Computational insights into selective CO2 hydrogenation to CH3OH catalysed by ZnO based nanocages†

Shyama Charan Mandal and Biswarup Pathak∗

Cu and ZnO based nanostructures were extensively studied for CO2 hydrogenation reaction. In this study, we have performed density functional theory (DFT) calculations for understanding the CO2 hydrogenation reaction mechanism on ZnO and Cu doped ZnO based nanocages (NCs). Two different ZnO based NCs and three different Cu doped ZnO based NCs have been considered for the investigation. The stabilities of the NCs have been investigated using the formation energy, cohesive energy, phonon dispersion and ab initio molecular dynamics (AIMD) calculations. Our calculated adsorption energy values show that the CO2 hydrogenation reaction intermediates adsorb strongly on the NCs compared to that on the bulk Cu(111), Cu(111) monolayer and Cu nanocluster. Besides, the detailed mechanistic investigation and the calculated ZPE corrected reaction energy values show that the ZnO and Cu doped ZnO based NCs show excellent selectivity for CH3OH. These catalysts also work under very low working potentials (0.55 V for ZnO NC and 0.39 V for Cu doped ZnO NC) compared to the bulk Cu(111), Cu(111) monolayer and Cu nanocluster. Hence, Cu@ZnO based nanocages can be highly efficient and selective catalysts compared to ZnO based nanocages and Cu based catalysts for CO2 hydrogenation to CH3OH. Moreover, the influence of *COOH and *COH coverage for ZnO NC, *COH and *CHOH coverage for Cu@ZnO NC on adsorption energy values show that the catalysts can be used at high surface coverage.

1. Introduction

Carbonaceous fossil fuel combustion increases the amount of CO2 in the environment. This is one of the main reasons for climate change and possible ocean acidification.1,2 Thus, CO2 chemistry has received significant attention among the scientific community to transform CO2 into valuable chemicals and fuels (such as CO, HCOOH, CH2O, CH3OH, CH3OCH3 and so on).3–11 Among all these, CH3OH is highly in demand due to its wide industrial application and fuel-based properties.8,9,12–17 Also, use of CH3OH as a fuel and its formation from CO2 form a carbon-neutral process. Therefore, research efforts are devoted to the hydrogenation of CO2 to CH3OH (CO2 + 3H2 → CH3OH + H2O). Here, the overall standard electrochemical potential for CO2 hydrogenation to CH3OH (CO2 + 3H2 → CH3OH + H2O) is −0.38 V, but this process competes with the methanation reaction (CO2 + 4H2 → CH4 + 2H2O).18 Liu et al. have reported the first copper–zinc oxide based catalyst for CO2 hydrogenation to CH3OH where conversion of CO2 and yield of CH3OH are low.19 Thus, efficient and selective catalysts that can activate CO2 and break only one C–O bond of the CO2 molecule are highly useful. An earlier report has shown that the process is dependent on the temperature and pressure of the reaction.20 Keeping all these in mind, several homogeneous and heterogeneous catalysts have been investigated for efficient CO2 hydrogenation to CH3OH.3,9,12–31 Besides, most of the industrial catalysts are metals supported by oxide-based nanoparticles.20,32 Industrial CH3OH is also obtained from the syngas mixture (CO, CO2 and H2) over the Cu/ZnO/Al2O3 catalyst at a temperature of 473–573 K and a pressure of 5–10 MPa.33 In this context, Chinchen et al. have reported that the C-atom of CH3OH is obtained from the C of CO2, i.e. CO2 is responsible for the formation of CH3OH.34 Several Cu/ZnO/Al2O3 based catalysts have been reported for the CO2 hydrogenation reaction.35–38 They demonstrated that the synergistic effect plays an important role in improving their catalytic activity, however, the industrial Cu/ZnO/Al2O3 catalyst does not cleave both the C–O bonds of the CO2 molecule and thus shows poor catalytic activity at low temperatures. The CO2 activation can be facilitated by increasing the temperature but undesirable products (CO and H2O) are also formed via the reverse water–gas shift reaction (RWGS). Furthermore, Kattel et al. have concluded that Cu/ZnO facilitates CH3OH formation.
in comparison to Cu–Zn.38 On this account, it is very important to explore the effect of Cu and ZnO for CH₃OH formation from CO₂ and H₂.

Besides, Cu based single-atom catalysts (SACs) have also been identified as promising catalysts for selective CH₃OH formation at a low overpotential.39,40 These SACs are highly beneficial due to their low metal use, i.e., maximum atom utilization efficiency. The different coordination numbers and unique electronic structures of SACs increase their catalytic activity in the reaction. In all cases, the nature of the catalyst’s active sites and the reaction route are two important factors. Earlier studies have shown that CO₂ hydrogenation to CH₃OH is achieved via two different pathways: (i) the formate (HCOO) pathway and (ii) the carboxyl (COOH) pathway.41,42 However, several experimentalists have confirmed that carbon monoxide (°CO) and formaldehyde (°CH₂O) are important intermediates, where °CO is obtained via the °COOH intermediate only.43,44 So, the CO₂ hydrogenation reaction proceeds via the °COOH pathway followed by °CO and °CH₂O. However, it is very difficult for experimentalists to identify all the intermediates. Hence, DFT studies can be very influential in understanding the underlying reaction mechanisms of such reactions.

Besides, ZnO based nanostructures are highly abundant and non-toxic. In addition, various ZnO based nanostructures (such as nanocombs, nanosprings, nanorings, nanobelts, nanocages and so on) have been synthesised very easily.45,46 Most of these nanostructures are also found to be promising for the hydrogenation reaction and more often than not, they have been identified as an efficient catalyst compared to their bulk catalysts.47,48 Recently, Wu et al. have synthesised (ZnO)n(n = 1–15) based nanostructures.49 Dmytruk et al. have shown that the (ZnO)34, (ZnO)60 and (ZnO)70 nanostructures are highly stable.50 Furthermore, Tian and his co-workers have described that the (ZnO)60 nanocluster is composed of a (ZnO)12 based structure where (ZnO)12 acts as a basic unit for the formation of ZnO based nanocage (NC) structures.51 Thus, we have considered Zn₁₂O₁₂ and Zn₂₄O₂₄ based NCs (Fig. 1) for our study. Between these two NCs, the energetically most stable NC has been considered for the CO₂ hydrogenation reaction. The main objective of this study is to understand the catalytic activity of a single Cu-atom based catalyst compared to the previously reported Cu-bulk and Cu-nanostructure based catalysts. Therefore, we have investigated the CO₂ hydrogenation reaction over the Cu doped ZnO system and then compared our results with the previously reported Cu-bulk and Cu-nanostructure based catalysts (Cu(111), Cu ML, and Cu NCs). The most favourable pathways for the CO₂ hydrogenation reaction have been identified to gain insights into the catalytic activity of the single Cu-atom based catalyst compared to the previously reported catalytic systems.

2. Computational details

All the density functional theory (DFT) calculations have been performed using the Vienna ab initio simulation package (VASP) through the projector augmented wave (PAW) method.52–54 The generalized gradient approximation (GGA) for the Perdew–Burke–Ernzerhof (PBE) functional has been used for the description of the exchange–correlation interaction.55,56 The Grimme’s D3 semi-empirical dispersion correction has also been included to account for the long-range dispersion forces.57 More than 15 Å of vacuum space has been considered along all three directions to avoid two successive periodic image interactions. We have calculated the energies of the NCs with 3 x 3 x 3 and 1 x 1 x 1 gamma centred k-points and found that the difference in energy is negligible (∼0.0009 eV). Hence, the plane-wave basis cutoff energy has been set to 470 eV with a 1 x 1 x 1 gamma centred k-point. All the structures have been optimised until the electronic energies and forces became less than 1 x 10⁻⁴ eV and 0.02 eV Å⁻¹, respectively. The adsorption energy (Ead) of the intermediates has been calculated using the following equation:

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

Here, E_{NC-adsorbate} is the total energy of the optimized nanocage with the adsorbate, and E_{NC} and E_{adsorbate} are the single-point energies of the NC and adsorbed intermediate from the optimized geometry of the nanocage with the adsorbate. The computational hydrogen electrode (CHE) model has been used for the calculation of H atom energy.58 The reaction energy (ΔG) has been calculated using the following equation:

\[ \Delta G = \Delta E + \Delta ZPE - T \Delta S \]

Here, ΔE is the total energy difference between the final and initial states of the considered path, ΔZPE is the change in the zero-point energy, T is the temperature, and ΔS is the change in entropy of the reaction. In this context, the zero-point energy can be determined by the \[ \sum_{i} \frac{1}{2} \nu_{i} \] term, where \( h \) and \( \nu_{i} \) denote the Planck’s constant and the vibrational frequencies of the intermediates, respectively. All the calculations have been performed at 0 K temperature (T = 0 K). So, the \( T \Delta S \) term is
zero. Therefore, the reaction energy (ΔE₀) reported in the manuscript is actually the ZPE corrected reaction energy (ΔE + ΔZPE). On the other hand, if the considered temperature is non-zero, entropy will have contributions from translation, rotational and vibrational degrees of freedom of each atom. In general, translation and rotational entropies are negligible for intermediates adsorbed on solid material-based catalysts whereas the vibrational entropy contribution can be calculated using the following statistical thermodynamics equation:

$$S_{\text{vib}} = R \sum \left( \frac{\hbar \nu_i}{k_B T \left( \exp \left( \frac{\hbar \nu_i}{k_B T} \right) - 1 \right)} \right) - \ln \left( 1 - \exp \left( \frac{-\hbar \nu_i}{k_B T} \right) \right)$$

In the above equation, $S_{\text{vib}}$ is the vibrational entropy, $k_B$ is the Boltzmann constant, $T$ is the temperature and $\hbar = h/2\pi$. From the above equation, it is clear that the vibrational entropy will be less for solid-state materials, i.e., the change in entropy can be neglected during reaction energy calculations. Moreover, in the presence of an external potential ($U$), the chemical potential of the reaction shifts by $-eU$ where $e$ is the elementary potential charge of the considered step.60 Besides, vibrational frequencies have been used for the characterisation of the reaction intermediates. Furthermore, we have calculated Bader atomic charges of some important intermediates using Henkelman code with the near-grid algorithm refine-edge method for the comparison of the adsorption energies of intermediates.61,62 Hereafter, all the adsorbed intermediates in the manuscript have been represented by an asterisk sign (*).

### 3. Results and discussion

In the beginning of this section, we have checked the stability of the considered NCs through energetic, dynamic and thermal stability calculations. Based on the stability calculations, we have considered the most stable NC for the CO₂ hydrogenation reaction. We have compared our results with earlier reports to understand the catalytic activity of the NC.

#### 3.1. Stability of the NCs

The stability of the considered NC based structures has been explored in various ways. In this context, we have considered the energetic stability of Zn₁₂O₁₂ and Zn₂₄O₂₄ NCs through the calculation of formation and cohesive energies, which are listed in Table 1. Our calculated formation energy values indicate that the formation of the Zn₂₄O₂₄ NC is 0.2 eV more favourable compared to the formation of the Zn₁₂O₁₂ NC. Similarly, the cohesive energy values also show that the Zn₂₄O₂₄ NC is more stable compared to the Zn₁₂O₁₂ NC. For this reason, we have considered the Zn₂₄O₂₄ NC for further studies. Moreover, it is worth mentioning that the formation energy of the bulk ZnO has been calculated and found to be $-2.96$ eV per formula unit, which is comparable to the previously reported $-3.04$ eV per formula unit.63 Therefore, the level of theory used in this study is good enough for further study.

Next, the energetically stable Zn₂₄O₂₄ NC has been considered for further study. Hereafter, all the possible Zn sites of the Zn₂₄O₂₄ NC have been substituted with Cu atoms to understand the effect of Cu doping on ZnO for the CO₂ hydrogenation reaction. The Zn₂₄O₂₄ NC has three different Zn sites that have been replaced by Cu atoms (Fig. 2a–f) and the energetically stable structure has been considered. Fig. 2a, b, c, d and e, f show the first-, second- and third-layer Cu doped structures, respectively. We have considered all the three possible Zn sites for Cu doping in the modelled ZnO NC. The calculated total energies show that the Cu doping at the top layer is 0.02 and 0.19 eV more stable compared to the doping in the second and third layer, respectively. Moreover, we have noticed that the doping with the Cu atom in the ZnO NC does not change the skeleton of the nanocage, which can be confirmed by the similar atomic radius of Cu and Zn atoms (Cu: 1.28 and Zn: 1.34 Å). This could also be one of the reasons why Cu/ZnO/Al₂O₃ based catalysts have been found to be some of the best catalysts for such reactions. So, the first layer Cu doped ZnO NC has been considered for the CO₂ hydrogenation reaction. From here on, the Zn₂₄O₂₄ NC and the most stable Cu doped Zn₂₄Cu₂₄O₂₄ NC have been represented as ZnO NC and Cu@ZnO NC, respectively. Furthermore, dynamic stability calculations were performed for ZnO and Cu@ZnO using phonon calculation as implemented in VASP.64 Our phonon results show a small imaginary frequency up to 9 i cm⁻¹ for ZnO NC and up to 7 i cm⁻¹ for Cu@ZnO NC. Previous studies have reported that clusters showing very small imaginary frequencies can be considered as a dynamically stable structure.65

In general, CO₂ hydrogenation reactions are carried out in the temperature range of 473–573 K.63 Hence, the catalyst must be stable in this temperature range. So, we have performed thermal stability calculations of ZnO and Cu@ZnO to find out the structural stability at the operational temperature. Ab initio molecular dynamics (AIMD) simulations with a Nosé thermostat model have been used to check the thermal stability of the considered NCs.66 The simulations have been performed with the NVT ensemble at temperatures of 300 K, 500 K and 700 K, with a time step of 1 femtosecond (fs) for 20 picoseconds (ps). Our simulations show that there are no significant changes in the energy throughout the simulation at 300 K for both the NCs (Fig. 2g and h). Also, at a temperature of 500 K and 700 K, the overall energy fluctuation is less for the considered NCs. So, the possibility of interconversion of ZnO and Cu@ZnO NCs into other local minimum energy structures is not possible within the 300–700 K temperature range. Thus, we can say that ZnO...
and Cu@ZnO NCs are thermally stable up to 700 K and can be used for the CO₂ hydrogenation reaction.

3.2. Adsorption of different intermediates

The applicability of ZnO and Cu@ZnO NCs has been investigated in detail through the adsorption of different CO₂ hydrogenation reaction intermediates on the NCs. We have considered all the possible adsorption sites on the ZnO NC (Fig. 1) and also adsorption sites close to the Cu atom on the Cu@ZnO NC (Fig. 2a and b). We have chosen adsorption sites close to the Cu atom to determine the role of the single atom catalyst in the catalytic activity. Therefore, all the possible top, bridge and hollow sites of the ZnO NC and Cu@ZnO have been taken into consideration. We could not compare our calculated results with the Cu/ZnO/Al₂O₃ catalyst as the previously reported values were not calculated using the same level of theory. For example, Liu and his co-workers theoretically investigated the CO₂ hydrogenation reaction on a Cu/ZnO/Al₂O₃ based catalyst to support their experimental findings. However, they used the GGA/PW91 level of theory for their theoretical calculations. Therefore, we have compared our results only with the Cu-based catalytic systems that were calculated at the GGA/PBE level of theory. Therefore, the adsorption energies of the intermediates on ZnO and Cu@ZnO NCs have been compared with the adsorption energies of the intermediates on bulk Cu(111), hexagonal Cu(111) monolayer (Cu(111) ML), and a Cu nanocluster and compared our results with the synergistic effects of the Cu/ZnO based catalyst.38,67,68 The most stable adsorption patterns of the intermediates on ZnO and Cu@ZnO NCs are given in Fig. S1 and S2 (ESI†) and their respective adsorption energies are given in Table 2. We find that the most stable adsorption sites of the considered intermediates are different on both the NCs. Here, the first intermediate, i.e. the CO₂ molecule, adsorbs strongly on both the NCs whereas CO₂ interacts weakly with the extensively studied Cu based materials.67–69 Therefore, the considered NCs can be promising for the activation of CO₂ molecules such that the following reaction steps are facilitated.

Besides, we find that the calculated adsorption energies of the considered intermediates are higher on the ZnO and Cu@ZnO NCs compared to those on bulk Cu(111), Cu(111) ML, Cu nanocluster and Cu–ZnO based catalysts.38,67,68 Furthermore, our calculated adsorption energy values show that the *COOH intermediate adsorbs strongly on the ZnO NC compared to that on the Cu@ZnO NC, whereas the adsorption energies of the other considered intermediates are almost
the same on ZnO and Cu@ZnO NCs. To understand the reason behind the strong *COOH adsorption on ZnO NC compared to that on Cu@ZnO NC, we have calculated the Bader atomic charges, which showed that 0.03 |e| charge is transferred from the Zn atom of ZnO NC to the O of *COOH, whereas 0.06 |e| charge is gained by the O atom of ZnO NC from the C atom of *COOH. Moreover, there is no charge transfer from Cu of Cu@ZnO NC to the C atom of *COOH whereas 0.05 |e| charge is gained by the O atom of Cu@ZnO NC from the H atom of *COOH. The amount of transferred charge is more in the case of ZnO NC compared to Cu@ZnO NC. So, the adsorption energy of the *COOH intermediate is higher on ZnO NC compared to Cu@ZnO NC. However, intermediates *COOH, *CO, *CHO, *CH₂O, *CH₃OH, *CH₂OH, *CH₃ and *H₂O adsorb more strongly on ZnO NC compared to Cu@ZnO NC whereas intermediates *CO₂, *COH, *CHOH, *H, *O and *OH adsorb more strongly on Cu@ZnO NC compared to ZnO NC. On the other hand, the adsorption energies of the products should be lower so that they can be removed easily from the catalytic surface for further steps. In our study, *CH₃OH and *CH₂ are two expected products and the calculated adsorption energy values of the *CH₃OH and *CH₂ intermediates are −0.87 eV and −5.02 eV on ZnO NC whereas −0.78 eV and −4.82 eV are the adsorption energies on Cu@ZnO NC. As a result, the removal of *CH₃OH is easier compared to *CH₂.

### 3.3. CO₂ hydrogenation reaction mechanism

In this section, we have considered different CO₂ hydrogenation reaction pathways that are discussed in detail with their calculated ZPE corrected reaction energies. Here, Scheme 1 represents the possible reaction pathways with their ZPE corrected reaction energies whereas Tables S1 and S2 (ESI†) give the details of the energy.

\[
\text{CO}_2 + * \rightarrow \text{CO}_2 \quad \Delta E_0 = -0.36 \text{ eV for ZnO} \quad -0.42 \text{ eV for Cu@ZnO}
\]

![Scheme 1](image-url)
At first, the CO₂ molecule has been examined for the adsorption on ZnO and Cu@ZnO NCs. Our calculated ZPE corrected reaction energies for the CO₂ adsorption steps are found to be exergonic. The calculated ZPE corrected reaction energies are −0.36 and −0.42 eV for ZnO and Cu@ZnO NCs, respectively. However, the ZPE corrected reaction energy values show that the CO₂ adsorption is almost the same on both NCs. This may be due to the similar adsorption energy of CO₂ on the NCs.

In the next step, adsorbed CO₂ can be reduced to *CO via direct and/or indirect reduction pathways. However, earlier reports have suggested that the direct *CO₂ reduction to *CO is unfavourable, whereas indirect *CO₂ reduction to *CO is favourable via the *COOH intermediate. Therefore, we have studied the indirect CO₂ reduction procedure.

In the indirect mechanism, *CO₂ reacts with the adsorbed/free H atom for the hydrogenation, and forms *COOH via weakening of one of the C=O bonds. This hydrogenation step is highly dependent on the proton source and transfer mechanism of the proton. In most of the cases, hydrogen can react via the Langmuir–Hinshelwood (LH) or Eley–Rideal (ER) type of mechanism. In general, CO₂ hydrogenation proceeds via the Langmuir–Hinshelwood (LH) mechanism.67–69 Therefore, we have considered the Langmuir–Hinshelwood mechanism for the *CO₂ hydrogenation procedure.

\[ *\text{CO}_2 + \cdot \text{H} \rightarrow *\text{COOH} \quad \Delta E_0 = 0.18 \text{ eV for ZnO} \\
0.39 \text{ eV for Cu@ZnO} \]

Our calculated ZPE corrected reaction energies for the formation of the *COOH intermediate are lower compared to that on the bulk Cu(111) surface and Cu(111) ML.67,68 However, these calculated ZPE corrected reaction energy values suggest that the formation of *CHO is more favourable on ZnO NC compared to Cu@ZnO NC. In the next step, the *COOH intermediate reacts with the *H atom and may form *CO and *H₂O. Earlier reports have suggested that CH₂OH formation is associated with the *CO intermediate.17,68 Sometimes *CO desorbs from the catalytic surface, which decreases the overall product formation. In this case, the adsorption energy of *CO is −2.06 and −2.05 eV on ZnO and Cu@ZnO NCs, respectively. Therefore, the considered NCs may be promising for CH₂OH formation.

\[ *\text{COOH} + \cdot \text{H} \rightarrow *\text{CO} + *\text{H}_2\text{O} \quad \Delta E_0 = 0.55 \text{ eV for ZnO} \\
-0.01 \text{ eV for Cu@ZnO} \]

In most of the cases, the formation of *CO from *COOH is a downhill process. In this case, the calculated ZPE corrected reaction energies are endergonic compared to those of the Cu NC and Cu(111) ML-based catalysts for the formation of *CO from *COOH.67,68 This may be due to the strong adsorption energy of *COOH on ZnO NC compared to Cu@ZnO NC, which makes the step endergonic for ZnO NC and reversible for Cu@ZnO. Furthermore, the intermediate *CO can be hydrogenated to *CHO and *COH via hydrogenation at the C and O centres of *CO. Earlier reports have concluded that *CHO forms CH₃OH whereas *COH forms CH₄.67–70 Hence, this step is highly important for selective product formation (CH₃OH vs. CH₄).

\[ *\text{CO} + \cdot \text{H} \rightarrow *\text{CHO} \quad \Delta E_0 = \begin{cases} -0.41 \text{ eV for ZnO} \\ -0.43 \text{ eV for Cu@ZnO} \end{cases} \]

\[ *\text{CO} + \cdot \text{H} \rightarrow *\text{COH} \quad \Delta E_0 = \begin{cases} 0.37 \text{ eV for ZnO} \\ -0.22 \text{ eV for Cu@ZnO} \end{cases} \]

The calculated ZPE corrected reaction energies are −0.41 and −0.43 eV on ZnO and Cu@ZnO NCs, respectively, for the formation of the *CHO intermediate. Besides, the calculated ZPE corrected reaction energies for *COH formation are 0.37 and −0.22 eV on ZnO and Cu@ZnO NCs, respectively. Therefore, the formation of the *CHO intermediate is highly favourable compared to the formation of the *COH intermediate on both the NCs. Thus, we have considered *CHO as an important intermediate for our further study. Furthermore, *CHO can be converted to CH₃OH and *CHOH through hydrogenation at the C and O centres of *CHO, respectively.

\[ *\text{CHO} + \cdot \text{H} \rightarrow *\text{CH}_2\text{O} \quad \Delta E_0 = \begin{cases} -0.35 \text{ eV for ZnO} \\ 0.08 \text{ eV for Cu@ZnO} \end{cases} \]

\[ *\text{CHO} + \cdot \text{H} \rightarrow *\text{CHOH} \quad \Delta E_0 = \begin{cases} 0.48 \text{ eV for ZnO} \\ 0.35 \text{ eV for Cu@ZnO} \end{cases} \]

Our calculated ZPE corrected reaction energies suggest that the formation of *CH₃OH is 0.83 and 0.27 eV more favourable compared to the formation of *CHOH on ZnO and Cu@ZnO NCs, respectively. The calculated ZPE corrected reaction energies reveal that *CH₂OH formation is exergonic on ZnO NC and endergonic on Cu@ZnO NC. Therefore, the reaction will proceed via the *CH₂O intermediate, which is in agreement with the earlier reports.67–70 Afterwards, *CH₂O can form *CH₃OH and *CH₂O via hydrogenation at the O and C centres of *CH₂O for the formation of O–H and C–H bonds, respectively.

\[ *\text{CH}_2\text{O} + \cdot \text{H} \rightarrow *\text{CH}_3\text{O} \quad \Delta E_0 = \begin{cases} 0.27 \text{ eV for ZnO} \\ -0.29 \text{ eV for Cu@ZnO} \end{cases} \]

\[ *\text{CH}_2\text{O} + \cdot \text{H} \rightarrow *\text{CHO} \quad \Delta E_0 = \begin{cases} 1.19 \text{ eV for ZnO} \\ 0.49 \text{ eV for Cu@ZnO} \end{cases} \]

In this case, the formation of *CH₂OH is 0.92 and 0.78 eV more favourable on ZnO and Cu@ZnO NCs compared to *CH₂O. Besides, it is also clear that the formation of the O–H bond is 0.56 eV more favourable on ZnO NC compared to Cu@ZnO NC. Earlier reports have suggested that the formation of *CH₂O is more favourable on the Cu(111) ML, whereas the formation of *CH₂OH is more favourable on the Cu nanocluster.67,68 However, our calculated ZPE corrected reaction energies show that Cu@ZnO NC can be considered as an efficient catalyst for *CH₂OH formation.

\[ *\text{CH}_2\text{OH} + \cdot \text{H} \rightarrow *\text{CH}_3\text{OH} \quad \Delta E_0 = \begin{cases} -0.91 \text{ eV for ZnO} \\ -0.25 \text{ eV for Cu@ZnO} \end{cases} \]

\[ *\text{CH}_2\text{OH} + \cdot \text{H} \rightarrow *\text{CH}_2 + *\text{H}_2\text{O} \quad \Delta E_0 = \begin{cases} -0.02 \text{ eV for ZnO} \\ 0.08 \text{ eV for Cu@ZnO} \end{cases} \]
These steps are highly important for the formation of selective CO$_2$ hydrogenated products such as CH$_3$OH and CH$_4$. Here, CH$_2$OH may react with *H at the C and O centre of *CH$_2$OH for the formation of *CH$_2$OH via hydrogenation at the C centre of *CH$_3$OH or *CH$_3$ and *H$_2$O via cleavage of the C-O bond, followed by O-H bond formation. If the formation of *CH$_3$ is favourable, the final product will be CH$_4$. The calculated ZPE corrected reaction energies show that the formation of the *CH$_3$OH intermediate is highly exergonic on both the NCs and formation of the *CH$_3$ intermediate is reversible on ZnO NC and endergonic on Cu@ZnO NC. Moreover, *CH$_3$OH formation on ZnO NC is 0.66 eV more favourable compared to Cu@ZnO NC. This can also be explained by the adsorption energies of *CH$_3$OH and *CH$_2$. Therefore, the formation of CH$_4$ is not favourable on both the considered NCs.

$$\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OH} \quad \Delta E_0 = 0.65 \text{ eV for ZnO}$$

In the last step, *CH$_3$OH desorbs from the catalytic surface and NCs are regenerated for the next catalytic cycle. The calculated ZPE corrected reaction energies for this desorption step are 0.65 and 0.55 eV on ZnO and Cu@ZnO NCs, respectively. Hence, the desorption of the *CH$_3$OH intermediate is 0.10 eV more favourable on Cu@ZnO NC compared to ZnO NC.

Thus, our calculated ZPE corrected reaction energy values suggest that ZnO and Cu@ZnO NCs can be considered as highly active and selective catalysts for CH$_3$OH formation. Moreover, the CO$_2$ hydrogenation reaction to CH$_3$OH on ZnO and Cu@ZnO NCs proceeds via *CO$_2$ to *COOH to *CO to *CHO to *CH$_2$O to *CH$_3$OH to *CH$_3$OH to CH$_3$OH. Here, the *CO$_2$ + *H \rightarrow *COOH, *CHO + *H \rightarrow *CH$_2$O and *CH$_3$OH + *H \rightarrow *CH$_3$OH steps are favourable on ZnO NC whereas the * + CO$_2$ to *CO$_2$, *COOH + *H \rightarrow *CO + *H$_2$O, *CO + *H \rightarrow *CHO, *CH$_2$O + *H \rightarrow *CH$_2$OH and *CH$_3$OH \rightarrow * + CH$_3$OH steps are favourable on Cu@ZnO NC. In this study, we have calculated the Bader atomic charges of Zn and Cu atoms in ZnO and Cu@ZnO NCs to understand the role of the single atom catalyst. Our calculated Bader atomic charges show that the charge on the Zn atom of ZnO NC is +1.16 [e] whereas the charge on the Cu atom of Cu@ZnO NC is +0.90 [e]. Therefore, the Zn atom in ZnO NC possesses a high positive charge compared to the Cu atom in Cu@ZnO. So, this indicates that the single Cu atom is available for the CO$_2$ reduction reaction compared to the Zn site as Cu can be oxidised easily compared to the Zn atom. Therefore, Cu doping of ZnO NC increases the catalytic activity, which could be due to the synergistic effects between the metal atoms. Similarly, Wang and his co-workers have reported that synergic effects between Cu and zinc oxides are responsible for efficient CO$_2$ hydrogenation to methanol. $^{71}$ Similarly, many other previous studies have shown that a synergic effect plays an important role in high methanol production.$^{37,38}$

3.4. Comparison between ZnO and Cu@ZnO NCs

Our considered ZnO and Cu@ZnO NCs can selectively hydro- genate CO$_2$ for the formation of CH$_3$OH. In this context, the most endergonic elementary step of the reaction is the potential limiting step.$^{46}$ These potential limiting steps are highly important to find out the applied electrode potential of the reaction. On the basis of the energies obtained above, Fig. 3 presents the calculated ZPE corrected reaction energies of the intermediates and their dependence on the applied electrode potential. Considering the electrochemical steps of CO$_2$ hydrogenation reaction to CH$_3$OH, the formation of *CO from *COOH is the potential limiting step (Fig. 3) for ZnO NC and *COOH formation from *CO$_2$ is the potential limiting step for Cu@ZnO NC.

The calculated ZPE corrected reaction energies of the considered potential limiting steps are 0.55 and 0.39 eV on ZnO and Cu@ZnO NCs, respectively. Therefore, at applied potentials of 0.55 V for ZnO NC and 0.39 V for Cu@ZnO NC, all the CO$_2$ hydrogenation reaction steps become exergonic/reversible. Hence, Cu@ZnO NC requires 0.16 V less potential compared to ZnO NC for CH$_3$OH formation. Our earlier reports have

![Fig. 3](image-url) Relative CO$_2$ hydrogenation ZPE corrected reaction energies and their dependence on the applied electrode potential for (a) ZnO NC, and (b) Cu@ZnO NC.
concluded that *CO to *CHO is the potential limiting step for a Cu nanocluster with an applied electrode potential of 0.53 V whereas *CO₂ to *COOH and *CO to *CHO are the potential limiting steps for Cu(111) ML with an applied electrode potential of 0.46 V.65,66 Besides, the bulk Cu(111) surface has been reported to have an applied electrode potential of 0.71 V.67 Therefore, the calculated results show that Cu@ZnO NC can be a very active catalyst for CH₃OH formation compared to the previously reported bulk Cu(111), Cu nanocluster, Cu(111) ML, ZnO NC and Cu@ZnO NC. Besides, the catalytic performance of ZnO NC is comparable with that of the Cu nanocluster.

In this study, we have considered intermediate coverages of ZnO and Cu@ZnO based NCs. We have focused on the coverage study of *COOH and *CO intermediates on ZnO NC, and *COH and *CHOH intermediates on Cu@ZnO NC based on their respective adsorption energy values. Here, the average adsorption energies of the important intermediates were calculated at different coverages and the calculated adsorption energies are summarised in Table 3. Our calculated results show that the average adsorption energy value mostly reduces at high coverage. However, the adsorption energy values are still significant at high surface coverage, which indicates that the catalytic activity of the NCs may not change significantly due to surface coverage. The skeleton of the NCs also remains the same even at high surface coverage, i.e., there is no surface reconstruction. This indicates that the attraction between Zn and O atoms is quite strong in the NC for the CO₂ hydrogenation reaction even at high surface coverage. Therefore, the NCs can be used as an active catalyst for CO₂ hydrogenation reaction at high surface coverage.

### 4. Conclusion

In conclusion, DFT calculations have been performed on the CO₂ hydrogenation reaction to CH₃OH on ZnO and Cu@ZnO NCs. Different adsorption possibilities of all the considered intermediates and various possible reaction pathways have been considered to understand the catalytic activity of ZnO and Cu@ZnO NCs. Our calculated adsorption energy values show that the considered intermediates bind strongly on both the NCs. However, intermediate *COOH binds strongly on ZnO NC compared to Cu@ZnO NC. Moreover, *CHO formation is favourable over *COH on the considered NCs for selective CO₂ hydrogenation to CH₃OH via a *CHO intermediate. Our calculated ZPE corrected reaction energy values show that *CHO formation is 0.78 and 0.21 eV more favourable over *COH on ZnO and Cu@ZnO NCs, respectively. Hence, the catalysts are selective for CH₃OH formation. Furthermore, the considered reaction mechanisms show that *CO₂ hydrogenation to *COOH is the potential limiting step for ZnO NC, whereas formation of *CO from *COOH is the potential limiting step for Cu@ZnO NC. Here, the calculated applied electrode potential to make all the steps exergonic and/or reversible is 0.53 and 0.39 V for ZnO and Cu@ZnO NCs, respectively, which is lower compared to earlier Cu based catalysts. Moreover, the adsorption energy values are still significant even at high surface coverage. Therefore, the NCs can be used as an efficient catalyst at high coverage. Therefore, our detailed mechanistic study shows that ZnO and Cu@ZnO NCs can be efficient and selective catalysts for the CO₂ hydrogenation reaction to CH₃OH. Moreover, Cu@ZnO NC was found to be a more promising catalyst compared to ZnO NC.

### Conflicts of interest

There are no conflicts to declare.

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