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Direct coupling of two inert CO₂ molecules to form a C–C bond on the Cu⁰ atomic interfaces of the nitrogen-doped graphene-supported Cu₄ cluster†

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The electrochemical reduction reaction of CO₂ (CO₂RR) to C₂₊ products is strongly related to the C–C coupling reaction. In general, deoxidation productions of CO₂ have been assigned as the active species for the C–C coupling reaction. For example, the direct coupling of two *CO, *CO and *CHO, and two *CHO species are always proposed to be the three main pathways for the formation of the C–C bond in CO₂RR. In this case, a direct coupling of two inert CO₂ molecules to form a CO₂ dimer with strong C–C bond over the Cu⁰ atomic interfaces of the Cu₄ cluster, which was anchored on a nitrogen-doped graphene support (Cu₄/N₃GN), has been proposed based on our periodic density functional theory (DFT) calculations. The mechanistic investigation shows that the atomic interface formed by the three Cu⁰ species of Cu₄/N₃GN can simultaneously adsorb two CO₂ molecules, and two adsorbed CO₂ molecules could be reduced to a CO₂^{•−} anionic radical with [O=C[•]=O][−] configuration via an electron-transfer process from the three Cu⁰ species to the two adsorbed CO₂ molecules. Furthermore, the direct coupling of two CO₂^{•−} anionic radicals results in the formation of a C–C bond. The calculated free energy profiles reveal that the direct coupling of two CO₂ molecules should be the main reaction relevant to the coupling of *OCHO and CO, *COOH and *CO, and two CO molecules over the catalyst surface. Electronic structural analysis indicates that the bent arrangement of two adsorbed CO₂ molecules is a key factor in the determination of the formation of the C–C bond in the CO₂ dimer via effective orbital interactions. In addition, the CO₂ dimer could be reduced to ethane in the series of electrochemical elementary steps. The high ethane selectivity of the Cu₄/N₃GN catalyst studied here mainly arises from the strong Cu–O bonding interaction. Regarding the direct coupling of two inert CO₂ molecules over the atomic interface of the Cu₄ cluster, these findings would be very useful to guide the search for potential catalysts for the formation of the C–C bond in CO₂RR into the subnanometer cluster with various active sites.

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1. Introduction

Subnanometer copper (Cu)-based clusters have received considerable attention in the conversion of CO₂ to valuable chemicals because of their unique electronic structure and excellent catalytic performance.^{1–6} Compared with bulk Cu surfaces and large Cu-based nanoparticles, subnanometer Cu-based clusters possess a larger surface-to-volume ratio and more active sites.⁷ Owing to the high surface energy, they have several advantages in the adsorption of the inert

CO₂ molecule. The adsorption and activation of the CO₂ molecule by catalysts is the first step for the conversion of CO₂ to any valuable chemicals.^{8,9} An activated CO₂ molecule, which has the lengthening of the C–O bond and the bending of the O–C–O bond angle, is always generated from an efficient electron-transfer process between catalysts and the CO₂ molecule.^{10–12} For this purpose, the oxidation state of the active Cu cluster has been well investigated by using experimental and theoretical methods. It has been reported that the ionic form of Cu⁺ was the active center for the activation of CO₂ molecule by the Cu-based clusters;^{13–15} however, other investigations suggested that the measured Cu⁰ species is strongly correlated to the activation of CO₂ molecule.^{16–18} Meanwhile, the cluster size and support composition are also key factors in the determination of the catalytic activity for the reported subnanometer Cu-based clusters.^{19–22} To date, a clear assignment of the active Cu

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site has not been achieved yet, and is still under debate for the subnanometer Cu-based clusters.

Recently, several theoretical and experimental studies have been reported for the reduction of CO₂ to methanol/ethanol catalyzed by a four-atom Cu cluster (Cu₄) on the surface of various supports.^{23–25} Liu and co-workers reported that a carbon-supported Cu_n (*n* = 3, 4) cluster achieved a single-product faradaic efficiency (FE) of 91% at –0.71 V (*versus* the reversible hydrogen electrode).²⁶ The FE of ethanol was found to be closely associated with the initial dispersion of Cu atoms. In their density functional theory (DFT) calculations, a supported Cu₃ cluster was assigned as a model to probe the possible reaction mechanism, assuming a Cu₄ cluster would share the similar mechanism. They found that the HCOOH* intermediate was reduced to CH₃* + H₂CO*, which underwent a C–C bond formation to form ethanol. Alternatively, the conventional CO* pathway was found to have a higher reaction free energy in several steps than the HCOO* pathway. In another case, the same group reported that a size-selected Cu₄ cluster is the most active low-pressure catalyst for the reduction of CO₂ to methanol.²⁷ DFT calculations showed that the unsaturated Cu sites in the Cu₄ clusters resulted in a strong adsorption of the adsorbates, which leads to an energetically low-lying reaction pathway. A systematic study of the size and support effects was carried out by using X-ray adsorption spectroscopy, catalytic activity measurement, and DFT calculations. They found that the catalytic activity for methanol synthesis varied strongly as a function of the Cu cluster size. The Cu₄/Al₂O₃ catalyst shows the highest turnover rate for methanol among all reported catalysts.^{27,28} By contrast, the Cu₃/Al₂O₃ catalyst showed less than 50% activity because the stronger charge transfer interaction with Al₂O₃ support for Cu₃ than Cu₄ leads to a less favorable energetic pathway for the reduction of CO₂ to methanol.²⁷ In addition to methanol and ethanol, the Cu₄ cluster was found to be an efficient catalyst for the conversion of CO₂ to CO and acetylene trimerization.²⁹ Rodriguez *et al.* reported that a small Cu₄ cluster in contact with TiC(001) displays a very high activity for the conversion of CO₂ to CO.³⁰ DFT calculations showed that the Cu₄/TiC(001) catalyst can bind CO₂ well, with the adsorption energy of –25.6 kcal mol^{–1}, which is about 2 times as large as that of the Cu₉/TiC(001) catalyst (–13.6 kcal mol^{–1}). Schlexer and co-workers found that the interaction between the Cu₄ cluster and a silica-surfaces can be enhanced by introduction of the hydroxyl groups,³¹ whereas the dopants have only a small effect on the interaction. Meanwhile, the possible reaction mechanism of acetylene trimerization catalyzed by the silica-supported Cu₄ cluster has been probed based on their DFT calculations. All of these instructive studies showed that (i) the catalytic activity of the Cu₄ clusters is unique and relevant to its analogues, such as Cu₃, Cu₉, Cu₁₃ and C₂₉ clusters, *etc.*; (ii) the reactivity of the Cu₄ cluster may be tuned in a desired manner by the support composition; (iii) the active Cu site in the Cu₄ cluster is strongly sensitive to the interaction between the Cu₄ clusters and support surfaces. These

factors encouraged us to probe the potential catalytic properties of the Cu₄ cluster for C₂ product synthesis.

Nitrogen-doped carbon materials have attracted considerable attention in the field of CO₂RR because of their adjustable pore structure, high specific surface area, and good electrochemical stability.^{32–37} Especially in the study of M–N–C catalysts based on metal elements such as Cu, Ni, Fe, and Co, *etc.*, it has been demonstrated that these catalysts have high activity and selectivity for the reduction of CO₂ to CO.^{38–42} Among the various reported metals, the carbon-loaded Cu-based catalyst shows high activity in CO₂RR.^{43–46} These reported catalysts are of particular interest because of their ability to generate large amounts of hydrocarbons, including HCOOH, CH₄, C₂H₄, *etc.*^{47–51} Shen and co-workers found that the anchoring of Cu atoms on defective diamond graphene results in excellent catalytic performance for the selective conversion of acetylene to ethylene.⁵² Baturina *et al.* reported that introduction of the Cu atomic chains into nitrogen-doped carbon materials can break the scaling relationship by providing secondary adsorption sites, thus effectively reducing the overpotential of the electrocatalytic reduction of CO₂ to methanol.⁵³ Shi and co-workers proposed that the morphology of the carbon support has a significant effect on the catalytic performance of these Cu-based materials in CO₂RR.⁵⁴ They found that the selectivity for CO₂RR is very sensitive to the carbon support morphologies. An onion-like carbon support can effectively improve the stability, activity, and selectivity for the reduction of CO₂ to C₂H₄.⁵⁵ DFT calculations show that the defect site of the nitrogen-doped carbon support not only promotes the electron transport to the key intermediate corresponding to the potential limiting step, but also prevents the sintering of Cu atoms because the defect sites can bind the Cu atom with the strong Cu–N bonding interaction.^{56,57}

In previous investigations, the formation of the C–C bond in CO₂RR generally comes from the coupling reactions between two deoxidation productions of CO₂, such as the direct coupling of two *CO species, direct coupling of the *CO and *CHO species, and direct coupling of two *CHO species.^{28,58–61} In this case, a direct coupling of two inert CO₂ molecules to form a CO₂ dimer with a C–C bond over the atomic interface of the Cu₄ cluster, which was anchored on a nitrogen-doped graphene substrate (Cu₄/N₃GN), has been proposed based on our DFT calculations. Our mechanistic investigation shows that the atomic interface formed by the three Cu⁰ species of Cu₄/N₃GN can simultaneously adsorb two CO₂ molecules. The two adsorbed CO₂ molecules were firstly reduced to a CO₂^{•–} anionic radical with [O=C[•]=O][–] configuration *via* an electron-transfer process from the three Cu⁰ species of Cu₄/N₃GN catalyst to the two adsorbed CO₂ molecules. The direct coupling of the two CO₂^{•–} anionic radicals then resulted in the formation of a CO₂ dimer with a C–C bond. Furthermore, the produced CO₂ dimer could be reduced to ethane in the series of electrochemical elementary steps. This study provided a new mechanism for the formation of the C–C bond, and shed light on further improving the CO₂RR catalysts through the rational design of a subnanometer Cu-based catalyst.

2. Computation details

All of the first-principles calculations are based on DFT⁶² to calculate the Perdew–Burke–Ernzerhof (PBE) functional and projector augmented wave (PAW)^{63,64} pseudopotential using the generalized gradient approximation (GGA)⁶⁵ realized in the Vienna *ab initio* simulation program (VASP).^{66,67} For all graphene supporting structures, a $6 \times 6 \times 1$ original graphene supercell was used for the doping of nitrogen atoms and loading of metal clusters, and the geometrically optimized convergence threshold was set to an effective $0.03 \text{ eV } \text{\AA}^{-1}$. The cutoff energy of the plane wave basis group is 500 eV. In order to prevent the interaction between periodic images along the *z*-direction, the vacuum of 26.7 \AA is used for the flat plate calculation, and a dipole correction is applied. The Brillouin zone of the surface is sampled with the Monkhorst-K point grid of $2 \times 2 \times 1$ γ center, while only γ points are sampled for molecular calculations and higher $7 \times 7 \times 1$ for the projected density of states (pDOS) calculations.⁶⁸ The climbing image miniature elastic band method is used to calculate the transition state (TS).^{69,70} Some atomic charges are calculated by the Bader charge analysis method.⁷¹

The computational hydrogen electrode (CHE) method was applied in free energy diagrams, which assumes that half of the free energy of gaseous hydrogen is equivalent to the free energy of a proton–electron pair at 0 V, all pH values, and 1 atm. Thus, the energy of $\text{H}_2(\text{g})$ is used as an electrochemical ref. 72 The adsorption energy (E_{ad}) is obtained from the following formula:

$$E_{\text{ad}} = E_{\text{total}} - E_{\text{slab}} - E_{\text{adsorbate}}.$$

Among them, E_{total} represents the total energy of the catalyst surface adsorbed by the adsorption species, E_{slab} represents the surface energy of the catalysts without the adsorption species, and $E_{\text{adsorbate}}$ represents the energy of the adsorption species. Therefore, the more negative the adsorption energy, the stronger the adsorption capacity. The binding energy E_{b} was calculated as:

$$E_{\text{b}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$$

where E_{AB} denotes the total energy of the whole system of the catalyst, E_{A} denotes the energy of the Cu_4 cluster, and E_{B} denotes the energy of the nitrogen-doped carbon graphene carrier. The Gibbs free energy (ΔG) is modified by the VASPKit⁷³ program at 298 K and 100 kPa,⁷⁴ as follows:

$$\Delta G = E_{\text{DFT}} + \Delta \text{ZPE} - \text{TS}$$

$$\Delta \text{ZPE} = \sum_i \frac{1}{2} h \nu_i$$

where h is the Planck constant, ν_i is the calculated actual frequency of the system, and E_{DFT} is the calculated total energy. The total entropy (S) is calculated from ref. 75

The frequency of the optimized adsorption species at γ point is determined by the VASP method, and the convergence accuracy is improved. When calculating the frequency of the

adsorbent, the whole catalyst system is fixed and only the adsorbent is released. For the free energy correction of adsorbed matter, VASPKit attributes the contribution of vibration to the translational or rotational part; in other words, the 3N vibration of the surface-adsorbed molecules (except the imaginary frequency) is used to calculate the correction of the thermal energy. In addition, the solvation program VASPsol was used to implicitly describe the effects of electrolytes and solvents.⁷⁶ The solvent molecule was regarded as a continuous medium model, and the dielectric constant ($\epsilon = 78.4$) was used to express the solvent. In this work, the free energy of all isomers, intermediates, transition state (TS), and products along the reaction pathways was calculated in the solvent.

3. Results and discussion

3.1. Geometric and electronic structure of $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst

In order to ascertain the adsorption and activation of CO_2 by the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst, we first need to determine the stable structure of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst. In the present paper, all of the possible structures of the initial geometries for the Cu_4 cluster, which already were reported recently in the literature for a study of the adsorption of CO_2 on Cu-based clusters, have been considered.^{77,78}

As shown in Fig. 1, our periodic DFT calculations obtained five possible geometric arrangements as anchoring of these Cu_4 clusters onto the nitrogen-doped graphene supports (1, 2, 3, 4, and 5). Based on these optimized geometries, we calculated the free energy of these isomers (see Fig. 1). The calculated relative free energy of these isomers increased in the following order: 4 (0.00 eV) < 1 (0.19 eV) < 2 (0.21 eV) < 5 (5.80 eV) < 3 (10.92 eV), indicating that the most stable species comes from anchoring the Cu_4 cluster with a rhombus-like structure onto the nitrogen-doped graphene supports, in which one Cu atom residing at the vertices of the rhombus-like structure coordinates to the three nitrogen atoms of the nitrogen-doped graphene support. The second higher energy isomer for the Cu_4 cluster is an inverted-tetrahedron-like structure, and is only 0.19 eV higher in energy than the lowest energy isomer optimized with the PBE functional. The third higher energy isomer is found to be another rhombus-like structure for the anchored Cu_4 cluster, which is only 0.21 eV higher in energy than the most stable isomer.

To further evaluate the stability of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst, we carried out calculations of the binding energy (E_{b}) between the Cu_4 cluster and nitrogen-doped graphene supports. The calculated E_{b} value of all possible isomers also has been compared in Fig. 1. It can be found that the calculated E_{b} value increases in the following order: 1 (−2.68 eV) < 4 (−1.77 eV) < 2 (−1.45 eV) < 3 (−0.58 eV) < 5 (2.66 eV). The negative E_{b} value indicates a strong interaction of the Cu_4 cluster and nitrogen-doped graphene supports, and thus a good stability. Thus, the isomer 1 with inverted-tetrahedron-like structure possesses the strongest interaction of the Cu_4 cluster and nitrogen-doped graphene supports among all isomers for the $\text{Cu}_4/\text{N}_3\text{GN}$ cata-



Fig. 1 The geometric arrangement and charge density difference of all possible isomers for the $\text{Cu}_4/\text{N}_3\text{GN}$ catalysts studied here, where the calculated relative free energy of these isomers and binding energy of the Cu_4 cluster and nitrogen-doped graphene support also have been compared. ((a) and (f) for 1, (b) and (g) for 2, (c) and (h) for 3, (d) and (i) for 4, (e) and (j) for 5.).

lysts studied here. The calculated E_b value of the inverted-tetrahedron-like isomer is about two times as large as that for the two rhombus-like isomers 2 and 4 (-2.68 vs. -1.45 and -1.77 eV). Our optimization calculations also provide the same results, in which the average Cu–N bond length of the inverted-tetrahedron-like isomer is optimized to be shorter than that of the two rhombus-like isomers (2.00 vs. 2.04 Å and 2.01 Å). Meanwhile, the Bader charge analysis shows that the charges of the coordinated Cu atom binding to the three N atoms in the inverted-tetrahedron-like isomer is about $-0.57e$. Furthermore, the charge density difference shows that electrons accumulate on the three N atoms and adjacent C atoms on the support surface of the inverted-tetrahedron-like isomer 1, which indicates an electron-transfer process from the coordinated Cu atom to the nitrogen-doped graphene support. Moreover, the extra electrons were entirely delocalized over the surface of nitrogen-doped graphene support. Such delocalized effects effectively improve the stability of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst. Meanwhile, these results support a donor–acceptor bonding interaction of the coordinated Cu atom and the nitrogen-doped graphene supports in the inverted-tetrahedron-like isomer. By the same logic, the donor–acceptor bonding interaction also can be found in two rhombus-like isomers. The charge density difference also shows that electrons accumulate between the three N atoms and coordinated Cu atom in the two rhombus-like isomers. However, no delocalization effects of the extra electrons have been observed on the nitrogen-doped graphene supports in the rhombus-like isomers. Thus, the stability of both isomers is not better than that of the inverted-tetrahedron-like isomer. All of these results indicate that the strong interaction of the Cu_4 cluster with the inverted-tetrahedron-like structure and the nitrogen-doped graphene substrate experimentally provide good feasibility in terms of synthesis of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst. We will focus on the inverted-tetrahedron-like isomer in the following discussions.

3.2. Adsorption and activation of CO_2 over the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst

In the inverted-tetrahedron-like isomer, the four Cu atoms are tightly coupled through metal bonds to form a cluster (see ESI Table S1†). One Cu atom in the Cu_4 cluster is anchored to the defects of the nitrogen-doped graphene substrate, and interacts with the three N atoms on the substrate. The calculated Bader charge of the Cu atoms, which does not directly attach to the N atom, is about zero (see ESI Table S2†). Thus, the Cu_4 cluster in the inverted-tetrahedron-like isomer may be described as a $\text{Cu}^+-\text{Cu}^0_3$ configuration, in which the three Cu^0 species form an atomic interface over the Cu_4 cluster. The transition metal center in a lower oxidation state always displays stronger ability to bind the adsorbates, according to previous investigations. Furthermore, the atomic interface formed by the unsaturated three Cu^0 species in the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst may have the ability to interact with molecules. Thus, they should be viewed as potential sites for the adsorption and activation of the inert CO_2 molecule. The effective combination of three possible Cu^0 sites may adsorb one or two CO_2 molecules over the surface of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst.

For the adsorption of the first CO_2 molecule, our DFT calculations provide three possible adsorption configurations (top, bridge_1, and bridge_2 models). For the top model, the CO_2 molecule was adsorbed on the top of three Cu^0 sites, in which the C and two O atoms of the CO_2 molecule directly interact with three Cu^0 sites. Meanwhile, in the bridge_1 model, the CO_2 molecule was localized at a position between two Cu atoms, in which two O atoms of the CO_2 molecule directly interact with the two Cu^0 sites. On the other hand, in the bridge_2 model, the C atom and one O atom of the CO_2 molecule directly interact with two Cu^0 sites.

In order to identify the stability of these adsorption configurations, the adsorption energy (E_{ad}) has been calculated by using our DFT calculations. The calculated E_{ad} values also have been compared in Fig. 2. It was found that the calculated



Fig. 2 The key geometric parameters and adsorption energy analysis of the possible adsorption configuration of the CO₂ molecule on the Cu₄/N₃GN catalyst with the (a) top, (b) bridge_1, (c) bridge_2, (d) coupling and (e) isolating models.

E_{ad} value increases in the following order: E_{ad} (bridge_2) (−0.87 eV) < E_{ad} (bridge_1) (−0.19 eV) < E_{ad} (top) (0.01 eV), indicating a strong adsorption of CO₂ on the Cu₄/N₃GN catalyst in the bridge_2 model. By contrast, the calculated E_{ad} values of the top and bridge_1 model are both higher than bridge_2, indicating that both adsorption configurations are not stable species. Such results indicate that the two Cu⁰ sites in the most stable adsorption configuration (bridge_2) are not occupied as the adsorption of the first CO₂ molecule, which is available for adsorption of the second CO₂ molecule.

For the adsorption of the second CO₂ molecule, two possible adsorption configurations have been obtained (coupling and isolating models). The most stable configuration is found to be the coupling model (see Fig. 2d), in which the three O atoms of the two CO₂ molecules direct interact with the three Cu⁰ sites. Meanwhile, a direct coupling of two adsorbed CO₂ molecules to form a CO₂ dimer with a C–C bond length of 1.55 Å has been found, according to our optimization calculations. The calculated E_{ad} value of the coupling model is about 0.94 eV lower in energy than that of the isolating model (−1.56 vs. −0.62 eV). It is well known that the selectivity of the catalyst to the C₂₊ products in CO₂RR is closely related to the formation of C–C bonds. According to previous reports, the formation of the C–C bond arises from three major pathways, including the *CO dimerization, *CO and *CHO dimerization, and *CHO dimerization over the catalyst surface. However, the direct coupling of two inert CO₂ molecules to form a CO₂ dimer with the strong C–C bond has not been found over the Cu-based catalysts. Interestingly, as shown in Fig. 2d, our optimization calculations provide a unique geometric arrangement, in which the two adsorbed CO₂ molecules are bound to each other *via* a strong C–C single bond over the atomic interface of the Cu₄/N₃GN catalyst. Such results strongly suggest a direct coupling of two inert CO₂ molecules to form a CO₂ dimer over the atomic interface of the Cu₄/N₃GN catalyst.

3.3. CO₂ dimerization

Electrochemical reduction of CO₂ is a very complicated system. The CO₂ molecule could be reduced to *OCHO, *COOH, *CO, *CHO, *CH, and *CH₂, and others in the series of electrochemical elementary steps, which would become the potential coupling species for the formation of the C–C bond in CO₂RR.^{49,79,80} These species may occupy the active sites of the catalyst and suppress the direct coupling of two CO₂ molecules

over the surface of the Cu₄/N₃GN catalyst. Owing to the low surface concentrations of *CHO, *CH, *CH₂, and other multiple reduced species of CO₂ molecule over the catalytic surface, the reaction pathway for the coupling of these species to form the C–C bond is not important when compared with the high concentration species *CO₂, *OCHO, *COOH, and *CO. In the present paper, starting from the *CO₂, *OCHO, *COOH, and *CO species, all possible coupling reactions for the combination of these species have been considered. According to our optimization calculations, four possible coupling pathways have been obtained. The calculated free energy curves for these reaction pathways are shown in Fig. 3.

It was found that the calculated free energy curve for the direct coupling of two *CO₂ molecules is located at the bottom, and has the lowest free energy barrier. By contrast, the calculated free energy curves of the direct coupling of two CO molecules are located in a third high-energy place, in which the calculated free energy barrier is about 0.62 eV higher in energy than that of the direct coupling of two CO₂ molecules. The calculated relative energy of the CO dimer is about 0.84 eV higher in energy than that of the CO₂ dimer. Thus, the direct coupling of two CO molecules over the surface of the Cu₄/N₃GN catalyst is both thermodynamically and kinetically unfavorable when compared with that of the two CO₂ molecules. As shown in Fig. 3, the calculated free energy curve of the coupling of *CO and *OCHO is located at the top, and has the highest energy barrier among them. Thus, such coupling reaction is not significant both thermodynamically and kinetically. Although the calculated free energy curve for the coupling of *CO and *COOH is located in a second high-energy place, the calculated free energy barrier is about 2 times as high as that of the direct coupling of two CO₂ molecules (0.94 vs. 0.52 eV). Thus, the competition effects of this coupling reaction may not be significantly relevant to the direct coupling of two CO₂ molecules. All these results indicate that the direct coupling of two CO₂ molecules over the surface of the Cu₄/N₃GN catalyst could be the main reaction for the formation of the C–C bond in the complicated electrochemical system.

The optimized geometric arrangements of the key transition states and intermediates for the direct coupling of two CO₂ molecules are shown in Fig. 3. It was found that the two CO₂ molecules firstly approach the three Cu⁰ species to form an adsorption complex *CO₂ + *CO₂ (isolating models). In *CO₂ + *CO₂, the optimized O₂C...CO₂ distance is 3.355 Å,



Fig. 3 The calculated free energy profiles for the direct coupling of two $^*\text{CO}_2$, $^*\text{OCHO}$ and CO , $^*\text{COOH}$ and $^*\text{CO}$, and two CO molecules to form a C–C bond on the surface of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst.

indicating a very weak interaction between the two CO_2 molecules over the surface of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst. The calculated Bader charge of the two adsorbed CO_2 molecules is +0.78 e and +0.49 e in $^*\text{CO}_2 + ^*\text{CO}_2$, respectively. The calculated Bader charge of the three Cu atoms in $^*\text{CO}_2 + ^*\text{CO}_2$, which are not attached to the N atom of the nitrogen-doped graphene substrate, is -0.25, -0.44, and -0.25 e, respectively. The calculated Bader charge of the Cu atom coordinated to the three N atoms of the nitrogen-doped graphene substrate is -0.46 e in $^*\text{CO}_2 + ^*\text{CO}_2$. Compared with the neutral CO_2 molecule and Cu_4 cluster with $\text{Cu}^+-\text{Cu}_3^0$ configuration on the clear surface of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst, such results indicate that the two adsorbed CO_2 molecules have been activated *via* an electron-transfer process from three Cu^0 species in the Cu_4 cluster of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst to the two adsorbed CO_2 molecules. Thus, the two CO_2 moieties in $^*\text{CO}_2 + ^*\text{CO}_2$ have been reduced and possess the bent structure with elongated C–O bond length relative to the free CO_2 molecule, and can be viewed as two $\text{CO}_2^{\cdot-}$ anionic radicals. A detailed analysis of the calculated Bader charge shows that the C atom is -2.10, -1.38, and -1.61 e for the free CO_2 molecule and two adsorbed CO_2 molecules, respectively. The calculated Bader charge of the two O atoms is (1.05 and 1.05 e), (1.08 and 1.08 e), and (1.04 and 1.06 e) for the free and two adsorbed CO_2 molecules, respectively. Such results indicate that the reduced electrons are mainly localized on the C atom adjacent to the O atoms for the two adsorbed CO_2 molecules in this electron-transfer process (Δq (C) = 0.72 and 0.49 e for the two adsorbed CO_2 molecules in this electron-transfer process, respectively). Thus, the electron configuration of the two adsorbed CO_2 molecules should be described as $[\text{O}=\text{C}^{\cdot-}=\text{O}]^-$. The C atom of the two adsorbed

CO_2 molecules would significantly contribute to the formation of a C–C single bond in the process of CO_2 dimerization. Then, our optimization calculation shows the direct coupling of two anionic CO_2 radicals with $[\text{O}=\text{C}^{\cdot-}=\text{O}]^-$ configuration over the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst *via* **TS1**, which needs an activation energy of 0.52 eV with an imaginary frequency of 244.83 cm^{-1} . At **TS1**, the $\text{O}_2\text{C}\cdots\text{CO}_2$ distance was shortened to 2.205 \AA , indicating that a new bond may form between the two adsorbed CO_2 molecules. In **TS1**, the calculated Bader charge of the two C atoms in the adsorbed two CO_2 molecules is -1.47 and -1.72 e, respectively, compared with the Bader charge of the C atoms in free CO_2 (-2.10 e), indicating the distinct radical feature for the two adsorbed CO_2 molecules in **TS1**. After **TS1**, the two CO_2 anionic radicals come together to form a CO_2 dimer, $^*\text{OOCO}^*\text{O}^*$, over the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst. This coupling process is calculated to be exoergic by 0.94 eV, indicating that $^*\text{OOCO}^*\text{O}^*$ has a high thermodynamic stability. Furthermore, the direct coupling of two CO_2 molecule over the surface of $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst has a large thermodynamic driving force. All of these results indicate that the CO_2 dimerization reaction over the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst should be viewed as a free-radical-coupling reaction.

As mentioned above, the two adsorbed CO_2 molecules over the atomic interface of $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst were reduced and possess bent structure. The reduced electron is mainly localized over the C atom of the adsorbed CO_2 molecule, according to the Bader charge analysis. The frontier molecular orbitals (FMOs) of the free CO_2 molecule are listed in Fig. 4. It can be seen that the two degenerated LUMOs of the free CO_2 molecule consist of 2p orbitals of the C atom and two O atoms with π^* antibonding feature, and mainly localized over the C atom

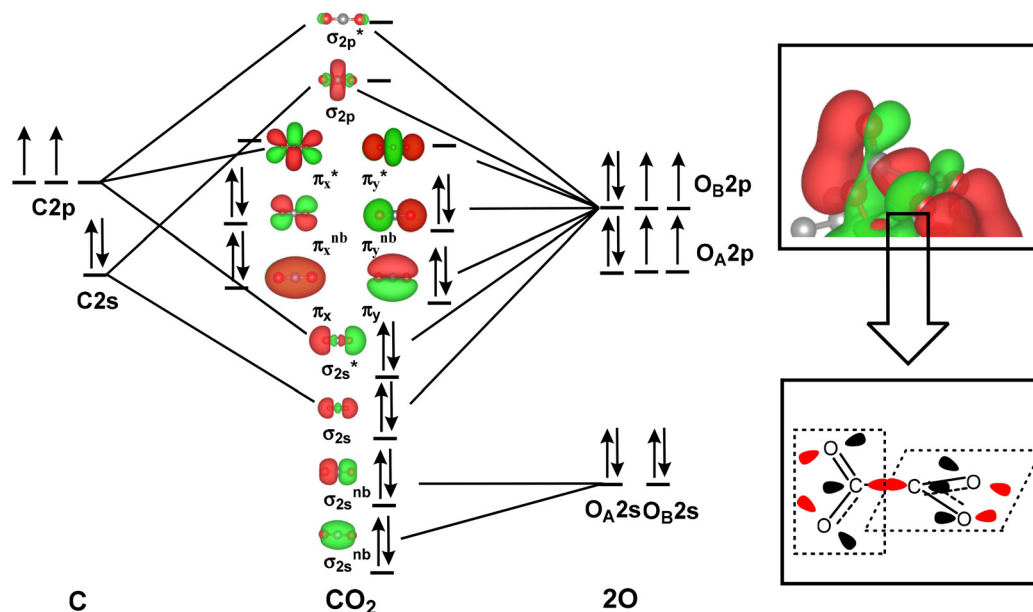


Fig. 4 The frontier molecular orbitals of free carbon dioxide molecules and the HOMO of the $^*\text{OOCO}^*\text{O}^*$ dimer, highlighting that the effective overlapping of two distorted π^* antibonding orbitals of two bent CO_2 molecules results in the formation of the C–C bond in the CO_2 dimer.

adjacent to the O atoms. Thus, injection of extra electrons into the LUMOs would localize on the C atom of the CO_2 molecule, which are in good agreement with our Bader charge analysis.

Meanwhile, our electronic structural analysis shows that $^*\text{OOCO}^*\text{O}^*$ provided a unique molecular orbital topology for the formation of the C–C bond in the CO_2 dimer. As shown in Fig. 4, our optimization calculations show that the two adsorbed CO_2 molecules with bent structure define two planes, in which the dihedral angle of the two planes is calculated to be 121.9° . Such geometric arrangement could effectively avoid the repulsion effects from the O atoms of the CO_2 molecule, and make the two C atoms of the adsorbed CO_2 molecules get closer in the process of CO_2 dimerization. The molecular orbital topology (HOMO) of $^*\text{OOCO}^*\text{O}^*$ represents the C–C bonding interaction. It can be seen that HOMO could be viewed as an effective overlapping of two distorted π^* antibonding orbitals of the CO_2 molecule. The bent arrangement of the adsorbed CO_2 molecule leads to a mixing of 2p orbitals of the two O atoms in the CO_2 molecule, which effectively polarizes the 2p orbital of the C atom in the CO_2 molecule. The polarized 2p orbital of the C atom promotes the overlapping of two distorted π^* antibonding orbitals, and significantly contributes to the formation of the C–C bond in the CO_2 dimer. All of these results indicate that the bent arrangement of the CO_2 molecule is the key factor in the determination of the formation of the C–C bond *via* effective orbital interactions.

The nature of the CO_2 dimer, $^*\text{OOCO}^*\text{O}^*$, is a key factor in the determination of the formation of the C_2 product in CO_2RR . As shown in Fig. 5, the four oxygen atoms in $^*\text{OOCO}^*\text{O}^*$ are the potential sites in the following elementary steps. In the present paper, we firstly considered the possible dissociated products of $^*\text{OOCO}^*\text{O}^*$ *via* cleavage of the four

C–O bonds, respectively. The calculated relative energy of the four dissociated products has been compared in Fig. 5. It can be found that the calculated relative energy of the four dissociated products increases in the following order: O_3 (0.34 eV) < O_2 (0.48 eV) < O_4 (0.82 eV) < O_1 (1.28 eV), indicating that these four dissociated processes are all endergonic. Furthermore, the most stable species among them comes from dissociation of the O_3 atom from the $^*\text{OOCO}^*\text{O}^*$ intermediate to form a $^*\text{OCCOO}^*$ species and a remaining $^*\text{O}^*$ species. Owing to the high thermodynamic stability of $^*\text{OOCO}^*\text{O}^*$, this dissociated process is calculated to have a high free energy barrier of 1.75 eV. However, this high barrier can be compensated by the following reduction reaction of the remaining $^*\text{O}^*$ species to H_2O over the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst.

After **TS5**, the O_3 atom moves from the top site of the Cu atom into the bridge site between the two Cu atoms. Meanwhile, the dissociated fragment of $^*\text{OCCOO}^*$ was bound over the surface of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst *via* a new Cu– C_2 bond and a Cu– O_2 bond. The remaining O_3 atom would be reduced to H_2O and leave the surface of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst. Although a lot of efforts have been made, we did not find any rational geometric arrangement for the hydrogenation of $^*\text{OOCO}^*\text{O}^*$. As shown in Fig. 3, three out of the four oxygen atoms in $^*\text{OOCO}^*\text{O}^*$ were bound to the three Cu atoms of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst *via* three strong Cu–O bonds. Thus, the three O atoms are located in the Cu–O–C units and in the chemical saturated states. Such structural arrangement of the three O atoms significantly weakens the reactivity with the proton–electron pairs. The O_4 atom, which was bound to the $^*\text{OOCO}^*\text{O}^*$ *via* a $\text{C}_2\text{–O}_4$ bond, also cannot react with the proton–electron pair to form a hydrogenation product because of the weak reactivity. All of these results indicate that the con-

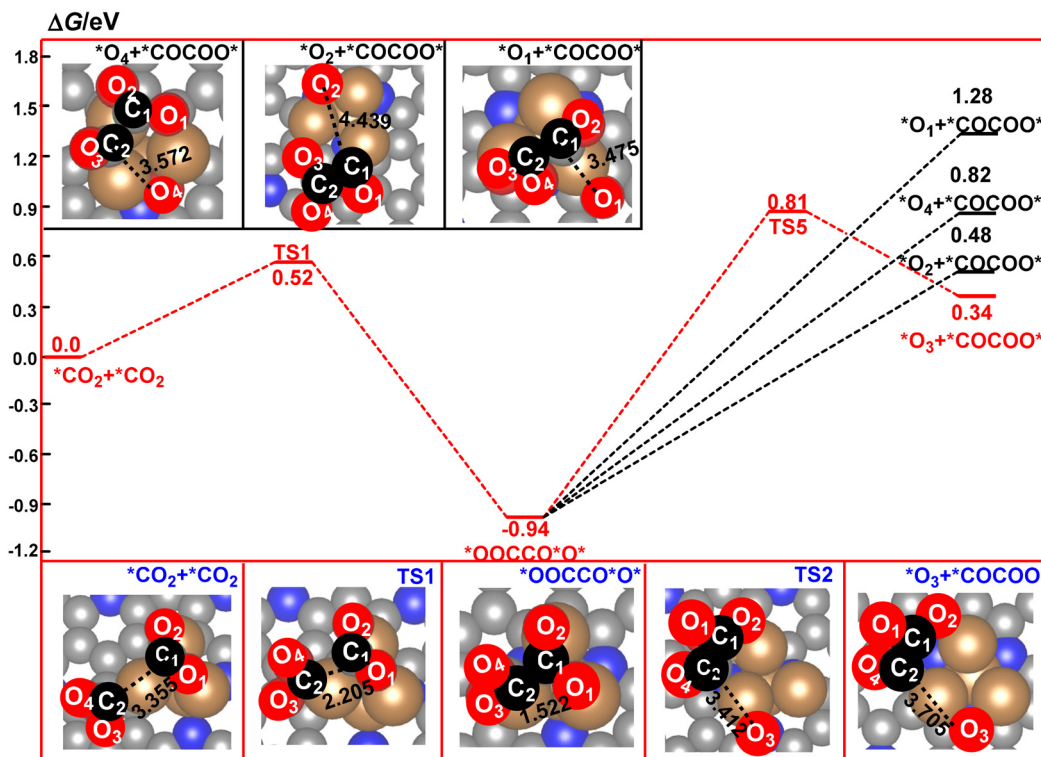


Fig. 5 Calculated reaction pathways for the formation and decomposition of the CO₂ dimer on the surface of the Cu₄/N₃GN catalyst.

version of the stable *OOCO*O* to *OCCOO* over the surface of the Cu₄/N₃GN catalyst could be triggered by a heating process because dissociation of the stable CO₂ dimer is an endergonic process with a high free energy barrier. By contrast, implementing of the electroreduction process at room temperature may not produce the C₂ product for our studied system in this work.

3.4. Formation of ethane

In previous literature, the number of oxygen atoms in the C–C coupling product is up to two, such as *OCCO .^{81,82} In general, the proton–electron pair preferentially attacks at the O atom of the C–C coupling product because of the high basicity of the O atom relative to the C atom.^{82,83} Thus, the nature of the O atom in the C–C coupling product would significantly affect the selectivity of the catalyst in CO₂RR. For our studied system, the decomposition product of the CO₂ dimer, $\text{*O}_3 + \text{*OCCOO*}$, contains four O atoms. The possible reaction pathways corresponding to the generation of the C₂ products entirely differ from the reported mechanism. The calculated free energy profiles of the whole reaction pathway for the hydrogenation of $\text{*O}_3 + \text{*OCCOO*}$ to ethane is shown in Fig. 6 and 7. All of the O sites of the $\text{*O}_3 + \text{*OCCOO*}$ intermediate have been considered for the first hydrogenation step. As expected, the reduction of the *O_3 atom to a *OH group is calculated to be energetically much more favorable among them. According to our free energy calculations, hydrogenation of $\text{*O}_3 + \text{*OCCOO*}$ to the $\text{*COCOO*} + \text{*OH}$ intermediate is calculated to be exoergic by

1.19 eV, indicating that the $\text{*COCOO*} + \text{*OH}$ intermediate is a thermodynamically stable species, and will remain on the catalyst surface long enough for further reduction to H₂O.

For the second reduction step, the hydrogenation of the $\text{*COCOO*} + \text{*OH}$ intermediate to $\text{*COCOO*} + \text{*H}_2\text{O}$ is calculated to be exoergic by 0.29 eV. Next, desorption of the produced H₂O molecules from the catalyst surface to form a *COCOO* intermediate is calculated to be endergonic by 0.72 eV.

Subsequently, the proton–electron pair preferentially attacks at the C₂ atom of *COCOO* , which binds to the Cu atom, to generate *CHOCOO* intermediates with a free energy downhill of 0.12 eV. This step leads to a complete cleavage of the Cu–C₂ bond, and the *CHOCOO* moiety was bound to the catalyst surface *via* a Cu–O₂ bond. Owing to the strong Cu–O₂ bonding interaction, the hydrogenation of the O₂ site in the conversion from *COCOO* to *COCOHO is calculated to be energetically unfavorable. Then, the proton–electron pair preferentially attacks at the O₄ atom of *CHOCOO* to produce *CHOHCOO* with a free energy downhill of 0.41 eV. The optimized Cu–O₂ bond length increases from 1.892 Å in *CHOCOO* to 1.896 Å in *CHOHCOO* , indicating that this hydrogenation step does not largely affect the Cu–O₂ bonding interaction. In the following two hydrogenated steps, the *CHOHCOO* was hydrogenated to form $\text{CH}_2\text{OHCOHO*}$ with two exothermic steps by 0.18 and 0.48 eV, respectively. For the thermodynamically unstable $\text{CH}_2\text{OHCOHO*}$ species, it was immediately hydrogenated to form the second H₂O molecule in $\text{CH}_3\text{COO*} + \text{H}_2\text{O}$ over the Cu₄/N₃GN catalyst. This hydrogen-

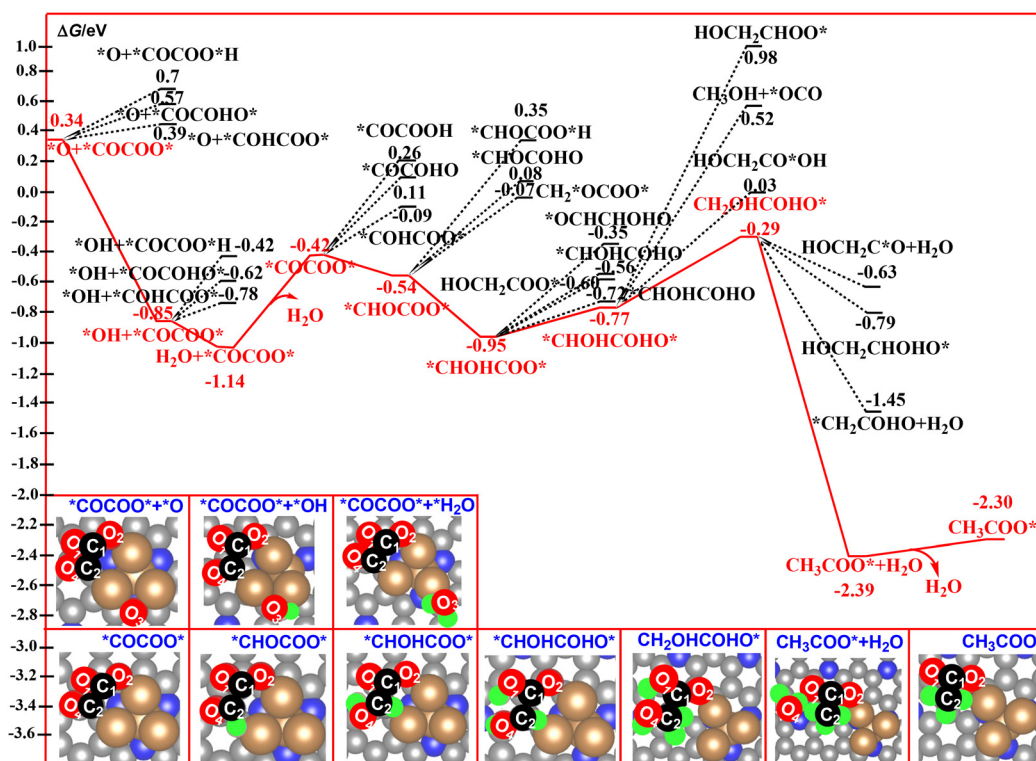


Fig. 6 Calculated free energy profiles for the electrocatalytic reduction of $*O_3 + *OCCOO^*$ to CH_3COO^* .

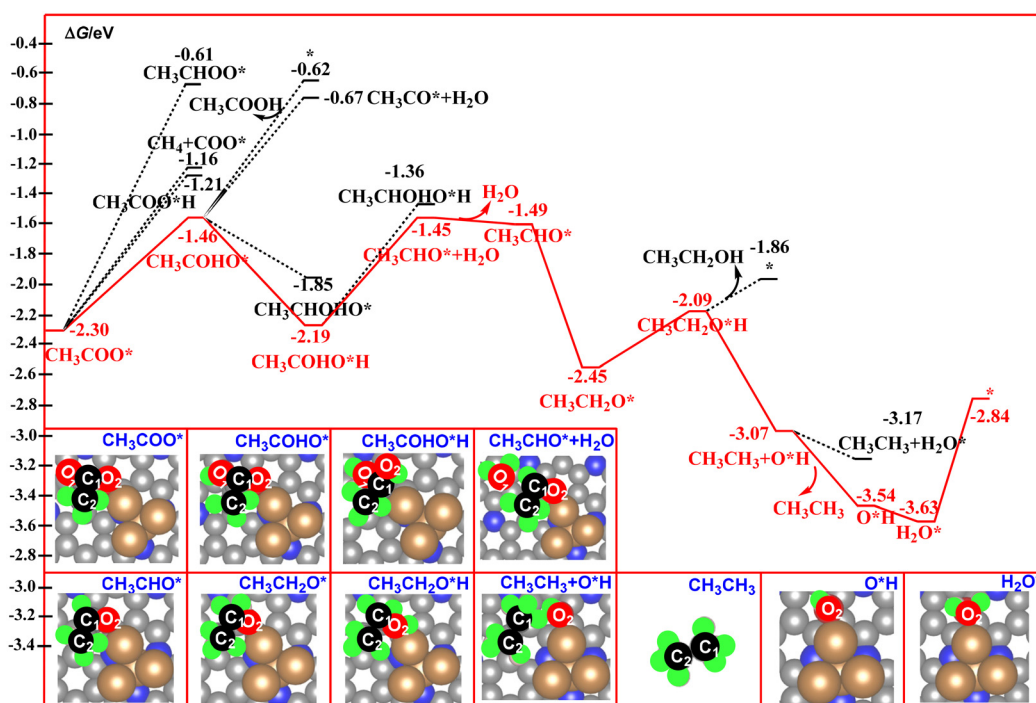


Fig. 7 Calculated free energy profiles for the electrocatalytic reduction of CH_3COO^* to acetic acid, ethanol, and ethane.

ation step is calculated to be most exoergic by 2.10 eV among all of the reaction steps studied here. Desorption of the second H_2O molecule from the catalyst surface leads to the formation

of CH_3COO^* . The calculated desorption energy for this process is 0.09 eV, indicating a very weak interaction of the produced H_2O molecule and the catalyst surface.

For the CH_3COO^* intermediate, it could be reduced to CH_3COOH *via* hydrogenation of the O_2 atom. As shown in Fig. 7, the C_2 atom in CH_3COO^* is in a saturated state *via* formation of three C–H bonds and one C–C bond. Thus, the O_1 , O_2 , and C_1 atoms have been assigned as the potential sites for the reaction with the proton–electron pairs. According to our free energy calculations, hydrogenation of the O_1 atom to form CH_3COHO^* is much more favorable compared to the O_2 and C_1 atoms.

This step is calculated to be exoergic by 0.84 eV. By contrast, hydrogenation of the O_2 atom to form a CH_3COOH molecule over the catalyst surface is calculated to be exoergic by 1.09 eV, and the release of the produced CH_3COOH molecule from the catalyst surface *via* cleavage of the Cu– O_2 bond needs a desorption energy of 0.59 eV. Such results indicate that the strong Cu– O_2 bonding interaction suppresses the formation of the CH_3COOH molecule. By contrast, the continuous hydrogenation of the CH_3COHO^* to $\text{CH}_3\text{COHO}^*\text{H}$ is a favorable path, in which this step is calculated to be exoergic by 0.73 eV. Next, hydrogenation of $\text{CH}_3\text{COHO}^*\text{H}$ to $\text{CH}_3\text{CHO}^* + \text{H}_2\text{O}$ results in the formation of the third H_2O molecule over the catalyst surface with a free energy downhill of 0.74 eV. After desorption of the third H_2O molecule from the catalyst surface, a CH_3CHO^* intermediate is formed with a free energy downhill of 0.04 eV. Further the hydrogenation of CH_3CHO^* results in the formation of the $\text{CH}_3\text{CH}_2\text{O}^*$ intermediate with a free energy downhill of 0.96 eV. For the $\text{CH}_3\text{CH}_2\text{O}^*$ intermediate, the hydrogenation of the O_2 atom of the $\text{CH}_3\text{CH}_2\text{O}^*$ intermediate would produce the $\text{CH}_3\text{CH}_2\text{OH}$ molecule. This step is calculated to be exoergic by 0.36 eV. For the $\text{CH}_3\text{CH}_2\text{O}^*\text{H}$ intermediate, the pathway bifurcates into ethanol- and ethane-forming routes. As shown in Fig. 7, the releasing of the $\text{CH}_3\text{CH}_2\text{OH}$ molecule *via* cleavage of the Cu– O_2 bond is found to be more unfavorable than the formation of the ethane molecule in $\text{CH}_3\text{CH}_3 + ^*\text{OH}$, as the calculated free energy of the former is 1.21 eV higher than that of the latter. Furthermore, desorption of the CH_3CH_3 molecule from the catalyst surface is calculated to be exoergic by 0.47 eV. These results indicate that ethane is the main product of direct CO_2 reduction catalyzed by the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst. Furthermore, the hydrogenation of the produced $^*\text{OH}$ group results in the formation of the fourth H_2O molecule with a free energy downhill of 0.09 eV. Finally, the catalyst was resumed *via* release of the fourth H_2O with a free energy uphill of 0.79 eV. In the whole reaction pathway, the potential-limiting step is still the decomposition of the CO_2 dimer to $^*\text{O} + ^*\text{OCCOO}^*$ with an energy of 1.75 eV, which is lower than the direct coupling of two CO on the Cu (111) surface (1.81 eV). Thus, the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst possesses excellent catalytic activity and high ethane selectivity for direct CO_2 reduction.

4. Conclusions

We have systematically investigated the nitrogen-doped graphene-supported Cu_4 cluster with various structures. Our

optimization calculations show that anchoring the Cu_4 cluster with an inverted-tetrahedron-like structure onto the nitrogen-doped graphene supports results in a catalyst with strong interaction between them, which provides high feasibility in terms of the experimental synthesis of the catalyst. The electronic structure analysis shows that the atomic interface of the inverted-tetrahedron-like Cu_4 cluster possesses a $\text{Cu}^+-\text{Cu}_3^0$ configuration. Furthermore, the three unsaturated Cu^0 species in the Cu_4 cluster are the potential sites for the adsorption and activation of the CO_2 molecules. Our optimization and free energy calculations reveal that the adsorption of two CO_2 molecules over the catalyst surface results in a direct coupling of two inert CO_2 molecules to form a CO_2 dimer with a strong C–C bond. The calculated free energy profiles show that the CO_2 dimerization should be the main reaction relevant to the coupling reaction of $^*\text{OCHO}$ and CO, $^*\text{COOH}$ and $^*\text{CO}$, and two CO molecules. The mechanistic investigation shows that the two adsorbed CO_2 molecules were firstly reduced to $\text{CO}_2^{\cdot-}$ anionic radicals with $[\text{O}=\text{C}^{\cdot}=\text{O}]^-$ configuration *via* an electron transfer process from the surface Cu^0 species to the two CO_2 molecules. Furthermore, the direct coupling of two anionic radicals, $\text{CO}_2^{\cdot-}$, results in the formation of the C–C bond in the CO_2 dimer. The orbital analysis indicates that the bent arrangement of the CO_2 molecule effectively promotes the overlap of two distorted π^* antibonding orbitals, which significantly contribute to the formation of the C–C bond in the CO_2 dimer. The free energy calculation shows that the CO_2 dimer could be reduced to ethane in the series of electrochemical elementary steps. The high ethane selectivity of the $\text{Cu}_4/\text{N}_3\text{GN}$ catalyst mainly arises from the strong Cu–O bonding interaction. This study calls for more fundamental investigations on the mechanism for the formation of the C–C bond in CO_2RR .

Conflicts of interest

The authors declare no competing financial interest.

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