Electrocatalytic CO$_2$ hydrogenation to C$_2$ based products through C–C coupling over Cu(100) nanocube

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Abstract

In this study, we have considered a Cu nanocube (Cu-NC) based catalyst exposed with (100) facets for CO$_2$ hydrogenation reactions. All the feasible mechanistic pathways for the formations of C$_1$ (HCOOH, CH$_3$OH and CH$_4$) and C$_2$ (C$_2$H$_4$ and C$_2$H$_5$OH) based products have been explored using the density functional theoretical calculations and the most plausible pathways have been identified. The calculated results are compared with the previous reports on the periodic Cu(100) and Cu(111) surfaces, and also on the surface of Cu$_{85}$ nanocluster and Cu(111) monolayer. The in-depth mechanistic investigation shows that Cu-NC can be very selective towards the C$_2$ based products with a lower limiting potential (calculated) compared to the periodic surfaces. The underlying reasons for such findings have been explained and compared that with the periodic surfaces. We therefore, propose that the Cu-NC based catalysts can be more promising for C$_2$ based products.

KEYWORDS: Cu(100) nanocube, CO$_2$ hydrogenation, methanol, ethylene, ethanol, density functional theory
1. Introduction

Electrocatalytic CO₂ hydrogenation reaction can be a promising approach for renewable energy production through conversion of CO₂ to liquid fuel and such hydrogenation reactions are also very important for fundamental chemistry such as C-C coupling and C-H bond formation reactions.¹⁻³ Among various metals in heterogenous electrocatalytic CO₂ hydrogenation reaction, Cu has been found as an effective electrocatalyst for CO₂ hydrogenation reaction.⁴ In the case of other electrodes, Ti, Fe, Ni, or Pt-based electrodes are found to be promising for hydrogen productions⁵ whereas Ag, Au or Zn based electrodes are efficient for CO productions⁶,⁷ and Pb, Pd, Au, Cd, In, Sn, or Ru-based electrodes favor formate⁸⁻¹⁰ productions. Hori and co-workers have shown that CH₄ and C₂H₄ are the two major products on Cu based catalysts with high current density and Faradic efficiency (FE).⁴,¹⁰,¹¹ However, the required potential for CO₂ hydrogenation is relatively high (~1.0 V) and therefore, the efficiency of Cu based catalysts is less for such reaction.¹² Further to this, the selectivity of the product is less as various products can be achieved at comparable potential. Hence, the major difficulties in the electrochemical CO₂ hydrogenation reaction are high overpotential and low product selectivity which hamper the development and application of CO₂ hydrogenation reaction. Several research groups have reported that the selectivity and activity of CO₂ hydrogenation reaction are highly influenced by the morphology of the Cu surface. Hori and co-workers have demonstrated that CH₄ is the main product on Cu(111) surface whereas C₂H₄ is the major product on Cu(100) surface.¹³⁻¹⁵ In this context, Koper and co-workers have shown two different pathways on the periodic Cu(100) surface for the formation of C₂ based product.¹⁶⁻¹⁸ Both the pathways have some common intermediates which can form CH₄ at −0.8 to −0.9 V vs reversible hydrogen electrode (RHE). In this case, the most important step for C₂ based product formation is the dimerization of CO at −−0.4 V vs RHE. After these reports,
Calle-Vallejo et al. have investigated the C\(_2\) production mechanism using DFT calculations on periodic Cu(100) surface.\(^{19}\) Nørskov and co-workers have also explored the CO\(_2\) hydrogenation mechanism and shown that CO dimerization barriers on the periodic Cu(100) surface are less compared to that on the periodic Cu(111) surface.\(^{20}\) Recently a detailed mechanistic pathways, required potentials, and various product selectivity have been investigated by Asthagiri and co-workers on periodic Cu(100) surface.\(^{21}\) After this, Head-Gordon and co-workers have shown the mechanism of various C\(_2\) based products on Cu(100) surface and compared with Cu(111) surface.\(^{22}\) All of these reports show that the C–C bond formation step is favourable on the Cu(100) facet compared to that on the Cu(111) facet. Even if Cu based electrodes are a good choice for the development of CO\(_2\) hydrogenation reaction, the high potential and selectivity still needs to be developed. In an effort to produce highly selective C\(_2\) based products, Cu nanoparticles with (100) facets have been used in earlier studies.\(^{23-25}\) In the case of nanoparticles, exposed (100) facet surface area is more compared to that on the periodic Cu(100) surface i.e., catalytic activity is more. Recently, Nilsson and co-workers have reported that Cu nanocube exposed with (100) facet shows more selectivity towards C\(_2\) based product at a very low overpotential.\(^{26}\) Their report shows that C\(_2\)H\(_4\) can be formed at \(-0.60\) \(\text{V}\) and CH\(_4\) can be formed at \(-0.93\) \(\text{V}\) vs. RHE. However, C\(_2\) based product, C\(_2\)H\(_4\) and C\(_2\)H\(_5\)OH is obtained along with some undesired H\(_2\), HCOO\(^-\), CH\(_3\)OH and CH\(_4\) products. Even after several excellent experimental and theoretical reports, the underlying reason behind Cu surface structure and the selectivity of the product is still unknown. Specifically, the most favourable pathways of various products with their adsorption energy and reaction free energy are not fully understood. Therefore, finding out the most favourable mechanisms for all C\(_1\) and C\(_2\) based products are highly essential to get the idea about the product selectivity of any catalyst. Experimental mechanistic studies of CO\(_2\) hydrogenation reaction are very challenging.
due to the complexities of spectroscopic operation on the reactants and intermediates. Even if several experimentalists have shown via in situ IR spectroscopy and confirmed CO$_2$, CO, and formate are important intermediates, this cannot identify all the surface species during the reaction specially for two carbon atoms-based products.$^{27,28}$ Besides, Koper and co-workers have proposed a CO$_2$ hydrogenation mechanism, but it does not include all the possible pathways of CO$_2$ hydrogenation reaction.$^{16}$ Their study can identify only the stable intermediates and it is obtained after observing the product only. So, the theoretical free energy calculations of all the possible pathways are very promising in terms of identifying the reaction pathways. In an effort to this, Rossmeisl and co-workers have shown various important intermediates for alcohol formation.$^{29}$ Hence, it is highly essential to theoretically investigate the full mechanistic pathways due to the limitation in experimental studies. However, C$_2$H$_4$ and C$_2$H$_5$OH are highly useful C$_2$ based CO$_2$ hydrogenated product along with various C$_1$ based products (HCOOH, CH$_3$OH and CH$_4$)$^{30-34}$ For example, C$_2$H$_4$ is an important feedstock in chemical industries as C$_2$H$_4$ oligomerization can produce highly valuable ethylene oxide, polyethylene, and diesel. Besides, C$_2$H$_5$OH can be used as a chemical feedstock for C$_2$H$_4$, glycol ether, amines, and esters formation. Hence, the present study investigates the development of CO$_2$ hydrogenation reaction mechanistic pathways for the formation of C$_1$ as well as C$_2$ based products. For this, we have modelled a Cu nanocube (Cu-NC) exposed with Cu(100) facets (Figure 1), as such nanoparticles have been experimentally reported to be more efficient and selective catalyst compared to the periodic Cu(100) surface/facet for the C–C coupling and therefore formation of C$_2$ based products. As a part of the attempt, stability of the Cu-NC, adsorption energy of all the considered intermediates and reaction free energy of each elementary steps have been calculated. These adsorptions and reaction free energy information can give a quantitative idea of the Cu electrode for CO$_2$ hydrogenation reaction based on the surface
morphology, and which can guide the future direction of modelling efficient catalyst. Shortly, in this work, we have computationally investigated the most plausible pathways of C$_1$ and C$_2$ based CO$_2$ hydrogenated products (such as CH$_3$OH, HCOOH, CH$_4$, C$_2$H$_4$ and C$_2$H$_5$OH) on the Cu-NC and found out the factors responsible for favoring those reaction pathways.

Figure 1: Modelled Cu nanocube (Cu-NC) exposed with Cu(100) surface for CO$_2$ hydrogenation reaction.

2. Computational Details

All the first principles calculations have been performed using the projector augmented wave (PAW) method as employed in the Vienna Ab initio Simulation Package (VASP).$^{35-37}$ The description of the exchange-correlation interaction in the calculation has been incorporated with the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functional.$^{38-40}$ The Grimme’s D3 semiempirical dispersion energy corrections have also been included in our calculations to account the corrections for the non-covalent interactions.$^{41}$ More than 15 Å vacuum space has been considered in all the three directions to avoid any periodic interactions. The plane-wave basis cutoff energy has been set to 470 eV. Here all the structures were optimized until the
energy convergence criteria becomes less than that of $1 \times 10^{-4}$ eV and forces become less than 0.02 eV/Å. Moreover, we have calculated the total energies of the Cu NC using a series of k-points (1×1×1, 3×3×3 and 5×5×5 gamma centered k-points grid) and it has been observed a little improvement of $9.2 \times 10^{-4}$ and $7.1 \times 10^{-4}$ eV in the total energy using 3×3×3 and 5×5×5 gamma centered k-points, respectively compared to 1×1×1 gamma centered k-points. Hence, all the calculations have been performed using 1×1×1 gamma centered k-points. We have calculated adsorption energies of all the considered CO$_2$ hydrogenation intermediates using the following equation (1):

$$E_{\text{ad}} = E_{\text{NC+adsorbate}} - (E_{\text{adsorbate}} + E_{\text{NC}})$$

(1)

In the above equation (1), $E_{\text{ad}}$ is the adsorption energy of any intermediate, $E_{\text{NC+adsorbate}}$ is the total energy of the optimized NC with adsorbate whereas $E_{\text{adsorbate}}$ and $E_{\text{NC}}$ are the single point energies of adsorbate and Cu-NC (within the optimized geometry of NC+adsorbate) respectively. In the case of the H atom energy, we have used the computational hydrogen electrode (CHE) model concept as reported by Nørskov and co-workers.$^{42}$ Moreover, for the calculation of reaction free energy of each elementary steps we have used the following equation (2):

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

(2)

In the above equation (2), $\Delta G$ is the reaction free energy of the considered particular elementary step, $\Delta E$ is the total energy difference of the final and initial states of the considered step, $\Delta ZPE$ is the change in zero-point energy, $\Delta S$ is the change in entropy of the considered step and $T$ is the temperature. The zero-point energy has been calculated using $\sum \frac{1}{2}h\nu_i$ where $h$ is the Planck’s constant and $\nu_i$ is the vibrational frequency. Here, we have neglected the entropy term during the reaction free energy calculation of each elementary step. During an external applied potential ($U$),
the chemical potential of each step shifts by $eU$ where $e$ is the electronic charge transferred in each elementary step.\textsuperscript{43,44} Moreover, we have checked transition states and calculated the energy barriers for some of the important steps using the nudged elastic band (CI-NEB, six climbing-image) and dimer methods.\textsuperscript{45,46} In this case we have not considered the effect of pH as reversible hydrogen electrode (RHE) is considered as 0 V at all pH values.\textsuperscript{44} A set of 3×3×3 k-point grid has been used for some of the important intermediates to investigate the electronic structure of the intermediates. We have also characterized all the intermediates by examining the absence of vibrational frequency. Besides, the Bader atomic charges of some of the important intermediates have been calculated using the Henkelman code with the near-grid algorithm refine-edge method.\textsuperscript{47-49} The adsorbed intermediates have been represented by an asterisk sign (*) throughout the manuscript.

3. Results and discussion

In this section, we have discussed the Cu-NC stability using energetic, dynamic, and thermal stability analysis. After stability analysis, we have considered the stable form of the Cu-NC for the investigation of CO$_2$ hydrogenation reaction catalytic activity based on the adsorption energy of each considered intermediates and reaction free energy of every elementary step for C$_1$ and C$_2$ based product formation.

3.1. Stability analysis

The stability of the considered Cu-NC has been examined through various approaches. At first, we have investigated the energetic stability by calculating the formation and cohesive energies of the
Cu-NC to check the stability of the considered structure with respect to the bulk Cu structure. We have used equation 4 and equation 5 for the calculation of cohesive energy ($E_{\text{coh}}$) and formation energy ($E_{\text{for}}$) of the considered Cu-NC respectively.\textsuperscript{50,51}

$$E_{\text{coh}} = \frac{E_{\text{Cu-NC}}}{N} - E_{\text{Cu}} \quad (4)$$

$$E_{\text{for}} = \frac{E_{\text{Cu-NC}}}{N} - \mu_{\text{Cu}} \quad (5)$$

In the above equations, $E_{\text{Cu-NC}}$, $E_{\text{Cu}}$, $\mu_{\text{Cu}}$, and $N$ are the total energy of the Cu-NC, energy of an isolated Cu atom, chemical potential of a Cu atom and total number of atoms present in the Cu-NC, respectively. For comparisons, we have also calculated the formation energy and cohesive energy of the periodic Cu(100) and Cu(111) surface and then compared with the available experimental values. Our calculated formation and cohesive energy values are tabulated in Table 1. The calculated formation and cohesive energy values for periodic Cu(111) surface are in agreement with the experimental formation and cohesive energy values on periodic Cu(111) surface.\textsuperscript{52} Hence, the considered level of theory is acceptable for further study. Further to this, we have checked the dynamic stability of the Cu-NC using density functional perturbation theory which is implemented in VASP. Our calculated, dynamic stability analysis shows imaginary frequency in the order of \textasciitilde 40i cm\textsuperscript{-1}. Several earlier reports have shown that the systems can be considered as stable if the imaginary frequency is below 35i cm\textsuperscript{-1}.\textsuperscript{53,54} Therefore, the considered Cu-NC is dynamically unstable structure i.e., Cu-NC has a possibility of interconversion to other form. Even though our considered approach is electrochemical there will be some nonelectrochemical steps which can be performed at experimental thermal condition. In general, thermal CO\textsubscript{2} hydrogenation reaction is performed at 473–573 K temperature.\textsuperscript{55} So, it is highly important to check the stability of the considered Cu-NC at that temperature range for the operation of the reaction. To investigate these aspects, we have investigated the thermal stability of Cu-NC
at 300, 400 and 500 K (Figure 2a) using ab initio molecular dynamics (AIMD) simulations with Nose´ thermostat model and NVT ensemble with a time step of 1 femtosecond (fs) for 20 picoseconds (ps). We find that there is no significance change in the energy as well as structure throughout the simulation of the Cu-NC at 300 K. However, we have noticed fluctuation in energy at 400 K after 13 ps. The same has been observed at 500 K after 10 ps. Therefore, we have checked the structure of the Cu-NC after the completion of the simulation at 400 and 500 K. All the structures obtained after completion of the AIMD simulation have been shown in Figure S1. We have found a significant change in the Cu-NC structure after completion of the AIMD simulation at 400 and 500 K. The Cu-NC is now converted into another geometry, where the structure looks like an octahedral structure (Figure 2b). Therefore, there is a chance of interconversion of the Cu-NC during the operation of the CO₂ hydrogenation reaction. Hence, we have considered the distorted Cu-NC (Cu-dNC) and checked its stability using energetic, dynamic, and thermal stability analysis.

**Table 1**: Formation and cohesive energies of Cu-NC, Cu-dNC, periodic Cu(100) and Cu(111) surface. The experimental formation and cohesive energy values for the periodic Cu(111) surface are given in parenthesis for comparisons.

| Cu-NC and periodic systems     | Formation energy (eV/atom) | Cohesive energy (eV/atom) |
|-------------------------------|----------------------------|---------------------------|
| Cu-NC                         | 1.03                       | -2.96                     |
| Cu-dNC                        | 0.99                       | -3.01                     |
| periodic Cu(100) surface      | 0.46                       | -3.54                     |
| periodic Cu(111) surface      | 0.26 (0.31)²⁺               | -3.85 (-3.49)²⁺           |

Our calculated cohesive and formation energy values indicated that the simulated Cu-dNC is more stable than the Cu-NC. Furthermore, we have checked the dynamic stability of Cu-dNC using
phonon calculation as implemented in VASP. Our study shows very small imaginary frequency up to 10i cm$^{-1}$. Hence, the Cu-dNC structure is dynamically more stable compared to the Cu-NC structure. After confirmation of energetic and dynamic stability of the Cu-dNC, we have examined the thermal stability of the Cu-dNC at 300, 500 and 700 K for 20 ps with a time step of 1 fs (Figure 2b). All the structures obtained after completion of the AIMD simulation of Cu-dNC have been shown in Figure S2. Our AIMD simulations show there are no significant change in the energy as well as structure throughout the calculation at 300 K. The overall energy fluctuation is also less even at 500 and 700 K. Hence, the interconversion possibility to other local minimum energy structure of the Cu-dNC during the reaction is not expected in the 300 to 700 K temperature range. So, we can say Cu-dNC is a stable structure and therefore considered as a model catalyst for the CO$_2$ hydrogenation reaction.
**Figure 2:** (a) Optimized structures of the Cu-NC and ab initio molecular dynamics (AIMD) simulations of Cu NC at 300, 400 and 500 K. (b) Optimized structures of the Cu-dNC and AIMD simulations of Cu-dNC at 300, 500 and 700 K.

### 3.2. Adsorption of different intermediates

Here, we have checked the applicability of Cu-dNC for CO$_2$ hydrogenation reaction in detail. At first, all the possible intermediates are identified, which can be formed during the CO$_2$ hydrogenation for the formation of C$_1$ (HCOOH, CH$_3$OH and CH$_4$) and C$_2$ based products (C$_2$H$_4$ and C$_2$H$_5$OH). All the possible adsorption sites on the Cu-dNC have been identified for all the considered intermediates as shown in Figure 3. There are four top, four bridge and three possible hollow sites on the Cu-dNC surface. Therefore, all these adsorption sites have been taken into consideration for the adsorption energy calculations of the intermediates. The preferred adsorption sites and adsorption energies are listed in Table 2 whereas the respective geometries for C$_1$, H, O and H$_2$O intermediates are shown in Figure S3 and the respective geometries for C$_2$ based intermediates are shown in Figure S4.
The calculated adsorption energies of most of the C$_1$ based intermediates are higher on the Cu-dNC surface compared to that on the periodic Cu(111) surface. However, CO$_2$ interacts very weakly with an adsorption energy of -0.19 eV on the Cu-dNC surface. The same has been observed in several experimental and theoretical studies. The *COOH intermediate also binds weakly on whereas *HCOO binds strongly on the catalytic surface. This may be due to the presence of two strong Cu–O bonds in case of *HCOO whereas in case of *COOH one Cu–C bond is present along with one Cu–O bond. Furthermore, to understand the reason behind the trends of adsorption energy, we have checked the projected density of states (PDOS) for *COOH and *HCOO. From Figure 4a-b, it is clear that the overlap among Cu-d orbitals and C+O-p orbital is less compared to the overlap among Cu-d orbitals and 2O-p orbital. Moreover, our calculated Bader atomic charges show that 0.29 |e| and 0.25 |e| charges are transferred from the Cu surface to the two O atoms of *HCOO, respectively whereas 0.26 |e| and 0.12 |e| charges are transferred from the Cu surface to the O and C-atom of *COOH. So, the amount of charge transfer is more for *HCOO compared to that for *COOH. Hence, adsorption energy is more in case of *HCOO on Cu-dNC compared to that for the *COOH. Another two important intermediates of CO$_2$ hydrogenation to C$_1$ based product formation are *HCO and *COH. In general, *HCO and *COH are two crucial intermediates for the selective C$_1$ based product formation of CH$_3$OH and CH$_4$, respectively. Our calculated results show that *HCO binds weakly on the catalytic surface compared to the *COH. The calculated Bader atomic charges show that 0.13 |e| charges are transferred from the Cu surface to the C atom of *HCO whereas 0.15 |e| charges are transferred from the Cu surface to the C-atom of *COH. So, the amount of charge transfer is more for *COH compared to the *HCO from Cu-dNC i.e., adsorption energy is more for *COH compared to the *HCO. Besides, the
*H₂CO binds strongly on the catalytic surface compared to the periodic Cu(111) surface\(^\text{57}\) i.e., the *H₂CO can be hydrogenated further for CH₃OH formation rather than desorption from the catalytic surface.

**Table 2**: Preferred adsorption sites and the adsorption energies of all the CO₂ hydrogenation related intermediates on the Cu-dNC.

| C₁ based, H, O and H₂O intermediates | C₂ based intermediates |
|--------------------------------------|------------------------|
| Intermediates                        | Adsorption energy      | Intermediates                        | Adsorption energy |
|                                      | on Cu-dNC (eV)         |                                      | on Cu-dNC (eV)    |
| *CO₂ (T2)                            | -0.19                  | *HCO-HCO (B3)                        | -2.35             |
| *COOH (B3)                           | -2.84                  | *HCO-HCOH (B3)                       | -2.59             |
| *HCOO (B1)                           | -4.09                  | *HCO-CO (B3)                         | -3.14             |
| *HCOOH (T1)                          | -1.04                  | *COH-CO (B1)                         | -3.67             |
| *CO (T2)                             | -1.28                  | *C-CO (B4)                           | -5.40             |
| *HCO (T1)                            | -1.96                  | *C₂H₄ (T2)                           | -1.19             |
| *COH (B4)                            | -3.71                  | *HC-CO (B3)                          | -3.55             |
| *H₂COOH (B3)                         | -3.53                  | *H₂C-CO (B3)                         | -3.15             |
| *H₂CO (B1)                           | -1.94                  | *HC-HCO (H3)                         | -4.99             |
| *HCOH (B1)                           | -2.72                  | *H₂C-HCO (H2)                        | -3.20             |
| *H₂COH (B1)                          | -2.37                  | *H₂C-H₂CO (B1)                       | -4.64             |
| *H₃CO (H3)                           | -3.12                  | *HC-COH (H3)                         | -5.78             |
| *H₂COH (T2)                          | -0.76                  | *C-HC (H3)                           | -4.81             |
| *C (B4)                              | -6.24                  | *C-H₂C (B4)                          | -3.95             |
| *CH (B4)                             | -6.02                  | *HC-HC (H3)                          | -4.85             |
| *CH₂ (H3)                            | -4.21                  | *HC-H₂C (B3)                         | -3.26             |
| *CH₃ (T1)                            | -2.38                  | *H₂C-HCOH (T2)                       | -1.16             |
| *CH₄ (T2)                            | -0.25                  | *H₂C-HCO (B4)                        | -0.95             |
| *H (H3)                              | -2.70                  | *H₂C-H₂CO (H3)                       | -3.19             |
| *O (H3)                              | -5.60                  | *H₃C-HCOH (T1)                       | -2.41             |
| *H₂O (T4)                            | -0.44                  | *H₃C-H₂COH (T3)                      | -0.77             |

In case of C₂ based products, intermediates adsorption energies are more compared to the adsorption energies of C₁ based intermediates. However, *HC-HCO adsorption energy is more compared to the *H₂C-CO adsorption energy as one extra strong Cu–O bond (1.936 Å) is present in case of *HC-HCO (Figure S4). The same has been observed in case of *H₂C-H₂CO (Cu–O bond
length is 1.843 Å) where adsorption energy is 3.48 and 3.69 eV high compared to the *H₂C-HCOH and *H₃C-HCO adsorption energy, respectively. Moreover, the adsorption energy of *H₃C-H₂CO is 0.78 eV more compared to the adsorption energy of *H₃C-HCOH. In this case also higher adsorption energy is due to the O binding with the active surface.

**Figure 4:** Projected density of states plot of (a) *COOH, (b) *HCOO, (c) *C-H₂C, and (d) *HC-HC intermediates on Cu-dNC.

On the other hand, the adsorption energy of *HC-HC is 0.90 eV higher than that of *C-H₂C. This may be due to the presence of two single Cu-C in *HC-HC. To understand the reason behind the trends of adsorption energy we have checked the PDOS for *C-H₂C and *HC-HC. From Figure 4c and 4d it is clear that the overlap between Cu-d orbitals with C-p orbital is less for *C-H₂C compared to the overlap between Cu-d orbitals with C-p orbital of *HC-HC. Hence, adsorption energy is more in case of *HC-HC on Cu-dNC compared to that for *C-H₂C. Further to this, we
have noticed that presence of adsorbate on the catalytic surface does not distort the catalyst. Therefore, the nano catalyst is stable even in the presence of adsorbates.

3.3. CO$_2$ hydrogenation to C$_1$ based product formation

In this section, we have considered all the possible mechanistic pathways for C$_1$ based product formation from CO$_2$ and identified the most plausible pathways along with the potential determining steps (PDS) responsible for such reaction on the Cu-dNC. All the considered mechanistic pathways for the CO$_2$ hydrogenation to HCOOH, CH$_3$OH and CH$_4$ along with the calculated reaction free energies associated for each of those mechanistic steps are shown in Scheme 1.

3.3.1. Formation of HCOOH: Several earlier studies have confirmed that HCOOH is a common CO$_2$ hydrogenated product. Hence, we have started our discussion of mechanistic investigation from CO$_2$ to HCOOH. The adsorption energy analysis shows that CO$_2$ interacts weakly with the Cu-dNC surface. However, the calculated reaction free energy value shows that the CO$_2$ adsorption process is exergonic by 0.22 eV. Our earlier report has also shown that the reaction free energy of CO$_2$ adsorption step is exergonic on ZnO and Cu dopped ZnO based nanocages.$^{61}$ In the presence of H, one of the C=O bonds of *CO$_2$ can be weakened due to the hydrogenation at the C-center for the formation of *HCOO. Moreover, the *HCOO intermediate can be hydrogenated further at the O-center of *HCOO for the production of *HCOOH. Lastly, the HCOOH can be removed from the catalytic surface and the removal of HCOOH is 0.95 eV endergonic in nature. So, a massive input of energy is required for the separation of HCOOH from the catalytic surface.
The formation of *HCOOH from *HCOO is calculated to be the potential rate determining step with a reaction free energy of 0.55 eV and the most favourable pathway for CO₂ hydrogenation to HCOOH on the Cu-dNC is * + CO₂ → *CO₂ → *HCOO → *HCOOH → * + HCOOH.

**Scheme 1**: All the possible mechanistic pathways with reaction free energies (in eV) for CO₂ hydrogenation reaction to HCOOH, CH₃OH and CH₄ on Cu-dNC. The values given in the parenthesis are the activation barriers in eV at 0 V vs. RHE. The common intermediates of most favourable pathways are highlighted in magenta color and the intermediates determine the selectivity of HCOOH, CH₃OH and CH₄ are highlighted in green, blue and red colors, respectively. The solid and hollow arrow heads represent the exergonic and endergonic steps, respectively.

3.3.2. Formation of CH₃OH: The CH₃OH is another important C₁ based CO₂ hydrogenated product. In this context several experimental studies have reported that *CO is an essential
intermediate for the formation of CH$_3$OH.$^{27,28}$ The adsorbed $^*$CO$_2$ can be hydrogenated at the O-center for the formation of $^*$CO. Our calculated results demonstrate that the formation of $^*$CO ($^*$COOH→$^*$CO) is calculated to be very much reversible with a reaction free energy of 0.07 eV. Subsequently, $^*$CO can be hydrogenated for the formation of $^*$HCO/$^*$COH. Previous reports have shown that the $^*$HCO is responsible for CH$_3$OH formation whereas $^*$COH is responsible for CH$_4$.$^{57,61-63}$ Therefore, the product selectivity is very much dependent on the $^*$CO hydrogenation step. Scheme 1 shows that $^*$HCO formation is 0.54 eV more favourable compared to the formation of $^*$COH. Moreover, our calculated activation barriers also shows that CH$_3$OH formation will proceeds via $^*$HCO intermediate. Hence, we can conclude that CH$_3$OH formation is more favourable compared to CH$_4$ formation on the Cu-dNC. We have also found out that $^*$HCO formation is 0.10 eV more favourable on Cu-dNC compared to the $^*$HCO formation on the periodic Cu(100) surface as reported by Asthagiri and co-workers using the same level of theory.$^{21}$ Besides, $^*$COH formation is 0.32 eV is more favourable on the periodic Cu(100) surface compared to that on the Cu-dNC as reported by Asthagiri and co-workers.$^{21}$ All these results indicate that Cu-dNC can be more selective towards CH$_3$OH formation compared to the periodic Cu(100) surface. In the next step, $^*$HCO can be hydrogenated for the formation of $^*$H$_2$CO/$^*$HCOH. Besides, $^*$H$_2$CO/$^*$HCOH can be produced via other pathways as shown in scheme 1. The calculated results show that the formation of $^*$H$_2$CO is 1.14 eV more favourable compared to the formation of $^*$HCOH. Subsequently, $^*$H$_2$CO can be hydrogenated to $^*$H$_3$CO/$^*$H$_2$COH whereas $^*$HCOH can be hydrogenated to $^*$H$_2$COH. The $^*$H$_3$CO formation is exergonic whereas $^*$H$_2$COH formation is endergonic from $^*$H$_2$CO i.e., the reaction will proceed via $^*$H$_3$CO. Further to this, $^*$H$_3$CO and $^*$H$_2$COH can be hydrogenated for the formation of CH$_3$OH. Eventually, CH$_3$OH can be separated, and the calculated results show that the removal of CH$_3$OH requires an amount of
0.73 eV energy. Considering all the above pathways and the most favourable CO₂ hydrogenation to CH₃OH pathway is * + CO₂ → *CO₂ → *COOH → *CO → *HCO → *H₂CO → *H₃CO → *H₃COH → * + CH₃OH, where the formation of the *CO → *HCO is the PDS with a reaction free energy of 0.52 eV. The previous reports on various Cu based surfaces [Cu(100) surface,²¹ Cu₈₅ nanocluster,⁵⁷ periodic Cu(111) surface⁶³ and Cu(111) monolayer⁶²] have also reported that *CO → *HCO is the PDS for CO₂ hydrogenation to CH₃OH reaction. However, the calculated reaction free energy value of the PDS indicates that Cu-dNC can be used as an active catalyst compared to the periodic Cu(100), Cu(111) surface and Cu₈₅ nanocluster for CH₃OH formation.²¹,⁵⁷,⁶³

3.3.3. Formation of CH₄: Along with HCOOH and CH₃OH, we have also investigated the mechanistic pathways of CO₂ hydrogenation to CH₄ formation via *COH intermediate. Here, *COH can be hydrogenated at the O-center followed by removal of H₂O and produce *C. Subsequent hydrogenations of *C would lead to the formation of *HC, *H₂C, *H₃C and *H₄C. Our calculated reaction free energy values indicate that all these subsequent hydrogenation steps are exergonic. In the final step, CH₄ can be separated from the catalytic surface of Cu-dNC with a reaction free energy of 0.25 eV. The *CO → *COH is the PDS for CO₂ hydrogenation to CH₄ with a reaction free energy of 1.06 eV. Hence the selectivity towards CH₄ formation would be less on the Cu-dNC. Earlier reports have shown that the reaction free energy of *CO → *COH step is 0.74, 1.11 and 0.71 eV on the periodic Cu(100) surface,²¹ Cu(111) monolayer⁶² and Cu₈₅ nanocluster,⁵⁷ respectively. Hence, formation of CH₄ is highly unfavourable on the Cu-dNC compared to the periodic Cu(111) surface and Cu₈₅ nanocluster and therefore, Cu-dNC can be highly selective towards CH₃OH formation compared to the CH₄ formation.
3.4. CO$_2$ hydrogenation to C$_2$ based product formation

Here we have considered all the possible mechanistic pathways for C$_2$ based products formation from CO$_2$ and identified the most plausible pathways with minimum applied potential on the Cu-dNC. It has been revealed in the previous section that at first CO$_2$ is converted to CO and several studies have shown that by CO$_2$ hydrogenation to C$_2$ based products formation proceeds via CO. Hence, we have considered all the mechanistic pathways from *CO as shown in Scheme 2.

3.4.1. Formation of C$_2$H$_4$: The C$_2$H$_4$ is the simplest and highly useful C$_2$ based hydrocarbon which can be obtained from CO$_2$. Various mechanistic pathways have been investigated via *HCO and *COH pathways as illustrated in Scheme 2. As shown in scheme 2, *CO can be hydrogenated to *HCO and *COH and can be dimerized to form C$_2$ based intermediates. There can be various nonelectrochemical steps to obtain C$_2$ based intermediates like *COH-CO, *HCO-HCO, *HCO-CO and *CO-CO. We have not discussed the *CO dimerization step as we could not able to optimize the *CO-CO intermediate on the Cu-dNC catalytic surface. Most of these nonelectrochemical dimerization steps are exergonic whereas the formation of *COH-CO formation is calculated to be more or less reversible and the *HCO-CO formation is endergonic. Our calculated activation barriers also reveal that dimerization of *HCO to *HCO-HCO is 1.61 eV more favourable compared to the *HCO-CO formation. Recently, Wang and co-workers have shown that the *HCO dimerization step is exergonic on the Cu(111) and F–Cu(111) facets. The same has been observed by Asthagiri and co-workers on the periodic Cu(100) surface. Hence, the CO$_2$ hydrogenation to C$_2$ based product may mainly proceed via *HCO-HCO intermediates. After the nonelectrochemical dimerization steps, subsequent proton transfer leads to the formation of various intermediates like *C-CO from *COH-CO, *HCO-HCO from *HCO-CO and *HCO-
HCOH from *HCO-HCO. All of these proton transfer steps are exergonic in nature. Subsequently, *HCO-HCOH can be hydrogenated at the OH-center for the formation of *HC-HCO. Subsequent hydrogenation at the CH-center of the *HC-HCO leads to the formation of *H2C-HCO with a reaction free energy of -0.44 eV. Then, *H2C-HCO can form *H2C-HCOH which is also an exergonic step. The successive hydrogenation and removal of water will form *HC-H2C which can be a reversible step (0.02 eV). The further hydrogenation of *HC-H2C would lead to the formation of *C2H4. Moreover, we have investigated the further hydrogenation of *C-CO even though this pathway is unfavourable. The subsequent hydrogenation of *C-CO would result in the formation of *C2H4 via *HC-CO, *HC-COH, *C-HC, *C-H2C/*HC-HC and *HC-H2C intermediates. We have also identified the *C2H4 formation pathway via nonelectrochemical *H2C dimerization step. Ultimately, C2H4 can be removed from the surface for the regeneration of the catalyst. This step requires an amount of 1.08 eV energy. Among all the probable pathways, the most favourable pathway for CO2 hydrogenation to C2H4 is * + CO2 → *CO2 → *COOH → *CO → *HCO → *HCO-HCO → *HCO-HCOH → *HC-HCO → *H2C-HCO → *H2C-HCOH → *HC-H2C → *C2H4 → * + C2H4 with a reaction total free energy of -1.02 eV. Hence, CO2 hydrogenation to C2H4 is thermodynamically favourable. Nørskov and co-workers have also shown that C2H4 pathways proceeds via *CHO and *HCO-HCO intermediates at -0.74 V.44 Moreover, our investigated route for C2H4 formation is similar as reported by Asthagiri and co-workers on the periodic Cu(100) surface.21 Conversely, the most favourable pathway is different from Head-Gordon’s report as they have shown *COCHO formation is exergonic for C2 based products formation.22 Moreover, our calculated results show that *CO → *HCO is the PDS for C2H4 formation with a reaction free energy of 0.52 eV. Besides, the *CO → *HCO, *H2C-HCOH → *HC-H2C, *HC-H2C → *C2H4 and *C2H4 → * + C2H4 steps are endergonic which can be
downhill at applied potential of -0.52 V. Astagiri and co-workers have also shown that the *CO → *HCO step is most endergonic step with a reaction free energy of 0.62 eV on the periodic Cu(100) surface for C₂H₄ formation.²¹ Along with this, Nilsson and co-workers have reported that CO₂ can be converted to C₂H₄ at -0.60 V on the Cu cube.²⁶ Hence, formation of C₂H₄ is highly favourable on the Cu-dNC compared to that on the periodic Cu(100) surface.

Scheme 2: All the possible mechanistic pathways with reaction free energies (in eV) for CO hydrogenation reaction to C₂H₄ and C₂H₅OH on Cu-dNC. The values given in the parenthesis are the activation barriers in eV at 0 V vs. RHE. The common intermediates of most favourable pathways are highlighted in blue color and the intermediates determine the selectivity of C₂H₄ and
C₂H₅OH are highlighted in magenta and green colors, respectively. The solid and hollow arrow heads represent the exergonic and endergonic steps, respectively.

3.4.2. **Formation of C₂H₅OH:** Along with C₂H₄ another important C₂ based CO₂ hydrogenated product is C₂H₅OH. Therefore, we have investigated the CO₂ hydrogenation to C₂H₅OH mechanistic pathways. There are some common intermediates for C₂H₅OH and C₂H₄ formations. The common intermediates of most favourable pathway for C₂H₄ formation are *CO, *HCO, *HCO-HCO, *HCO-HCOH, *HC-HCO, and *H₂C-HCO. In case of C₂H₅OH, the formation of *HCO-HCO is more favourable as it can be reduced to C₂H₅OH. The *HCO-HCO intermediate has also been identified for C₂H₅OH formation by several groups on periodic Cu(100) surfaces.²¹,²² After identifying the common intermediates, possible pathways for C₂H₅OH formation have been investigated by calculating the reaction free energy of all the possible elementary step. The *H₂C-HCO can form C₂H₅OH via hydrogenation at three different positions and may form *H₂C-HCOH, *H₃C-HCO and *H₂C-H₂CO. The calculated reaction free energy values show that the hydrogenation step of *H₂C-HCO is exergonic if protonation occurs only at the O-center of the *H₂C-HCO. Then, further hydrogenation at the H₂C-center of *H₂C-HCOH and hydrogenation at the O-center of the *H₃C-HCO may form *H₃C-HCOH. Besides, hydrogenation at the HC-center of *H₃C-HCO and hydrogenation at the H₂C-center of *H₂C-H₂CO produce *H₃C-H₂CO with reaction free energies of -0.51 and -0.64 eV, respectively. In the next step, *H₃C-HCOH and *H₃C-H₂CO can be converted to *H₃C-H₂COH. Eventually, C₂H₅OH can be removed from the catalytic surface of Cu-dNC. This step is highly endergonic with a reaction free energy of 1.30 eV. Therefore, the amount of C₂H₅OH production is expected to be less. However, the most favourable pathway for CO₂ hydrogenation to C₂H₅OH is * + CO₂ → *CO₂ → *COOH → *CO → *HCO → *HCO-HCO → *HCO-HCOH → *HC-HCO → *H₂C-HCO → *H₃C-HCO → *H₃C-H₂CO →
\[
\text{H}_2\text{C}-\text{H}_2\text{COH} \rightarrow * + \text{C}_2\text{H}_5\text{OH} \text{ with a total reaction free energy of } -1.54 \text{ eV. Besides, *CO } \rightarrow \text{ HCO is the PDS with a reaction free energy of } 0.52 \text{ eV. Recently, Yeo and co-workers have shown } \text{C}_2\text{H}_5\text{OH pathway via *CH and *CO coupling on Cu(111) surface which are different than that of our favourable pathway on the Cu-dNC.}\]

\text{However, the *CO } \rightarrow \text{ HCO has also been reported to be the PDS by several other studies on periodic Cu(100) surface but the required reaction free energy of the PDS step is higher in those studies than that on the Cu-dNC for } \text{C}_2\text{H}_5\text{OH formation.}\]

\text{Therefore, Cu-dNC can be an efficient catalyst for } \text{C}_2\text{H}_5\text{OH formation from CO}_2.\]

4. \textbf{Comparison among C}_1 \text{ and C}_2 \text{ based products}

In this section, we have compared the C\textsubscript{1} and C\textsubscript{2} based products on the basis of working potential. The working potential is the minimum required potential at which all the elementary reaction steps become exergonic or reversible.\textsuperscript{43} Hence, the required working potential is the potential of the most endergonic step i.e., PDS. In this case we have considered the most plausible mechanistic pathway for HCOOH, CH\textsubscript{3}OH, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{5}OH formation from CO\textsubscript{2}. The relative reaction free energies and their dependencies on the applied potential are shown in Figure 5 and S5. Here, in case of HCOOH formation, *HCOOH from *HCOO is the most endergonic step with a reaction free energy of 0.55 eV. Hence, at -0.55 V all the steps of HCOOH formation will be thermodynamically favourable. Besides, for CH\textsubscript{3}OH formation *CO } \rightarrow \text{ HCO step is the most endergonic step and an amount of -0.52 V potential is required for CH\textsubscript{3}OH formation. For CH\textsubscript{4}, an amount of -1.06 V potential is required as *CO } \rightarrow \text{ COH step is endergonic by 1.06 eV. Along with CH\textsubscript{3}OH, *CO } \rightarrow \text{ HCO is the most endergonic step for C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{5}OH formation. Hence, at -0.52 V we can expect CH\textsubscript{3}OH, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{5}OH on the Cu-dNC surface. Even if working potential is same for C\textsubscript{2}H\textsubscript{5}OH and C\textsubscript{2}H\textsubscript{4}, the calculated total reaction free energies show that
C$_2$H$_5$OH formation is 0.52 eV more favourable than that of C$_2$H$_4$ on the Cu-dNC surface. Hence, the amount of C$_2$H$_5$OH formation will be more compared to C$_2$H$_4$ on the Cu-dNC. Earlier reports suggest that *CO to *HCO is the potential limiting step on the Cu$_{85}$ nanocluster and periodic Cu(111) surface with required potential of -0.53 and -0.71 V respectively for CH$_3$OH formation.$^{57,63}$

**Figure 5**: Reaction free energies of CO$_2$ hydrogenation to CH$_3$OH, C$_2$H$_4$ and C$_2$H$_5$OH and their dependencies on the applied potentials.

Moreover, earlier reports have reported the most endergonic step with 0.62 and 0.65 eV on the periodic Cu(100) surface for C$_2$ based product formation from CO$_2$.\textsuperscript{21,22} Thus, Cu-dNC can be
considered as an efficient and promising catalyst for CO$_2$ hydrogenation reaction to C$_2$ based product formation. To understand the reason behind the superior catalytic activity of the Cu(100) facet of the Cu-dNC compared to the periodic Cu(100) surface, we have investigated the d-band-center energies. The calculated d-band-center energies are -2.45 and -2.43 eV for periodic Cu(100) surface and Cu(100) facet, respectively. Therefore, the calculated d-band-center energies of the Cu(100) and Cu(100) facet are more or less same. The Cu-Cu bond distances are 2.47 Å on the periodic Cu(100) surface whereas the Cu-Cu average bond distance is 2.52 Å as various Cu-Cu bond lengths are observed (2.56, 2.76, 2.42 and 2.35 Å) on the Cu-dNC surface. So, Cu-dNC is highly distorted compared to the periodic Cu(100) surface. Our calculated strain value shows that Cu-dNC is under tensile strain (10.99%) compared to the periodic Cu(100) surface. Therefore, the formation of *HCO from *CO is favourable on the Cu-dNC as distorted surface can stabilize the intermediates as also reported by Rojas and co-workers, who have shown that the lattice distortion of the catalyst can influence the activity, higher distortion results higher catalytic activity.\textsuperscript{67}

5. Conclusion

We have used DFT studies for the investigation of the most favourable pathways of CO$_2$ hydrogenation to various C$_1$ and C$_2$ based products on the Cu(100) facet of a Cu-NC based nanocluster. At first, the stability of the modelled Cu-NC has been examined and we have found out that the formation of the Cu-NC is energetically favorable though the structure is not dynamically and thermally stable as the structure converts to a minimum energy structure at higher temperatures. The structure distorts to another structure (Cu-dNC) which is calculated to be stable. Hence, the CO$_2$ hydrogenation reaction to C$_1$ and C$_2$ based products has been studied on the Cu-dNC catalyst. Our calculated adsorption energies and mechanistic pathways explains various
important observations including the reason behind the superior activity of Cu-dNC for product selectivity towards C₂ based products. We find that that most of the considered intermediates adsorb strongly on the Cu-dNC compared to that on the periodic Cu(111) surface. The trend in adsorption energies of the intermediate can be explained using the PDOS and Bader charge analysis. We have also studied the effect of applied potential on the product formation steps and the calculated results indicate that the formation of CH₃OH, C₂H₄ and C₂H₅OH are favourable at -0.52 V. On the other hand, our calculated reaction energy values (-0.38 eV for CH₃OH, -1.02 eV for C₂H₄, and -1.54 eV C₂H₅OH) show that the formation of C₂ based products are highly exergonic compared to C₁ (methanol) formation. Hence, Cu-dNC can be considered as efficient catalyst for the C₂ based products compared to that on the periodic Cu(100) surface. This may be due to the distorted surface of Cu-dNC which stabilize the intermediates responsible for C₂ based products formation. To the best of our knowledge, this is the first theoretical reports of CO₂ hydrogenation reaction for various C₁ and C₂ based product formation on a Cu-NC based model. We believe that these finding will be helpful for theorists as well as experimentalists working on the CO₂ hydrogenation reaction for the designing of efficient and selective catalyst.
Associated content

Supporting Information: Snapshots of the Cu-NC and Cu-dNC at the end of the AIMD simulations, adsorption patterns of the considered C₁ and C₂ based intermediates, relative reaction free energies and dependencies on the applied potential of CO₂ hydrogenation to HCOOH and CH₄.

Conflicts of interest

There are no conflicts to declare.

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