A brief review on the reaction mechanisms of CO\textsubscript{2} hydrogenation into methanol

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Abstract

The catalytic reduction of CO\textsubscript{2} to methanol is an appealing option to reduce greenhouse gas concentration as well as renewable energy production. In addition, the exhaustion of fossil fuel, increase in earth temperature and sharp increases in fuel prices are the main driving factor for exploring the synthesis of methanol by hydrogenating CO\textsubscript{2}. Many studies on the catalytic hydrogenation of CO\textsubscript{2} to methanol were published in the literature over the last few decades. Many of the studies have presented different catalysts having high stability, higher performance, low cost, and are immediately required to promote conversion. Understanding the mechanisms involved in the conversion of CO\textsubscript{2} is essential as the first step towards creating these catalysts. This review briefly summarizes recent theoretical developments in mechanistic studies focused on using density functional theory, kinetic Monte Carlo simulations, and microkinetics modeling. Based on these simulation techniques on different transition metals, metal/metal oxide, and other heterogeneous catalysts surfaces, mainly, three important mechanisms that have been recommended are the formate (HCOO), reverse water–gas shift (RWGS), and trans-COOH mechanisms. Recent experimental and theoretical efforts appear to demonstrate that the formate route in which the main intermediate species is H\textsubscript{2}CO\textsuperscript{*} in the reaction route, is more favorable in catalytic hydrogenation of CO\textsubscript{2} to chemical fuels in various temperature and pressure conditions.

Keywords: CO\textsubscript{2} hydrogenation, methanol synthesis, DFT, kMC, Reaction mechanism, RWGS

1. Introduction

The production of hydrocarbons, such as methanol (CH\textsubscript{3}OH) from CO\textsubscript{2}/CO/H\textsubscript{2} feeding, is a considerable method which strongly depends on the reaction conditions and the nature of the catalyst applied. The liquid yields like methanol are much favorable due to their application in lessening the lack of fossil fuels. Methanol is synthesized by CO\textsubscript{2} hydrogenation through
CO₂(g) + 3H₂(g) = CH₃OH(g) + H₂O(g) reaction scheme, which is a reverse process of methanol-reforming at the same time. The standard enthalpy for this reaction at room temperature is -49.3 kJ mol⁻¹ [1]. This negative enthalpy means that the reaction is thermodynamically desirable and that the reaction temperature has to be regulated to repel side and reverse reactions at a moderately low level. Mostly, among all the metals, transition metals and their oxides are recognized as the effective catalysts to hydrogenate CO₂ into methanol on a wider industrial range. The Cu/ZnO/Al₂O₃ catalyst is actually used to industrially transform syngas mixtures (H₂/CO₂/CO) to methanol at the modest 50–100 bar pressures and 473–573 K temperatures [1]. While, the basic catalytic mechanism and the active sites remain a major challenge.

Beginning from this species, the mechanism involves successive hydrogenations that ultimately lead to methanol. Based on density functional theory (DFT) calculations, kinetic Monte Carlo (kMC) simulations, microkinetic modeling, and in situ investigations on different Cu, Cu/metal oxide, and non-copper heterogeneous catalysts surfaces, mainly, there are three important mechanisms which have been recommended so far including the formate (HCOO), reverse water–gas shift (RWGS), and trans-COOH mechanisms. The CO₂ hydrogenation process involves successive hydrogenations beginning with each precursor species ultimately leading to methanol [1]. This review highlights briefly the reaction routes of the three mechanisms on different heterogeneous catalytic systems and is discussed in the following section.

2. Literature review

2.1 Formate (HCOO) Mechanism

The main intermediate in the HCOO mechanism is the formate (HCOO) in the reaction route. HCOO* has been believed to be the primary intermediate for hydrogenating CO₂ to CH₃OH. Consequently, the rate-determining step (RDS) is thought to be regulated by HCOO* formation and hydrogenation. Accordingly, previous theoretical studies focused mainly on revealing low-barrier steps in the industrial catalyst Cu/ZnO following the development of HCOO* with regard to unique Cu surface structures and Cu–oxide interactions [2]. Kopač et al. [3] used the first principles of DFT calculations and kMC simulations to test the activation of carbon dioxide on the Cu(111) catalysts for methanol synthesis. They applied the hydrogenation route model of CO₂ resulting in the formate mechanistic steps. To state that the production of formaldehyde, H₂COO + H ↔ H₂CO + OH, is the rate-determining step for the synthesis of methanol. This step in the format pathway signifies the bottleneck even though it has the greatest activation energy, but the CO₂ hydrogenation remains as the selectivity control step. They examined the conversion, selectivity, and rate (TOF) dependence of the output of CH₃OH on operating process conditions, primarily temperature and pressure [3]. In methanol synthesis experiments using various Cu-type catalysts, the trends observed from their simulations, namely higher selectivity at a higher pressure and lower temperature, higher conversion at higher pressure are in good agreement with their method. As well as, higher TOF at higher pressure and temperature are commonly seen supporting their method [3]. In addition, the numerical stability analysis of kMC simulations has been statistically checked for activation regarding random
seed parameters and energy barriers. The distribution of surface products has been observed to be particularly susceptible to the smallest disruptions of the activation standard Gibbs energy [3]. Similarly, in accordance with the ab initio Hartree–Fock (HF) and the second-order Møller–Plesset (MP2) calculations, Hu et al. [4] used the dipped adcluster model (DAM) to test the hydrogenation process of CO$_2$ to methanol on a Cu(100) surface. They examined the promising reaction route with the Langmuir–Hinshelwood mechanism that initiated on the basis of that Cu cluster model from the co-adsorption of H$_2$ and CO$_2$ state. The chemisorbed CO$_2$ appears in the Cu(100) DAM as a bent anionic CO$_2^-$ species that bind all oxygen atoms to surface copper. They noticed five succeeding hydrogenation steps for the conversion of CO$_2$ to methanol with the reaction pathway given in the following equations (* indicating the adsorbed species) [4]:

$$\text{CO}_2^- + 2\text{H}^+ \rightarrow \text{HCOO}^+ + \text{H}^+$$  \hspace{1cm} (1)

$$\text{HCOO}^+ + \text{H}^+ \rightarrow \text{H}_2\text{COO}^-$$ \hspace{1cm} (2)

$$\text{H}_2\text{COO}^- + \text{H}^+ \rightarrow \text{H}_3\text{CO}^+ + \text{OH}^-$$ \hspace{1cm} (3)

$$\text{H}_2\text{CO}^+ + \text{H}^+ \rightarrow \text{H}_3\text{CO}^-$$ \hspace{1cm} (4)

$$\text{OH}^- + \text{H}^+ \rightarrow \text{HOH}$$ \hspace{1cm} (6)

Among all other steps, hydrogenation of adsorbed formate to adsorbed dioxomethylene (HCOO$^+$ + H$^+$ → H$_2$COO$^-$; Ea = 1.00 eV; $\Delta$E = 0.74 eV) is the highest elementary barrier. Besides this, the hydrogenation of adsorbed dioxomethylene producing formaldehyde was another high barrier reaction intermediate with Ea = 0.74 eV [4]. Besides Cu and metal oxide supported Cu catalysts, the combined Zn with Cu and Cu oxides act as the effective catalysts that show better performance in hydrogenation reaction of CO$_2$ into methanol. The direct comparison between ZnCu alloy behavior and ZnO/Cu model catalysts for hydrogenation of CO$_2$ into methanol was reported by Kattel et al. [2]. They carried out DFT calculations on the catalysts of the ZnCu and ZnO/Cu model to achieve a further mechanistic understanding of the methanol production from CO$_2$. The findings from their kMC simulations were consistent with the DFT predictions under the experimental conditions, indicating that CO$_2$ hydrogenation followed the format route on both catalyst systems. The HCOO$^+$ species are known on pure Cu catalysts as merely viewer in production of methanol. The addition of Zn or ZnO helped to stabilize the intermediate HCOOH$^+$ by direct Zn-O interaction for both ZnCu and ZnO/Cu systems and to activate HCOO$^+$ by hydrogenation. Their results highlighted an interface Cu and ZnO synergy which facilitates the formate intermediates formation to produce methanol [2]. Kakumoto et al. [5] also conducted ab initio calculations using a density functional approach to test the stability of the intermediate reaction in the production of methanol using clusters of Cu, CuO, and CuZnO. They provided some valuable insights but the models are too simplistic when opposed to the catalyst’s actual surfaces. Their findings showed that CO$_2$ and other intermediate reaction agents were able to adsorb on C$^+$ sites while H$_2$ molecules adsorb on Cu and ZnO to generate H atoms and ions.

In addition to ZnO, zirconia (ZrO$_2$) is also an important promoter and supporter for the Cu catalyst. Hong and Liu [6] conducted a large study on the hydrogenation reaction of CO$_2$ on the surface of hybrid Cu/ZrO$_2$ catalyst using DFT calculations and kMC method to supply a comprehension understanding of the complex interfacial catalysis under experimental circumstances. They demonstrated that both methanol
and CO are generated primarily through the formate route, whereas the RWGS channel has only a slight involvement. Their theoretical findings showed that the key route at the oxygen-rich Cu/ZrO$_2$ interface is the formate pathway initiated by direct CO$_2$ hydrogenation, where H$_2$CO$^*$ was a key intermediate reaction species. Their kinetics simulation results exhibited the CO$_2$ conversion selectivity towards methanol and lower activation energies for methanol in contrast to production of CO. They also concluded that kMC is a more appropriate tool in comparison with the microkinetics method for simulating heterogeneous catalytic processes [6]. In addition, Tang and colleagues [7] researched the catalytic kinetics of CO$_2$ fastening to methanol over a Cu/ZrO$_2$ binary catalyst using kMC simulations with first principles. Two reaction pathways including the RWGS via CO$_2$ decomposition to CO and hydrogenation through formate intermediate for methanol synthesis were verified on the surface of Cu/ZrO$_2$ catalyst. The selectivity as a result of theoretical studies were 85% and 15% for methanol and CO, respectively. In the reverse RWGS path, the CO release as a by-product was predictable due to the existence of the CO$_2$ splitting channel. Although it is possible to recognize HCOO and H$_2$COO, but they are not the principal intermediate that results in methanol. Theoretically, the hydrolysis route plays an important role in the formation of methanol and the removal of oxygen atom on the surface of the catalyst, but the catalyst interface sites are commonly occupied by oxidative species, such as O atoms, OH and H$_3$CO groups, and, thus, the Cu atoms interface is cationic. The lack of active sites for CO$_2$ adsorption result in the low conversion rate of CO$_2$ fixation.

The increased catalytic efficiency of the combined catalyst in CO$_2$ hydrogenation highlights the position of Al$_2$O$_3$ together with Cu and ZnO. The reaction mechanism of methanol production using the Cu/ZnO/Al$_2$O$_3$, catalyst by CO$_2$ hydrogenation was investigated by French et al. [8] using hybrid quantum mechanics and molecular mechanics (QM/MM) embedding computational technique. Their mechanisms proposed the formation of formate intermediate through CO$_2$ chemisorption to produce methanol with further hydrogenation of CO$_2$. Their findings showed the creation of interstitial surface sites of oxygen vacancy that are responsible for methanol synthesis. They explained the adsorption of essential precursors of methanol including CO$_2$, HCOO$^-$ and H$_3$CO$^-$ ions. The interstitial oxygen site was the principal catalytically active site for the formation of anionic adsorbates. Two intermediate species, HCO$_2$ and H$_2$COO$^-$ were found to be particularly stable. The former (the formate ion) is considered a stable long-lived intermediate, but the latter has not been characterized experimentally although it is isomeric to the reported methoxy species [8].

The coupled-clusters singles and doubles theory [CCSD(T)] calculations were performed by Huš and his colleagues [9] to test the thermodynamics and equilibria of hydrogenation of CO$_2$ into methanol by using spinel-type catalyst Cu/ZnAl$_2$O$_4$. They evaluated the Gibbs free energy, enthalpy, entropy, and chemical equilibrium constants of the direct methanol synthesis and the opposing RWGS reaction at pressures 1, 20, 40, 60, and 100 bars and temperatures 25, 150, 200, 250, and 300ºC using ab initio quantum chemistry method of CCSD(T)/aug-cc-Pvqz. In addition, a thorough study of all possible intermediates in each elementary step, adsorption/desorption energies, geometries, barriers and adsorption rate were performed using the DFT method of plane wave. The reaction pathway for methanol
synthesis was via formate route as a result of their calculations, and the rate-limiting steps were the formations of H$_2$COO and H$_2$COOH species. The role of the DFT in modeling the current non-copper catalytic systems can also be reflected. Frei et al. [10] studied the reaction mechanism and kinetic behavior of CO$_2$ hydrogenation on the surface of In$_2$O$_3$ catalyst. They carried out DFT calculations using the Vienna Ab initio Simulation Package (VASP) and the exchange-correlation functional of the Perdew-Burke-Ernzerhof (PBE). The core electrons were represented with a 500 eV plane-wave cut-off energy via projector Augmented Wave Pseudopotentials (PAW) for the valence electrons. Theoretical modeling of CO$_2$ hydrogenation over this surface has shown that the oxygen vacancies generated under reaction conditions can activate CO$_2$ and heterolytically split H$_2$. There was a description of the plausible path to methanol which followed identical steps until the second addition of hydride. In this route, CO$_2$ was reduced along the path given in the following equations [10]:

\[
\begin{align*}
\text{CO}_2 + \text{H} & \rightarrow \text{HCO}_2 \quad (7) \\
\text{HCO}_2 + \text{H} & \rightarrow \text{HCOOH} \quad (8) \\
\text{HCOOH} + \text{H} & \rightarrow \text{H}_2\text{COOH} \quad (9) \\
\text{H}_2\text{COOH} + \text{H} & \rightarrow \text{H}_2\text{C(OH)}_2 \quad (10) \\
\text{H}_2\text{C(OH)}_2 & \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O} \quad (11) \\
\text{H}_2\text{CO} + \text{H} & \rightarrow \text{H}_3\text{CO} \quad (12) \\
\text{H}_3\text{CO} + \text{H} & \rightarrow \text{H}_3\text{COH} \quad (13)
\end{align*}
\]

In this path methanediol formation is strongly favored. They also led orders in methanol synthesis for reactants and products that usually matched the values which were obtained experimentally. In addition, Li and Ho [11] studied the CO$_2$ hydrogenation on the surfaces of Fe(111) and W(111) catalysts with quantum-chemical measurements using the PAW method based on DFT in the periodic boundary state. They proved that the reaction routes on the surfaces of Fe(111) and W(111) catalysts for the CO$_2$ hydrogenation were the same but the energies were dissimilar. Their calculation results showed that the most possible way to hydrogenate the CO$_2$ on the surfaces of Fe(111) or W(111) catalysts, was to construct a formate-vertical structure. They observed that all of the respective CO$_2$ hydrogenation intermediates on the W(111) surface were more stable than those on the Fe(111) equivalents, but all of the W(111) surface reaction barriers were greater than those on the Fe(111) analogs. It is due to the stronger interactions between adsorbates and the W(111) surface, which makes it more difficult to recombine H and CO$_2$ adsorbates compared to Fe(111) analogues.

The key argument in the HCOO process is the formation of HCOOH$^*$ or H$_2$COO$^*$ as the optimal product as a result of hydrogenation of HCOO$^*$. The HCOO mechanism has been proved to be more beneficial experimentally and theoretically in specific temperature and pressure environments for the catalytic hydrogenation of CO$_2$ to chemical fuels [1,4].

### 2.2 The Reverse Water-Gas Shift Mechanism

In the reverse water-gas shift reaction (RWGS) mechanism, the key intermediate is considered to be CO$^*$ instead of HCOO$^*$ as compared to the HCOO mechanism. Simply it can be seen that the CH$_3$O and CO generations share the same pathway. The CO$^*$ species was created when the COOH$^*$ intermediate was hydrogenated, whereas HCOO$^*$ was considered a dead-end spectator species due to the experimental finding that HCOO$^*$ hydrogenation kinetics did not suit that of methanol production. However, the RWGS route on pure
Cu surfaces is at least not feasible as most the theoretical studies confirmed [1]. Yang et al. [12] found that formyl (HCO\(^{\bullet}\)) was not stable and chose to dissociate into CO\(^{\bullet}\) and H\(^{\bullet}\) species instead of adopting the Cu reverse route. Consequently, only a small amount of CO\(^{\bullet}\) formed from the RWGS reaction on the surface of Cu catalyst could be changed to methanol and much of CO\(^{\bullet}\) would be desorbed on the surface, thereby considerably hindering methanol selectivity. In order to stabilize HCO\(^{\bullet}\), promoters or dopants were required. To enhance the performance of Cu on methanol synthesis, the Cu-based catalysts have been promoted or doped with various elements [13]. Using a combination of DFT and KMC simulations, Yang et al. [14] obtained the activity sequence of different metal doped Cu towards methanol synthesis. It was obtained that the Ni-supported Cu nanoparticle showed the highest catalytic activity because of the HCO stabilization, i.e., Ni dopants in Cu nanoparticles may promote the formation of CH\(_3\)OH through the RWGS mechanism and decrease the generation of CO side products, as many experimental studies have demonstrated [1].

Additionally, many forms of processed non-copper-based materials have remarkable catalytic performance in converting CO\(_2\) into CH\(_3\)OH through RWGS mechanisms. Through integrating DFT experiments, kMC simulations and experimental observations, Kattel and colleagues [15] got a comprehension mechanism of CO\(_2\) hydrogenation on the Pt nanoparticles catalyst. They performed DFT calculations using the VASP code. They used 400 eV plane-wave cutoff energy to calculate total energy. The generalized gradient approximation (GGA) with the functional PW91 was used to explain the electronic exchange and correlation effects. Their DFT calculations and kMC simulations result confirmed the reaction pathway to be the RWGS + CO-Hydro. The CO formed in the RWGS reaction can either desorb or continue to react with hydrogen to produce CH\(_4\) or CH\(_3\)OH. They found that while there are active low-coordinated sites, Pt nanoparticle itself cannot catalyze the reaction. The poor bonding to CO\(_2\) can impede the overall activity. The selectivity depends greatly on parameters including binding energy of CO, and energetics for intermediate reactions such as CO\(^{\bullet}\) + H\(^{\bullet}\) → CHO\(^{\bullet}\), CH\(_2\)OH\(^{\bullet}\) → CH\(_2\)^+ + OH\(^{\bullet}\), and CH\(_2\)OH\(^{\bullet}\) + H\(^{\bullet}\) → CH\(_3\)OH. The improved binding of CO and thus the facilitated hydrogenation of CO\(^{\bullet}\) to HCO\(^{\bullet}\) prevents CO yield and improves the synthesis of CH\(_4\) or CH\(_3\)OH [15]. The emergence of CO has also been detected besides from COOH\(^{\bullet}\) hydrogenation by direct dissociation of CO\(_2\) on endorsed Cu catalysts. The experimental attempts on Cu/ZnO/Al\(_2\)O\(_3\) [8] and DFT examination of Cu–ZrO\(_2\) ideal catalysts both verified that CO could be synthesized by direct CO\(_2\) dissociation (CO\(_2\)^+ → CO\(^{\bullet}\) + O\(^{\bullet}\)) without the key intermediate COOH\(^{\bullet}\). For the purpose of testifying the probability of CO hydrogenation to CH\(_3\)OH concerning CO\(_2\) under accurate reaction conditions, kMC simulations have been applied with a large time scale. The results exhibited that a ratio of 1:1 of CO\(_2\): CO mixture gas results in ∼2/3 CH\(_3\)OH generation by CO\(_2\) and ∼1/3 CH\(_3\)OH by CO, whereas the CO\(_2\) gas itself gives ∼85% CH\(_3\)OH and the rest ∼15% is from dissociation of CO\(_2\) involving CO. The kMC simulations showed that CO\(_2\) hydrogenation without CO\(^{\bullet}\) intermediate is predominant under the reaction conditions for CH\(_3\)OH synthesis while CO hydrogenation leads to a small amount of CH\(_3\)OH via the RWGS process [7].

The above discussions summarize that the RWGS mechanism cannot be entirely excluded even though
many theoretical studies declared the key intermediate to be \( \text{HCOO}^* \) in the formate route and \( \text{CH}_3\text{OH} \) synthesis followed the HCOO mechanistic pathway. The average hydrogenation limit for CO was just marginally higher than that for \( \text{HCOO}^* \) to hydrogenate to \( \text{CH}_3\text{OH} \). This may account for the observed levels of divergence between the production rates of \( \text{HCOO}^* \) and \( \text{CH}_3\text{OH} \).[1]

In the section below, the methanol synthesis from the mixed \( \text{CO}_2/\text{H}_2 \) gas will be discussed in a debatably different mechanism in the existence of water.

### 2.3 Trans-COOH Mechanism

Water is a critical factor influencing the thermocatalytic conversion of \( \text{CO}_2 \) as seen in industrial processes where the RWGS reactions can produce a considerable amount of gaseous water. Even though Tang et al. [7] determined that the mechanism of HCOO was overpowering in the synthesis of \( \text{CH}_3\text{OH} \) from \( \text{CO}_2 \), they found that the difficulty in surface \( \text{H}^* \) hydrogenation of \( \text{CH}_3\text{O}^* \) could be overwhelmed in the existence of \( \text{H}_2\text{O} \) through a smaller barrier. The theoretical studies indicated that water may influence \( \text{CO}_2 \) hydrogenation reaction barriers, and may even modify the preferred reaction pathways. In a recent study, Zhao et al. [16] suggested an alternative reaction pathway called the trans-COOH\(^*\) mechanism [16], with trans-COOH\(^*\) generation rather than HCOO\(^*\) being the key limiting step for Cu(111) due to the high hydrogenation barrier of HCOO\(^*\). It was observed that the trans-COOH\(^*\) formation barrier could be lowered in the existence of water and, therefore, promote the synthesis of \( \text{CH}_3\text{OH} \).

With water physisorbed or chemically absorbed, the \( \text{CO}_2 \) hydrogenation barrier was reduced to 0.17 or 0.77 eV, respectively, from 1.17 eV without water molecules. Their proposed trans-COOH\(^*\) could rapidly change into COOH\(^*\) and the RWGS mechanism pathway \( \text{CO}_2^* \rightarrow \text{trans-COOH}^* \rightarrow \text{CO}^* \rightarrow \text{HCO}^* \rightarrow \text{H}_2\text{CO}^* \rightarrow \text{H}_2\text{CO}^* \rightarrow \text{CH}_3\text{OH} \), which was more desirable than formate pathway from a kinetic viewpoint. The key intermediate in this mechanistic route of \( \text{CO}_2 \) hydrogenation on the surface of Cu(111) catalyst was COH\(^*\) with a high activation barrier. Upon the hydrogenation of COH\(^*\), \( \text{CH}_3\text{OH} \) was synthesized, excluding the presence of both HCOO\(^*\) and CO\(^*\) intermediates [16]. Besides this, Tang et al. [17] used the DFT calculation method on a stepped surface of the \( \text{Ga}_3\text{Ni}_5(111) \) catalyst to analyze the mechanistic route of \( \text{CO}_2 \) hydrogenation to methanol. Their calculation results demonstrated that the possible reaction route for conversion of \( \text{CO}_2 \) into methanol using \( \text{Ga}_3\text{Ni}_5(111) \) catalyst is as the following equations [17]:

\[
\begin{align*}
\text{CO}_2 + \text{H} & \rightarrow \text{trans-COOH} \quad (14) \\
\text{trans-COOH} + \text{H} & \rightarrow \text{t,t-COOH} \quad (15) \\
\text{t,t-COOH} & \rightarrow \text{t,c-COOH} \quad (16) \\
\text{t,c-COOH} & \rightarrow \text{c,c-COOH} \quad (17) \\
\text{c,c-COOH} & \rightarrow \text{COH} + \text{OH} \quad (18) \\
\text{COH} + \text{H} & \rightarrow \text{HCOH} \quad (19) \\
\text{HCOH} + \text{H} & \rightarrow \text{CH}_2\text{OH} \quad (20) \\
\text{CH}_2\text{OH} + \text{H} & \rightarrow \text{CH}_3\text{OH} \quad (21)
\end{align*}
\]

Remarkably, their findings showed that the formation of trans-COOH species was not the rate-limiting step and had a low activation barrier, however, \( \text{H}_2\text{O} \) formation from H and OH was observed as the rate-limiting step with the lowest rate constant and highest activation barrier (0.85 eV). The summary of the three main reaction mechanisms, the corresponding computational and simulation methods, and rate-limiting steps during \( \text{CH}_3\text{OH} \) production by the hydrogenation of \( \text{CO}_2 \) using different heterogeneous catalysts are given in Table 1.
Table 1: Summary of the comparison of the different heterogeneous catalytic systems, the corresponding computational and simulation methods, and rate-limiting steps in the hydrogenation of CO$_2$ into CH$_3$OH.

| Catalyst          | Computational/Simulation Method   | Reaction Mechanism     | Rate-Limiting Step (RLS)                     | Ref. |
|-------------------|-----------------------------------|------------------------|---------------------------------------------|------|
| Anatase TiO$_2$(101) | DFT (GGA-VASP)                    | Formate (HCOO)         | CH$_2$O$^-$ + H$^+$ → CH$_3$O$^+$         | [18] |
| Cu(100)           | DAM, HF, and MP2                   | Formate (HCOO)         | HCOO$^-$ + H$^+$ → H$_2$COO$^+$           | [14] |
| Cu(111)           | DFT (GGA-PW91) and Microkinetic model | Formate (HCOO)       | CH$_3$O$^-$ + H$^+$ → CH$_3$OH$^-$        | [19] |
| Cu(111)           | DFT (GGA-PW91)                     | Carboxyl (COOH)        | CO$_2$ + H$^+$ → COOH$^+$ + H$^+$         | [16] |
| Cu(111)           | DFT (GGA-PW91)                     | H$_2$O-promoted carboxyl (COOH) | COOH$^-$ + COH$^+$ + OH$^+$ + H$^+$         | [16] |
| Cu(111)           | DFT (GGA-PW91)                     | Formate (HCOO)         | H$_2$COO$^-$ + H$^+$ → H$_2$COO$^-$ + OH$^+$ + H$^+$ | [3] |
| Cu(111)           | DFT and kMC                        | Formate (HCOO)         | HCOO$^-$ + H$^+$ → H$_2$COO$^-$           | [20] |
| Cu/PbTiO$_3$      | DFT (VASP-PAW) and kMC (Zacros 2.0) | Formate (HCOO)       | -                                            |      |
| Cu/ZnAl$_2$O$_4$   | DFT (PWscf-PBE) and CCSD(T)/aug-cc-pVQZ | Formate (HCOO)         | HCOO$^-$ + H$^+$ → H$_2$COO$^-$ + H$^+$         | [9]  |
| Cu/ZnO            | DFT and kMC                        | Formate (HCOO)         | H$_2$COO$^-$ + H$^+$ → H$_2$COOH$^+$       | [2]  |
| Cu/ZnO/Al$_2$O$_3$ | DFT (GGA-PW91) and Microkinetic model | Formate (HCOO)       | CH$_3$O$^-$ + H$^+$ → CH$_3$OH$^-$        | [19] |
| Cu/ZrO$_2$        | DFT (GGA-PBE) and kMC              | Formate (HCOO)         | CH$_3$O$^-$ + H$^+$ → CH$_3$OH$^-$        | [7]  |
| Cu$_{25}$         | DFT (GGA-PW91)                     | Formate (HCOO)         | H$_2$COO$^-$ + H$^+$ → H$_2$CO$_2$ + OH$^+$ + H$^+$ | [12] |
| Fe(111) and W(111) | DFT (VASP-PAW-rPBE)               | Carboxyl (COOH)        | CO$_2$ + H$^+$ → trans-COOH$^+$ + H$^+$    | [11] |
|                    |                                   |                        | or cis-COOH$^+$                         |      |
| Ga$_3$Ni$_5$(111) | DFT (GGA-VASP-PBE) and Microkinetic model | Carboxyl (COOH)       | H$^+$ + OH$^-$ → H$_2$O                   | [17] |
| In$_2$O$_3$(111)  | DFT (GGA-VASP-PBE) and Microkinetic model | Formate (HCOO)       | CH$_3$O$^-$ + H$^+$ → CH$_3$O$^+$ + H$^+$ | [10] |
| InZr$_3$(110)     | DFT (GGA-PBE)                      | RWGS+CO-hydrogenation  | HCO$^-$ + H$^+$ → H$_2$CO$^+$ + H$^+$    | [21] |
| Mo$_6$S$_8$       | DFT (GGA-PBE)                      | RWGS+CO-hydrogenation  | CO$^-$ + H$^+$ → HCO$^+$ + H$^+$           | [22] |
| Pt(111)           | DFT (GGA) and Microkinetic model   | Carboxyl (COOH)        | COOH$^-$ + H$^+$ → CO$_2$ + H$^+$         | [23] |
| PdCu$_3$          | DFT (GGA-PW91)                     | Carboxyl (COOH)        | HCOH$^-$ + H$^+$ → H$_2$COH$^+$ + H$^+$   | [24] |
| Pd$_x$/In$_2$O$_3$ | DFT (VASP-GGA-PAW-PBE) and Microkinetic model | Formate (HCOO) | H$_2$COO$^-$ + H$^+$ → H$_2$CO$_2$ + OH$^+$ + H$^+$ | [25] |
| Pt nanoparticle   | DFT (VASP-GGA-PW91)                | Formate (HCOO)         | HCOO$^-$ + H$^+$ → H$_2$COO$^-$           | [15] |
| Rh$_3$Cu$_6$(111) | DFT (DMol$^3$-GGA-PW91)            | RWGS+CO-hydrogenation  | CO$_2$ + H$^+$ → trans-COOH$^+$ + H$^+$   | [24] |
3 Conclusion

To concludes all discussions, in the HCOO pathway, the crucial intermediate is highlighted to be HCOO*, while HCOO* in RWGS and trans-COOH mechanisms is regarded as a dead-end species. Moreover, the formation of CO* intermediate from CO₂ or COOH* in the RWGS mechanism remains a big challenge. It is widely accepted that the hydrogenation of HCOO* to H₂COO* is the rate-determining step in the HCOO mechanism, though the hydrogenation of HCOO into HCOOH* to be extremely important as suggested by most of the recent studies. In addition, consideration should be given to the position of promoters (dopants, water, etc.). This lowers the barrier of HCOO* hydrogenation or trans-COOH* formation and stabilizes HCO* and binds CO* more tightly to avoid direct CO desorption. The current summary reveals the presence of enormous prospects and incentives for further study in this region in the near future.

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Conflicts of Interest

The author does not report any conflict of interest about this work.

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