C<sub>3</sub>N<sub>4</sub>, the adsorption strength of H<sup>\*</sup> species is notably weaker than that of CO<sub>2</sub> molecule by 0.09–0.67 eV, implying that CO<sub>2</sub> reduction would prevail over HER on these catalysts with either high activity or superior selectivity. For Fe<sub>2</sub>@4N-V<sub>2</sub>, Fe<sub>2</sub>@6N-V<sub>4</sub>(a), and Fe<sub>2</sub>@6N-V<sub>4</sub>(b), the H<sup>\*</sup> adsorption strength is stronger than that of CO<sub>2</sub>, which may suppress the CO<sub>2</sub> reduction. Combining the information in Figures 6A and 6B, we conclude that four of our considered systems are eligible for catalysis of CO<sub>2</sub> reduction with high activity for C-C coupling toward C<sub>2</sub> products. Among them, Fe<sub>2</sub>@C<sub>2</sub>N has remarkable selectivity for ethanol; Fe<sub>2</sub>@5N-V<sub>3</sub> favors the formation of both ethanol and methane; Fe<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub> and 6N-V<sub>6</sub> have lower selectivity and may generate both C<sub>1</sub> and C<sub>2</sub> products. Therefore, dimeric transition metal clusters immobilized on the nitrogenated holey carbon substrates form a category of efficient electrocatalysts for reduction of CO<sub>2</sub> to high-value hydrocarbons and alcohols, with desired selectivity achievable by choosing proper substrate.

## Conclusion

In summary, we exploited dispersed 3d transition metal dimers for CO<sub>2</sub> reduction to selectively produce liquid fuels. Comprehensive first-principles calculations show that nitrogenated holey carbon materials not only serve as templates to stabilize small metal clusters but also dictate their electronic structures. Specifically, controlling the metal-substrate coupling strength allows effective modulation of both activity and product selectivity. As a consequence, the spatially confined dual reaction centers within the carbon matrix exhibit the following advantageous catalytic behavior: (1) simultaneous fixation of two CO<sub>2</sub> molecules, (2) prohibition of CO desorption, and (3) exclusive pathway for C-C coupling with high activity. The selectivity is tunable by choosing proper substrate materials. In particular, a Fe<sub>2</sub> dimer embedded in the C<sub>2</sub>N monolayer exhibits remarkable selectivity for C<sub>2</sub>H<sub>5</sub>OH against the other C<sub>1</sub> and C<sub>2</sub> products as well as HER. These theoretical findings provide vital knowledge of the design rules of subnano metal clusters for converting greenhouse gas to high-energy fuels and high-value chemicals and meanwhile call for more experimental and theoretical efforts to advance the technologies for precise synthesis of atomically dispersed catalysts with well-controlled composition and structures.

## Limitations of the Study

This study systematically exploited 3d transition metal dimers anchored on nitrogenated holey carbon monolayers for selective reduction of CO<sub>2</sub> to liquid fuels and screened suitable metal elements and carbon templates with high selectivity for ethanol. However, experimental realization of such superior subnano catalysts relies on the preparation of metal clusters with specific size supported on some given substrates, which may be challenging and requires the development of advanced synthesis methods.

## METHODS

All methods can be found in the accompanying [Transparent Methods](#) supplemental file.

## SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.isci.2020.101051>.

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## AUTHOR CONTRIBUTIONS

S. Zhou conceived the idea; Y. Zhao carried out the calculation; S. Zhou and J. Zhao supervise the research. All authors wrote the paper.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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**Supplemental Information**

**Selective C–C Coupling by Spatially  
Confined Dimeric Metal Centers**

**Yanyan Zhao, Si Zhou, and Jijun Zhao**

# Supplemental Information

## Transparent Methods

### Computational Methods

Our calculations were performed using the Vienna *ab initio* simulation package (VASP) based on spin-polarized density functional theory (DFT) (Kresse and Furthmüller, 1996), with the projector augmented wave (PAW) method for ion-electron interaction (Kresse and Joubert, 1999), and the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) for the exchange and correction functional (Perdew et al., 1996). We used the planewave basis set with the energy cutoff of 500 eV. The Grimme's semiempirical DFT-D3 scheme of dispersion correction was adopted for a reliable description of the interactions between catalysts and reaction species (Grimme, 2010). To incorporate a metal dimer, we considered defective graphene sheets comprising holes, whose edge atoms are partially substituted by N atoms (shown in Figure 1). The supercell consists of  $7 \times 7$  graphene unit cells with a lattice constant of 17.22 Å for the lateral directions, and a vacuum space of 20 Å for the perpendicular direction. We also considered two kinds of monolayer carbon nitrides with stoichiometry of  $C_2N$  and  $g-C_3N_4$ , using  $2 \times 2$  unit cells with supercell dimensions of 16.64 Å and 14.26 Å, respectively. One metal dimer was placed in the hole of each model supercell structure. The Brillouin zones of all the supercells were sampled by the  $2 \times 2 \times 1$  Monkhorst-Pack  $k$  grids. The geometry optimization was carried out for both ionic and electronic degrees of freedom, with the convergence criteria of  $10^{-4}$  eV and 0.02 eV/Å for energy and force, respectively. On-site charges were evaluated by the Mulliken population analysis (Mulliken, 1955) implemented in the CASTEP (Clark et al., 2005), using the planewave basis with energy cutoff of 1000 eV, the norm-conserving pseudopotentials, and the PBE functional. The climbing image nudged elastic band method was employed to search for the transition states of elementary steps and calculate the kinetic barriers (Henkelman et al., 2000).

The thermodynamic stability of a defective carbon substrate was characterized by



the formation energy per unit length defined as

$$E_{\text{form}} = (E_{\text{NxCy}} - x/2 E_{\text{N}_2} - yE_{\text{C}}) / L \quad (\text{S1})$$

where  $E_{\text{NxCy}}$  is the energy of the carbon substrate comprising  $x$  numbers of N atoms and  $y$  numbers of C atoms per supercell;  $E_{\text{N}_2}$  and  $E_{\text{C}}$  are the energies of a  $\text{N}_2$  gas molecule and a C atom in perfect graphene, respectively;  $L$  is the total edge length of a hole in the carbon substrate. The binding strength between the metal dimer and the carbon substrate was evaluated as

$$E_{\text{b}} = E_{\text{M}_2@\text{NxCy}} - E_{\text{M}_2} - E_{\text{NxCy}} \quad (\text{S2})$$

where  $E_{\text{M}_2}$  and  $E_{\text{M}_2@\text{NxCy}}$  are the energies of the metal dimer ( $\text{M}_2$ ) in vacuum and on the carbon substrate, respectively. The thermal stability of these carbon substrate anchored metal dimers was further assessed by *ab initio* molecular dynamics (AIMD) simulations.

To characterize the interaction between reaction molecules ( $\text{CO}_2$  and  $\text{CO}$ ) and catalyst, we defined the adsorption energy as

$$\Delta E = E_{\text{total}} - E_{\text{M}_2@\text{NxCy}} - E_{\text{mol}} \quad (\text{S3})$$

where  $E_{\text{total}}$  is the energy of the molecule adsorbed on the catalyst;  $E_{\text{mol}}$  is the energy of the molecule in gas phase. The Gibbs free energy of formation ( $\Delta G$ ) for each reaction step was calculated by including the zero-point energy and entropy (Table S3 and S4). The maximum  $\Delta G$  among all the reaction steps defines the rate-determine step (RDS) and is thus denoted as  $\Delta G_{\text{RDS}}$ . Then, the free energy diagrams of  $\text{CO}_2$  reduction were obtained based on the computational hydrogen electrode model (Peterson et al., 2010).

### **Random simulation of N-doped carbon monolayer**

To obtain the lattice structures of various N-doped carbon monolayers, we used a home-made program to generate random structures of graphene lattice with different N doping concentrations. The essential idea of the program is to produce a graphene lattice of a given size and add certain number of N dopants into it. Specifically, a lattice C atom is randomly selected to be substituted by N atom or deleted and replacing its adjacent sites with N atoms until the total number of N atoms reaches the target N content. There are three types of N atom: graphitic N, pyridinic N, and pyrrolic N. Experimentally, pyridinic N dopants in graphene are the major doping species at high

N contents (Sheng et al., 2011; Sarau et al., 2017). Thus, we mainly considered N contents from 3.6% to 15.6% (with pyridinic N and graphitic N of 3.3% ~ 15.3% and 0.3%, respectively). For each N content, we created several random lattice structures of N-doped graphene, as shown in Figure S1. In generally, the types and size of the holes increase as the nitrogen concentration increases. Particularly, 4N-V<sub>2</sub>, 5N-V<sub>3</sub> and 6N-V<sub>4</sub> exist as the N content lower than 7.5%, and 6N-V<sub>6</sub> would arise as the N doping content reaches 10%.

### **Dynamic movie of the MD simulation on CO<sub>2</sub> adsorption process**

As a respective, we have performed calculations to explore the dynamic process of CO<sub>2</sub> adsorption on Fe<sub>2</sub>@6N-V<sub>6</sub> at 100 K (Supplemental Video S1) and 300 K (Supplemental Video S2) by AIMD simulations, respectively. The results show that the molecule can quickly chemisorb on the dimeric metal centers within a simulation time of 1 ps. These two movies are provided as independent files for download. Related to Figure 4.

**Table S1.** Adsorption energies of single and dual CO molecules ( $\Delta E_{\text{CO}^*}$ ,  $\Delta E_{\text{CO.CO}^*}$ ), kinetic barriers of CO–CH and CO–CH<sub>2</sub> coupling, and the Gibbs free energy of formation for the rate-determine step ( $\Delta G_{\text{RDS}}$ ) of CH<sub>3</sub>OH, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH for the Fe<sub>2</sub> dimer anchored on various carbon substrates. Related to Figure 4.

Substrate	$\Delta E_{\text{CO}^*}$ (eV)	$\Delta E_{\text{CO.CO}^*}$ (eV)	Kinetic barrier (eV)		$\Delta G_{\text{RDS}}$ (eV)			
			CO–CH	CO–CH <sub>2</sub>	CH <sub>3</sub> OH	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>5</sub> OH
4N-V <sub>2</sub>	-2.14	-3.62	0	0.53	0.77	0.77	1.25	0.77
5N-V <sub>3</sub>	-2.21	-3.48	0	0.49	0.98	0.64	0.96	0.64
6N-V <sub>4</sub> (a)	-1.94	-2.94	0	0.62	0.82	0.82	0.82	0.82
6N-V <sub>4</sub> (b)	-2.31	-3.78	0	0.48	1.45	0.85	1.11	0.59
6N-V <sub>6</sub>	-2.70	-3.68	0	0	0.57	0.57	0.58	0.57
C <sub>2</sub> N	-2.41	-3.56	0.23	0.38	0.94	0.94	1.76	0.70
g-C <sub>3</sub> N <sub>4</sub>	-2.61	-4.04	0.22	0.19	1.01	1.01	1.69	1.01

**Table S2.** Adsorption energies of second CO<sub>2</sub> molecule ( $\Delta E'_{\text{CO}_2^*} = E_{\text{chem}} - E_{\text{phys}}$ , i.e. the difference of energies between chemisorption and physisorption of second CO<sub>2</sub> molecule) and kinetic barriers for activating the second CO<sub>2</sub> molecule for the Fe<sub>2</sub> dimer anchored on various carbon substrates, given in the unit of eV. Related to Figure 3.

Substrate	4N-V <sub>2</sub>	5N-V <sub>3</sub>	6N-V <sub>4</sub> (a)	6N-V <sub>4</sub> (b)	6N-V <sub>6</sub>	C <sub>2</sub> N	g-C <sub>3</sub> N <sub>4</sub>
$\Delta E'_{\text{CO}_2^*}$	0.12	0.52	0.44	0.20	0.42	0.68	0.22
Kinetic barrier	0.29	0.54	0.83	0.87	0.67	0.70	1.04

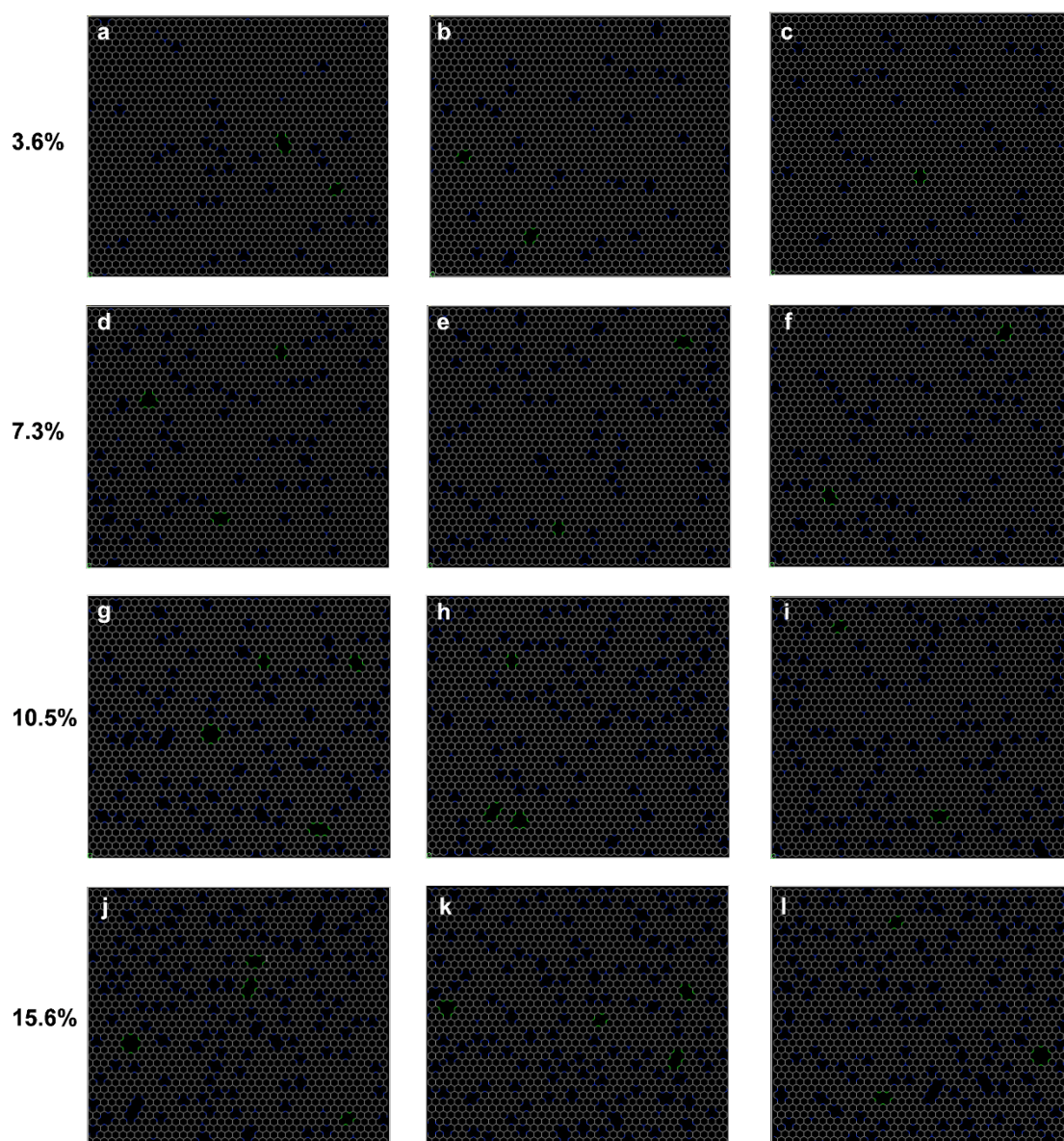
**Table S3.** Zero-point energy (ZPE) and entropic correction ( $TS$ ) at  $T = 298$  K for the molecules and intermediate species involved in  $\text{CO}_2$  reduction on  $\text{Fe}_2@6\text{N-V}_6$ . The ZPE and  $TS$  values were obtained from the NIST-JANAF thermodynamics table for gaseous molecules (Chase, 1998), and by calculating the vibrational frequencies for reaction intermediates (Reuter and Scheffler, 2001). The Gibbs free energy of formation for each elementary step was computed as  $\Delta G = \Delta E_{\text{DFT}} + \Delta \text{ZPE} - T\Delta S$  ( $\Delta E_{\text{DFT}}$  is the DFT energy difference between the initial and final states). Our test calculations show that the ( $\text{ZPE} - TS$ ) value of a certain intermediate is very similar for the  $\text{Fe}_2$  dimer supported by different carbon substrates, and thus the values of  $\text{Fe}_2@6\text{N-V}_6$  were used throughout this work. Related to Figure 5.

Species	ZPE (eV)	$TS$ (eV)	$\text{ZPE} - TS$ (eV)	Species	ZPE (eV)	$TS$ (eV)	$\text{ZPE} - TS$ (eV)
$\text{H}_2$	0.29	0.41	-0.12	$\text{CO}\cdot\text{COH}^*$	0.69	0.26	0.43
$\text{H}_2\text{O}$	0.60	0.59	0.01	$\text{CO}\cdot\text{HCOH}^*$	0.99	0.23	0.76
$\text{CO}$	0.14	0.62	-0.48	$\text{CO}-\text{CH}^*$	0.57	0.15	0.42
$\text{CO}_2$	0.31	0.67	-0.35	$\text{COH}-\text{CH}^*$	0.91	0.15	0.76
$\text{CH}_3\text{OH}$	1.39	0.79	0.60	$\text{HCO}-\text{CH}^*$	0.86	0.09	0.79
$\text{CH}_4$	1.20	0.58	0.62	$\text{CO}-\text{CH}_2^*$	0.88	0.17	0.71
$\text{C}_2\text{H}_4$	1.36	0.71	0.65	$\text{HCO}-\text{CH}_2^*$	1.17	0.10	1.07
$\text{C}_2\text{H}_5\text{OH}$	2.11	0.82	1.09	$\text{COH}-\text{CH}_2^*$	1.22	0.15	1.06
$\text{CO}_2^*$	0.32	0.13	0.19	$\text{HCOH}-\text{CH}_2^*$	1.50	0.21	1.29
$\text{COOH}^*$	0.65	0.19	0.46	$\text{CH}-\text{CH}_2^*$	1.07	0.10	0.97
$\text{CO}^*$	0.20	0.14	0.06	$\text{CH}_2\text{CH}_2^*$	1.39	0.16	1.23
$\text{CO}_2\cdot\text{CO}_2^*$	0.59	0.29	0.30	$\text{HCOH}-\text{CH}_3^*$	1.81	0.22	1.59
$\text{CO}_2\cdot\text{COOH}^*$	0.90	0.37	0.53	$\text{C}_2\text{H}_5\text{OH}^*$	2.16	0.24	1.92
$\text{COOH}\cdot\text{COOH}^*$	1.23	0.30	0.93	$\text{CO}\cdot\text{H}_2\text{COH}^*$	1.28	0.29	0.99
$\text{CO}\cdot\text{COOH}^*$	0.79	0.23	0.56	$\text{CO}\cdot\text{CH}_3\text{OH}^*$	1.60	0.31	1.29
$\text{CO}\cdot\text{CO}^*$	0.39	0.11	0.28	$\text{CO}\cdot\text{CH}_2^*$	0.82	0.17	0.65
$\text{CO}\cdot\text{HCO}^*$	0.69	0.19	0.50	$\text{CO}\cdot\text{CH}_3^*$	1.25	0.26	0.99

**Table S4.** Gibbs free energy of formation ( $\Delta G$ ) for each elementary step of CO<sub>2</sub> reduction on the Fe<sub>2</sub> dimer anchored on various carbon substrates. Related to Figure 5.

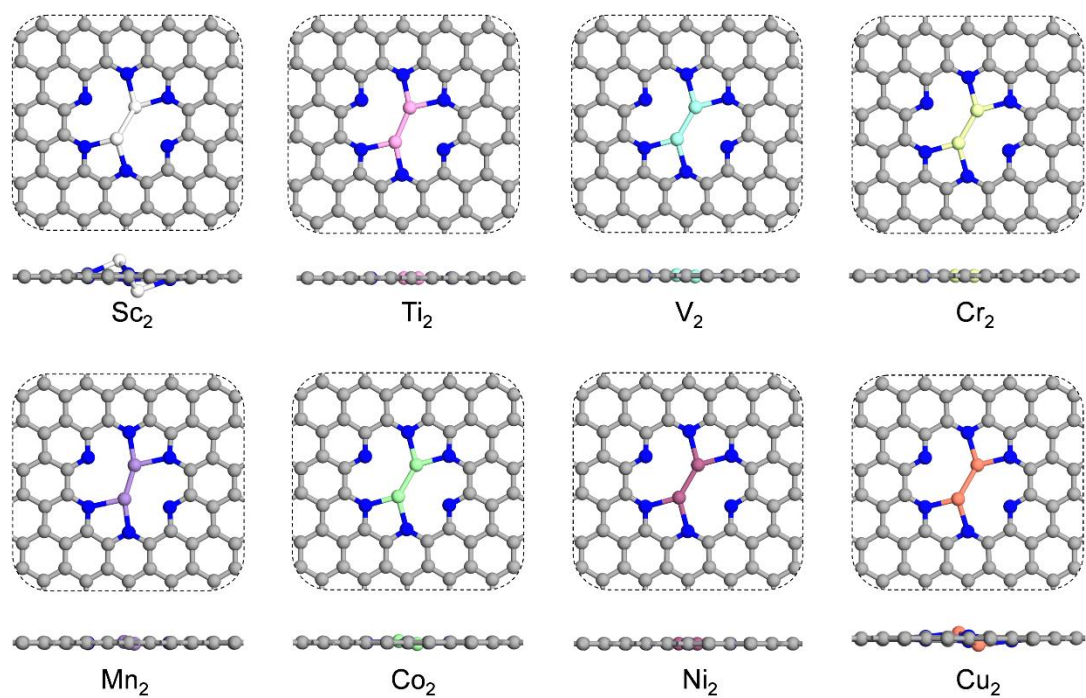
Reaction	$\Delta G$ (eV)						
	4N-V <sub>2</sub>	5N-V <sub>3</sub>	6N-V <sub>4</sub> (a)	6N-V <sub>4</sub> (b)	6N-V <sub>6</sub>	C <sub>2</sub> N	g-C <sub>3</sub> N <sub>4</sub>
2CO <sub>2</sub> → CO <sub>2</sub> .CO <sub>2</sub> *	-0.31	0.09	0.74	-0.18	0.48	0.67	-0.64
CO <sub>2</sub> .CO <sub>2</sub> * → CO <sub>2</sub> .COOH*	0.14	0.24	0.57	0.22	0.38	0.01	0.27
CO <sub>2</sub> .COOH* → COOH.COOH*	0.66	0.23	0.37	0.51	-0.80	0.39	0.87
COOH.COOH* → COOH.CO* + H <sub>2</sub> O	0.07	-0.64	-0.97	-0.80	-0.39	-1.10	-1.22
COOH.CO* → CO.CO* + H <sub>2</sub> O	-1.71	-0.90	-1.09	-0.96	-0.79	-0.95	-0.88
CO.CO* → CO.HCO*	0.77	0.49	0.70	0.53	0.57	0.70	1.01
CO.CO* → CO.COH*	1.34	1.10	1.83	1.13	0.88	0.76	1.03
HCO.CO* → CO.HCOH*	0.57	0.64	0.82	0.38	0.31	0.03	0.32
CO.HCOH* → CO-CH* + H <sub>2</sub> O	-0.27	-0.49	-1.17	-0.27	-0.28	-0.30	-0.81
CO.HCOH* → CO.H <sub>2</sub> COH*	-1.10	-0.73	-0.95	-0.72	-0.27	0.94	0.31
CO-CH* → CO-CH <sub>2</sub> *	-1.08	-0.32	0.03	-0.49	-0.49	-0.15	-0.04
CO.H <sub>2</sub> COH* → CO.CH <sub>2</sub> * + H <sub>2</sub> O	0.44	0.41	-0.50	0.85	0.36	-1.46	-1.22
CO.H <sub>2</sub> COH* → CO. CH <sub>3</sub> OH*	-0.35	-0.24	-0.59	-0.07	-0.79	-1.89	-1.39
CO-CH <sub>2</sub> * → HCO-CH <sub>2</sub> *	-0.13	0.35	-0.13	-0.66	0.13	-0.52	-0.78

CO-CH <sub>2</sub> * → COH-CH <sub>2</sub> *	0.28	0.14	0.32	0.28	0.28	0.46	0.10
CO. CH <sub>2</sub> * → CO. CH <sub>3</sub> *	-0.94	-0.97	0.56	-1.19	-1.06	-0.21	-0.33
HCO-CH <sub>2</sub> * → HCOH-CH <sub>2</sub> *	0.36	-0.18	0.15	1.06	-0.02	0.48	0.82
COH-CH <sub>2</sub> * → HCOH-CH <sub>2</sub> *	-0.06	0.04	-0.30	0.12	-0.26	-0.50	-0.06
CO. CH <sub>3</sub> * → CO. CH <sub>4</sub> *	-0.53	0.39	-2.04	0.65	-1.33	-1.27	-0.90
HCOH-CH <sub>2</sub> * → CH-CH <sub>2</sub> *+ H <sub>2</sub> O	-0.74	-0.59	-0.23	0.22	-0.21	-0.79	-0.46
HCOH-CH <sub>2</sub> * → HCOH-CH <sub>3</sub> *	0.03	0.18	-0.22	-0.03	0.01	0.02	-0.03
CH-CH <sub>2</sub> * → CH <sub>2</sub> CH <sub>2</sub> *	0.04	-0.26	-0.41	-1.04	0.14	0.05	-0.54
HCOH-CH <sub>2</sub> * → C <sub>2</sub> H <sub>5</sub> OH*	0.41	-0.55	-0.16	-0.30	0.73	-0.12	0.36
CH <sub>2</sub> CH <sub>2</sub> * → C <sub>2</sub> H <sub>4</sub>	1.25	0.96	0.23	1.11	0.58	1.11	1.69
C <sub>2</sub> H <sub>5</sub> OH* → C <sub>2</sub> H <sub>5</sub> OH	0.11	0.46	-0.04	0.59	-0.26	0.46	0.34

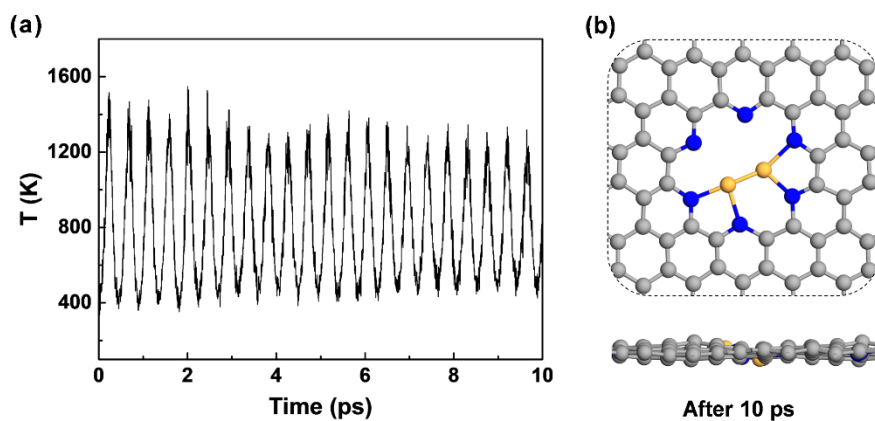


**Figure S1.** The N-doped carbon monolayer structures with various N content of (a, b, c) 3.6%, (d, e, f) 7.3%, (g, h, i) 10.5% and (j, k, l) 15.6%, respectively, created by our home-made program that randomly introduces pyridinic N and graphitic N into graphene lattice. The results show that 4N-V<sub>2</sub>, 5N-V<sub>3</sub> and 6N-V<sub>4</sub> exist as the N content lower than 7.5% and 6N-V<sub>6</sub> configuration emerges as the N doping content reaches 10%. The C and N atoms are shown in grey and blue/green colors, respectively. The green highlights the structural models considered in this work. Related to Figure 1.

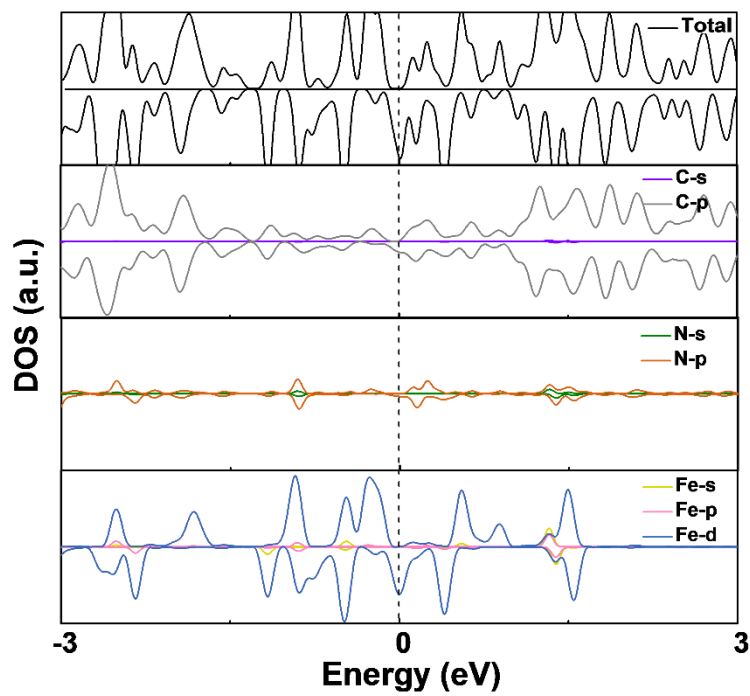




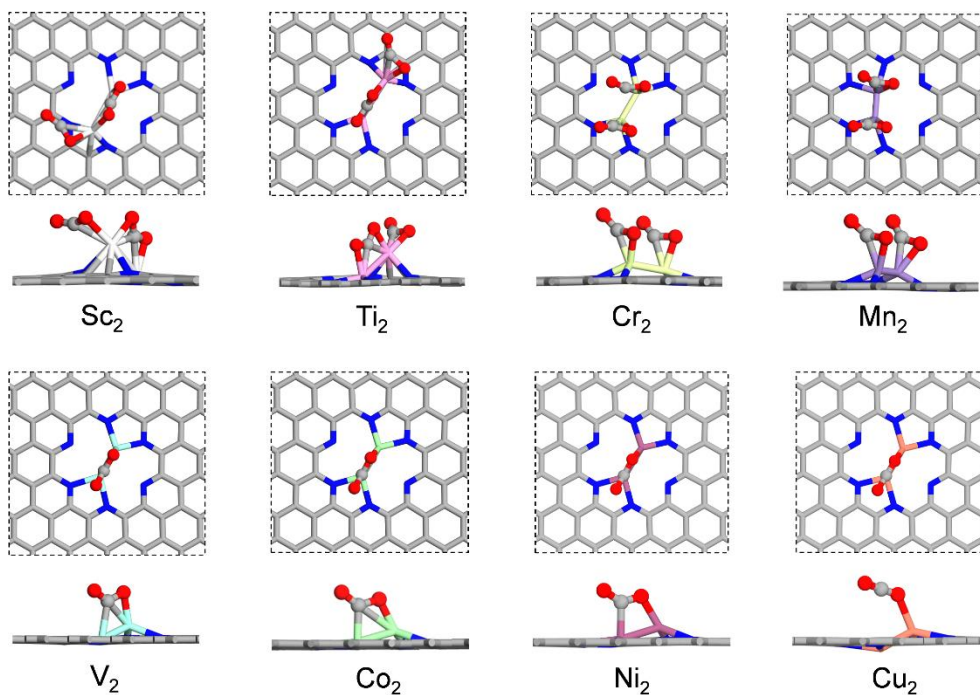
**Figure S2.** Atomic structures of 3d transition metal dimers anchored on the 6N-V<sub>6</sub> monolayer. The C and N atoms are shown in grey and blue colors, respectively. Related to Table 2.



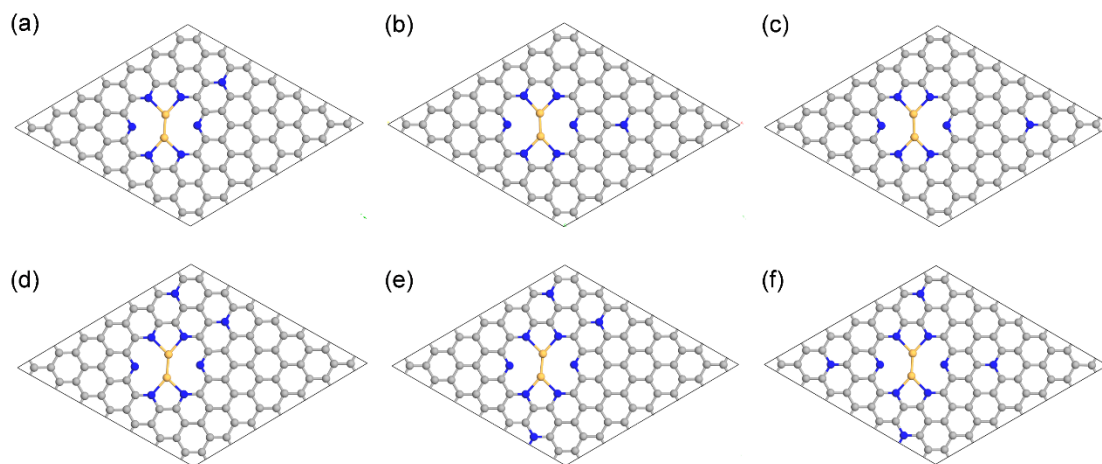
**Figure S3.** (a) Temperature profile and (b) snapshot atomic structure of  $\text{Fe}_2@6\text{N-V}_6$  from *ab initio* molecular dynamics simulation at 800 K for 10 ps, which well maintains the initial equilibrium geometry with an average atomic displacement of 0.16 Å in the vertical direction. The C, N and Fe atoms are shown in grey, blue and orange colors, respectively. Related to Figure 1.



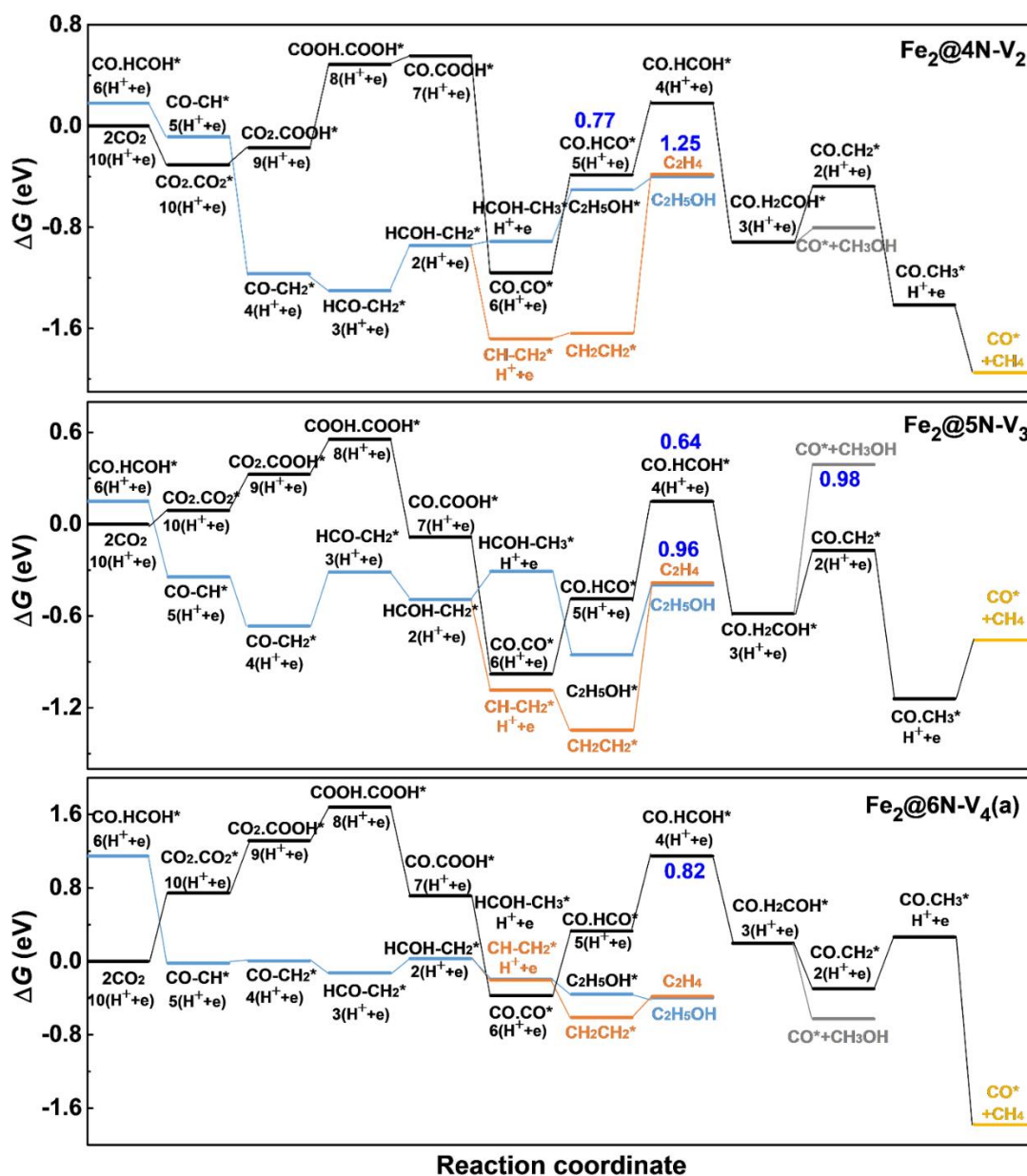
**Figure S4.** The projected density of states (DOS) of Fe<sub>2</sub>@6N-V<sub>6</sub>. The dashed line shows the Fermi level. Related to Figure 2.



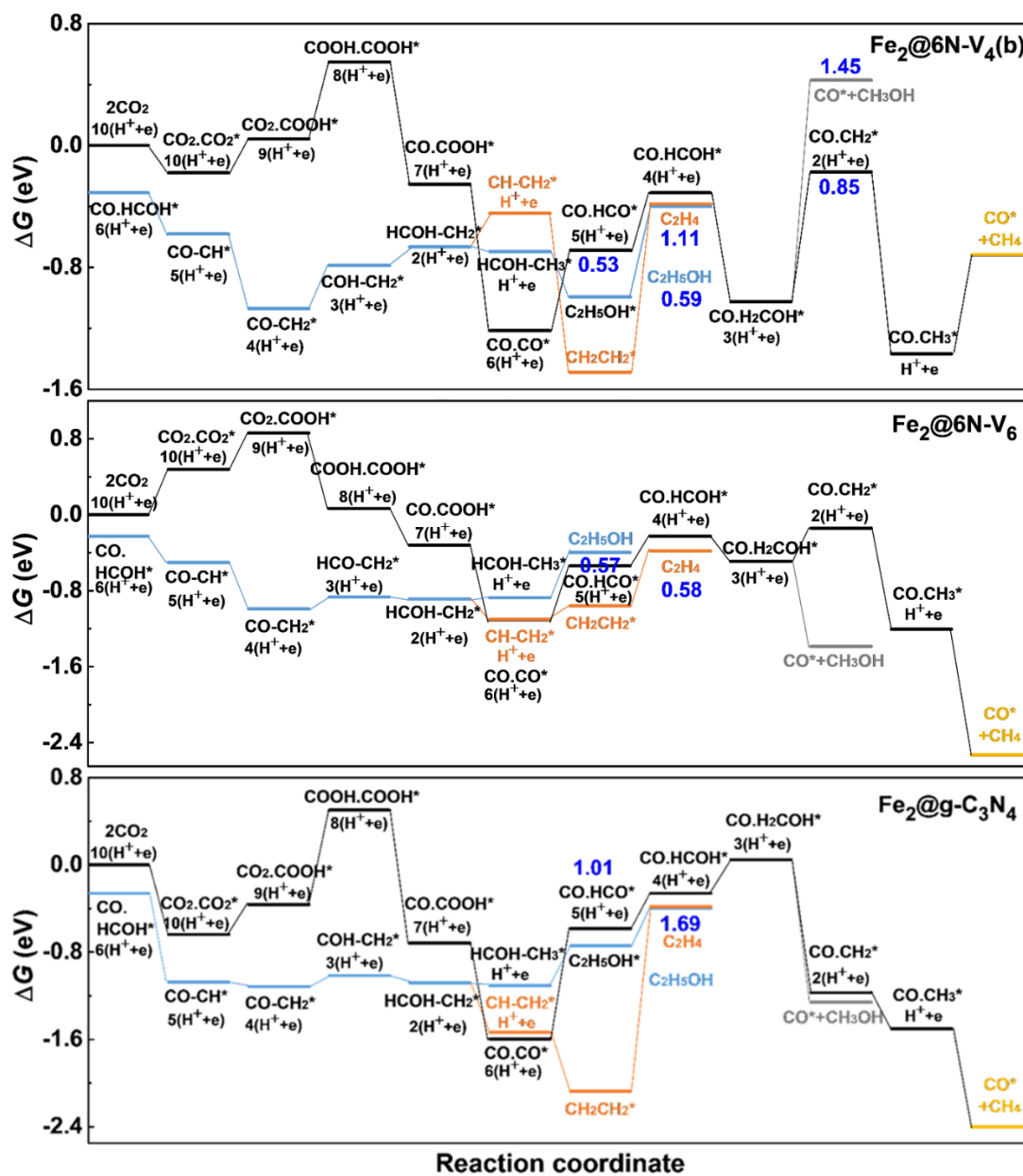
**Figure S5.** Atomic structures of dual or single CO<sub>2</sub> molecule adsorbed on 3*d* transition metal dimers anchored on the 6N-V<sub>6</sub> monolayer. The C, N and O atoms are shown in grey, blue and red colors, respectively. Related to Table 2.



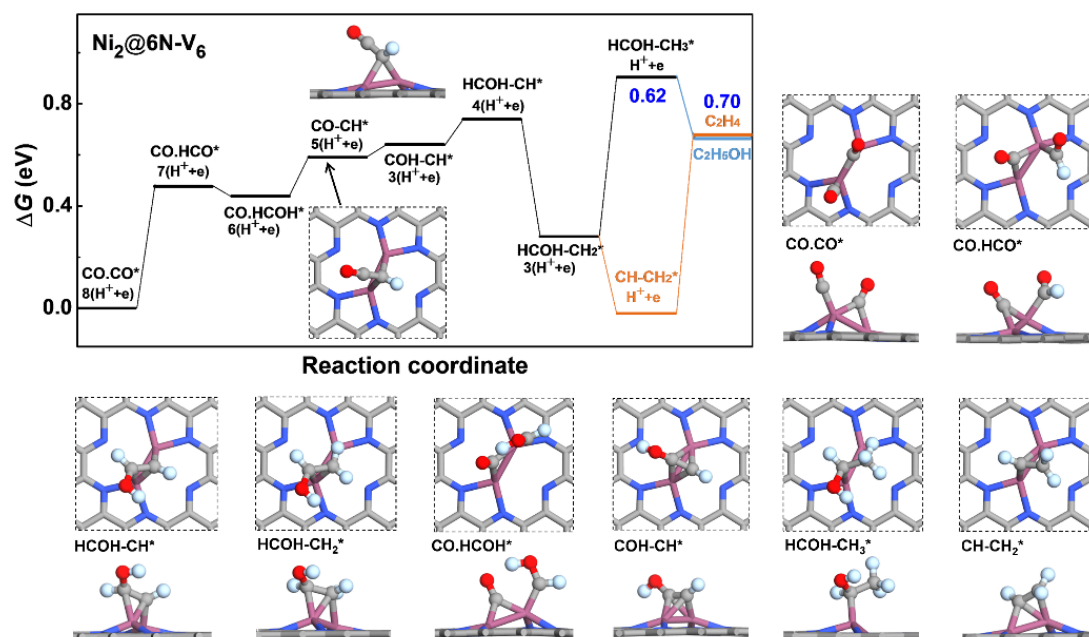
**Figure S6.** Model structures of  $\text{Fe}_2@6\text{N-V}_6$  with presence of the graphitic N atoms near or away from the hole. For models (a), (b) and (c), we placed the graphitic N atom at different distances from the  $\text{Fe}_2$  dimer, with  $d_a < d_b < d_c$ . For models (d), (e) and (f), we considered two, three and four graphitic N atoms per supercell, respectively. The C, N and Fe atoms are shown in grey, blue and orange colors, respectively. Related to Figure 1.



**Figure S7.** Free energy diagrams of CO<sub>2</sub> reduction to form various C<sub>1</sub> and C<sub>2</sub> products (indicated by different colors) on Fe<sub>2</sub>@4N-V<sub>2</sub>, Fe<sub>2</sub>@5N-V<sub>3</sub> and Fe<sub>2</sub>@6N-V<sub>4</sub>(a). The blue numbers indicate  $\Delta G_{\text{RDS}}$  values for every products. Related to Figure 5.

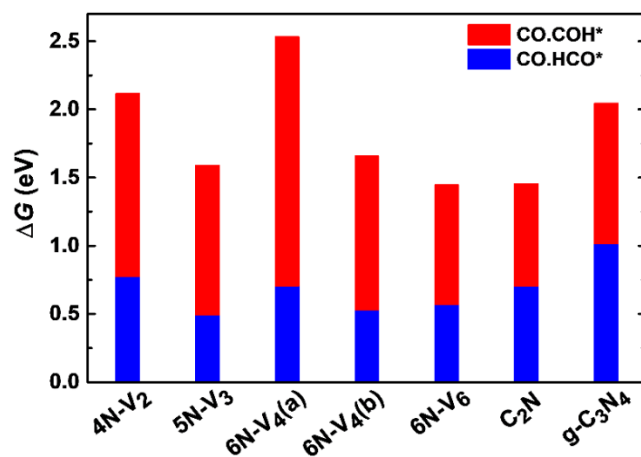


**Figure S8.** Free energy diagram of  $\text{CO}_2$  reduction to form various  $\text{C}_1$  and  $\text{C}_2$  products (indicated by different colors) on  $\text{Fe}_2@6\text{N-V}_4(\text{b})$ ,  $\text{Fe}_2@6\text{N-V}_6$  and  $\text{Fe}_2@g\text{-C}_3\text{N}_4$ . The blue numbers indicate  $\Delta G_{\text{RDS}}$  values for every products. Related to Figure 5.

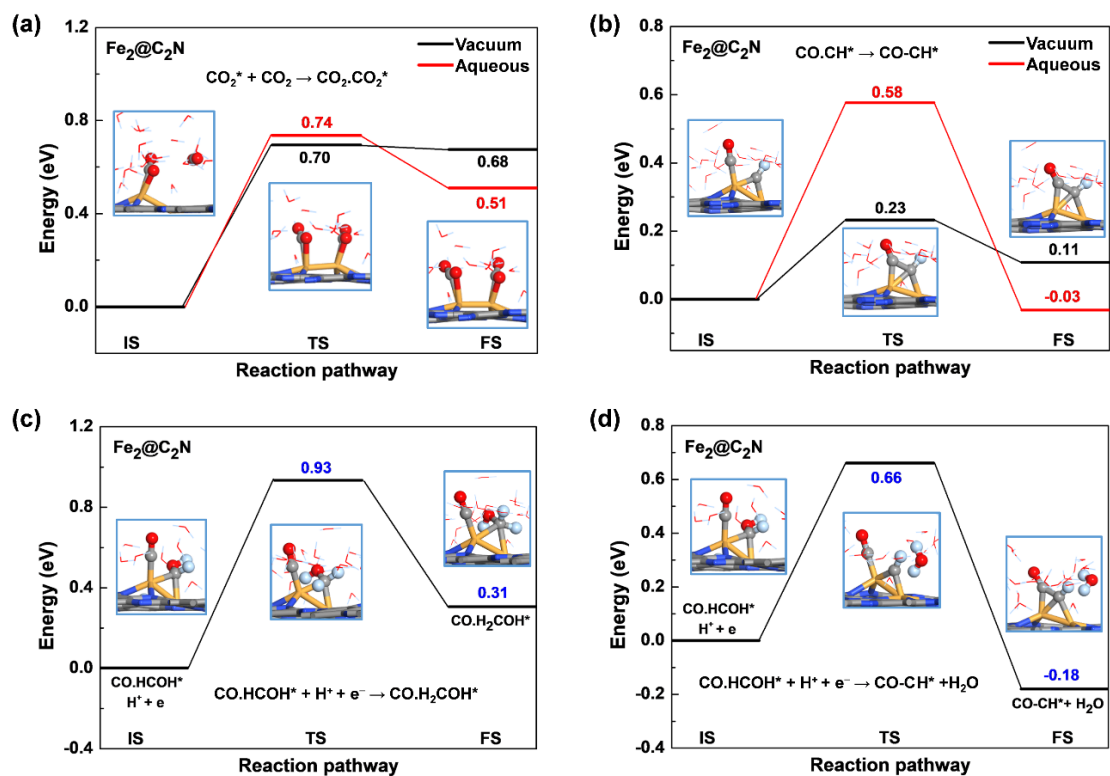


**Figure S9.** Free energy diagram and atomic structures of CO<sub>2</sub> reduction to form C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH products (indicated by different colors) on Ni<sub>2</sub>@6N-V<sub>6</sub>, the free energies of rate-determining step are 0.70 and 0.62 eV for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH products, respectively. The blue numbers indicate  $\Delta G_{\text{RDS}}$  values for every products. The H, C, N, O and Ni atoms are shown in light blue, grey, blue, red and claret colors, respectively. Related to Figure 5.





**Figure S10.** Gibbs free energy of formation ( $\Delta G$ ) for generating CO.HCO\* and CO.COH\* intermediates from protonation of CO.CO\*. Related to Figure 4.



**Figure S11.** (a) The kinetic process of second CO<sub>2</sub> activation in vacuum and in the aqueous condition. (b) The CO–CH\* coupling in vacuum and in the aqueous condition. Competing reactions of CO.HCOH\* to form (c) C<sub>1</sub> and (d) C<sub>2</sub> intermediates on Fe<sub>2</sub>@C<sub>2</sub>N in water environment, respectively. The insets display the structures of initial state (IS), transition state (TS) and final state (FS). The numbers give the kinetic barriers (middle) and heat of reaction (right). The H, C, N, O and Fe atoms are shown in light blue, grey, blue, red and orange colors, respectively. Related to Table 3.

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