



ISSN: 2617-6548

URL: www.ijirss.com



A Brief Review on the Reaction Mechanisms of CO₂ Hydrogenation into Methanol

Jawed Qaderi^{1,2}

¹Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

²Department of Physical Chemistry, Faculty of Chemistry, Kabul University, Kabul 1001, Afghanistan

(Email: najikarimi1986@gmail.com)

Abstract

The catalytic reduction of CO₂ 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 CO₂. Many studies on the catalytic hydrogenation of CO₂ 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 CO₂ 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 H₂CO* in the reaction route, is more favorable in catalytic hydrogenation of CO₂ to chemical fuels in various temperature and pressure conditions.

Keywords: CO₂ hydrogenation, methanol synthesis, DFT, kMC, Reaction mechanism, RWGS.

DOI: 10.53894/ijirss.v3i2.31

Funding: This study received no specific financial support.

History: Received: 17 February 2020/Revised: 25 March 2020/Accepted: 4 May 2020/Published: 11 May 2020

Licensed: This work is licensed under a [Creative Commons Attribution 4.0 License](https://creativecommons.org/licenses/by/4.0/)

Acknowledgment: Author wish to declare my sincere gratitude and profound appreciation to my main research supervisor, Dr. Che Rozid Mamat, senior lecturer at Faculty of Science, Universiti Teknologi Malaysia (UTM), for his support, encouragement, and guidance throughout preparing this paper. Without his continued support and interest, this review paper would not have been the same as presented here.

Competing Interests: The author declares that there are no conflicts of interests regarding the publication of this paper.

Transparency: The author confirms that the manuscript is an honest, accurate, and transparent account of the study was reported; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained.

Ethical: This study follows all ethical practices during writing.

1. Introduction

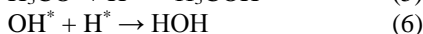
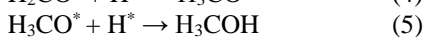
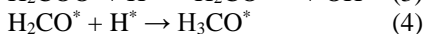
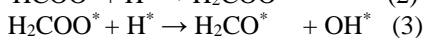
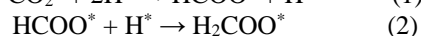
The production of hydrocarbons, such as methanol (CH₃OH) from CO₂/CO/H₂ feeding, is a considerable method which strongly depends on the reaction conditions and the nature of the catalyst applied. The liquid yields like methanol are much favorable due to their application in lessening the lack of fossil fuels. Methanol is synthesized by CO₂ 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 Kattel, et al. [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 CO₂ 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 H₂ and CO₂ state. The chemisorbed CO₂ appears in the Cu(100) DAM as a bent anionic CO₂⁻ species that bind all oxygen atoms to surface copper. They noticed five succeeding hydrogenation steps for the conversion of CO₂ to methanol with the reaction pathway given in the following equations (* indicating the adsorbed species) [4]:



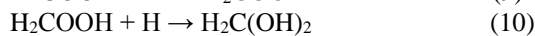
Among all other steps, hydrogenation of adsorbed formate to adsorbed dioxomethylene (HCOO* + H* → H₂COO*; E_a = 1.00 eV; ΔE = 0.74 eV) is the highest elementary barrier. Besides this, the hydrogenation of adsorbed dioxomethylene producing formaldehyde was another high barrier reaction intermediate with E_a = 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 CO₂ into methanol. The direct comparison between ZnCu alloy behavior and ZnO/Cu model catalysts for hydrogenation of CO₂ 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 CO₂. The findings from their kMC simulations were consistent with the DFT predictions under the experimental conditions, indicating

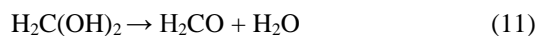
that CO₂ hydrogenation followed the formate route on both catalyst systems. The HCOO* species are known on pure Cu catalysts as merely viewer in production of methanol. The addition of Zn or ZnO helped to stabilize the intermediate HCOOH* by direct Zn-O interaction for both ZnCu and ZnO/Cu systems and to activate HCOO* by hydrogenation. Their results highlighted an interface Cu and ZnO synergy which facilitates the formate intermediates formation to produce methanol [Kattel, et al. \[2\]](#). [Kakumoto and Watanabe \[5\]](#) 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 CO₂ and other intermediate reaction agents were able to adsorb on C⁺ sites while H₂ molecules adsorb on Cu and ZnO to generate H atoms and ions.

In addition to ZnO, zirconia (ZrO₂) is also an important promoter and supporter for the Cu catalyst. [Hong and Liu \[6\]](#) conducted a large study on the hydrogenation reaction of CO₂ on the surface of hybrid Cu/ZrO₂ 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/ZrO₂ interface is the formate pathway initiated by direct CO₂ hydrogenation, where H₂CO* was a key intermediate reaction species. Their kinetics simulation results exhibited the CO₂ 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 CO₂ fastening to methanol over a Cu/ZrO₂ binary catalyst using kMC simulations with first principles. Two reaction pathways including the RWGS via CO₂ decomposition to CO and hydrogenation through formate intermediate for methanol synthesis were verified on the surface of Cu/ZrO₂ 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 CO₂ splitting channel. Although it is possible to recognize HCOO and H₂COO, 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 H₃CO groups, and, thus, the Cu atoms interface is cationic. The lack of active sites for CO₂ adsorption result in the low conversion rate of CO₂ fixation.

The increased catalytic efficiency of the combined catalyst in CO₂ hydrogenation highlights the position of Al₂O₃ together with Cu and ZnO. The reaction mechanism of methanol production using the Cu/ZnO/Al₂O₃ catalyst by CO₂ 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 CO₂ chemisorption to produce methanol with further hydrogenation of CO₂. 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 CO₂, HCOO⁻ and H₃CO⁻ ions. The interstitial oxygen site was the principal catalytically active site for the formation of anionic adsorbates. Two intermediate species, HCO₂⁻ and H₂COO⁻ 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, et al. \[9\]](#) to test the thermodynamics and equilibria of hydrogenation of CO₂ into methanol by using spinel-type catalyst Cu/ZnAl₂O₄. 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 300°C 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 H₂COO and H₂COOH 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 CO₂ hydrogenation on the surface of In₂O₃ 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 CO₂ hydrogenation over this surface has shown that the oxygen vacancies generated under reaction conditions can activate CO₂ and heterolytically split H₂. There was a description of the plausible path to methanol which followed identical steps until the second addition of hydride. In this route, CO₂ was reduced along the path given in the following equations [\[10\]](#):





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, Ye, et al. [11] studied the CO₂ 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 CO₂ hydrogenation were the same but the energies were dissimilar. Their calculation results showed that the most possible way to hydrogenate the CO₂ on the surfaces of Fe(111) or W(111) catalysts, was to construct a formate-vertical structure. They observed that all of the respective CO₂ 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 CO₂ adsorbates compared to Fe(111) analogues.

The key argument in the HCOO process is the formation of HCOOH* or H₂COO* 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 CO₂ to chemical fuels [1, 4].

2.2. The Reverse Water-Gas Shift Mechanism

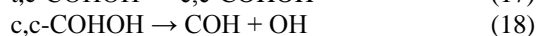
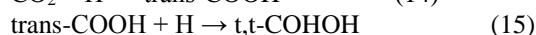
In the reverse water-gas shift reaction (RWGS) mechanism, the key intermediate is considered to be CO* instead of HCOO* as compared to the HCOO mechanism. Simply it can be seen that the CH₃O and CO generations share the same pathway. The CO* species was created when the COOH* intermediate was hydrogenated, 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 Li, et al. [1]. Yang, et al. [12] found that formyl (HCO*) was not stable and chose to dissociate into CO* and H* species instead of adopting the Cu reverse route. Consequently, only a small amount of CO* formed from the RWGS reaction on the surface of Cu catalyst could be changed to methanol and much of CO* would be desorbed on the surface, thereby considerably hindering methanol selectivity. In order to stabilize HCO*, 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 CH₃OH 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 CO₂ into CH₃OH through RWGS mechanisms. Through integrating DFT experiments, kMC simulations and experimental observations, Kattel, et al. [15] got a comprehension mechanism of CO₂ 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 CH₄ or CH₃OH. They found that while there are active low-coordinated sites, Pt nanoparticle itself cannot catalyze the reaction. The poor bonding to CO₂ can impede the overall activity. The selectivity depends greatly on parameters including binding energy of CO, and energetics for intermediate reactions such as CO* + H* → CHO*, CH₂OH* → CH₂* + OH*, and CH₂OH* + H* → CH₃OH. The improved binding of CO and thus the facilitated hydrogenation of CO* to HCO* prevents CO yield and improves the synthesis of CH₄ or CH₃OH [15]. The emergence of CO has also been detected besides from COOH* hydrogenation by direct dissociation of CO₂ on endorsed Cu catalysts. The experimental attempts on Cu/ZnO/Al₂O₃ [8] and DFT examination of Cu-ZrO₂ ideal catalysts both verified that CO could be synthesized by direct CO₂ dissociation (CO₂* → CO* + O*) without the key intermediate COOH*. For the purpose of testifying the probability of CO hydrogenation to CH₃OH concerning CO₂ under accurate reaction conditions, kMC simulations have been applied with a large time scale. The results exhibited that a ratio of 1:1 of CO₂: CO mixture gas results in ~2/3 CH₃OH generation by CO₂ and ~1/3 CH₃OH by CO, whereas the CO₂ gas itself gives ~85% CH₃OH and the rest ~15% is from dissociation of CO₂ involving CO. The kMC simulations showed that CO₂ hydrogenation without CO* intermediate is predominant under the reaction conditions for CH₃OH synthesis while CO hydrogenation leads to a small amount of CH₃OH 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 HCOO* in the formate route and CH₃OH synthesis followed the HCOO mechanistic pathway. The average hydrogenation limit for CO was just marginally higher than that for HCOO* to hydrogenate to CH₃OH. This may account for the observed levels of divergence between the production rates of HCOO* and CH₃OH [1]. In the section below, the methanol synthesis from the mixed CO₂/H₂ 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 CO₂ 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 CH₃OH from CO₂, they found that the difficulty in surface H* hydrogenation of CH₃O* could be overwhelmed in the existence of H₂O through a smaller barrier. The theoretical studies indicated that water may influence CO₂ 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 CH₃OH. With water physisorbed or chemically absorbed, the CO₂ 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 COHOH* and the RWGS mechanism pathway CO₂* → trans-COHOH* → CO* → HCO* → H₂CO* → H₃CO* → CH₃OH, which was more desirable than formate pathway from a kinetic viewpoint. The key intermediate in this mechanistic route of CO₂ hydrogenation on the surface of Cu(111) catalyst was COH* with a high activation barrier. Upon the hydrogenation of COH*, CH₃OH 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 Ga₃Ni₅(111) catalyst to analyze the mechanistic route of CO₂ hydrogenation to methanol. Their calculation results demonstrated that the possible reaction route for conversion of CO₂ into methanol using Ga₃Ni₅ (111) catalyst is as the following equations [17]:



Remarkably, their findings showed that the formation of trans-COOH species was not the rate-limiting step and had a low activation barrier, however, H₂O 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 CH₃OH production by the hydrogenation of CO₂ using different heterogeneous catalysts are given in Table 1.

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 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.

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 CO₂ into CH₃OH.

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* + *	Ji and Luo [18]
Cu(100)	DAM, HF, and MP2	Formate (HCOO)	HCOO* + H* → H ₂ COO*	Yang, et al. [14]
Cu(111)	DFT (GGA-PW91) and Microkinetic model	Formate (HCOO)	CH ₃ O* + H* → CH ₃ OH*	Grabow and Mavrikakis [19]
Cu(111)	DFT (GGA-PW91)	Carboxyl (COOH)	CO ₂ * + H* → COOH* + *	Zhao, et al. [16]
Cu(111)	DFT (GGA-PW91)	H ₂ O-promoted carboxyl (COOH)	COHOH* → COH* + OH* + *	Table 1
Cu(111)	DFT (GGA-PW91)	Formate (HCOO)	H ₂ COO* + H* → H ₂ CO* + OH* + *	Yang, et al. [12]
Cu(111)	DFT and kMC	Formate (HCOO)	H ₂ COO* + H* ↔ H ₂ CO* + OH* + *	[3]
Cu/PbTiO ₃	DFT (VASP-PAW) and kMC (Zacros 2.0)	Formate (HCOO)	HCOO* + H* → H ₂ COO*	Hus, et al. [20]
Cu/ZnAl ₂ O ₄	DFT (PWscf-PBE) and CCSD(T)/aug-cc-pVQZ	Formate (HCOO)	HCOO* + H* → H ₂ COO* + * H ₂ COO* + H* → H ₂ COOH*	Huš, et al. [9]
Cu/ZnO	DFT and kMC	Formate (HCOO)	-	Kattel, et al. [2]
Cu/ZnO/Al ₂ O ₃	DFT (GGA-PW91) and Microkinetic model	Formate (HCOO)	CH ₃ O* + H* → CH ₃ OH*	Grabow and Mavrikakis [19]
Cu/ZrO ₂	DFT (GGA-PBE) and kMC	Formate (HCOO)	CH ₃ O* + H* → CH ₃ OH*	Tang, et al. [7]
Cu ₂₉	DFT (GGA-PW91)	Formate (HCOO)	H ₂ COO* + H* → H ₂ CO* + OH* + *	Yang, et al. [12]
Fe(111) and W(111)	DFT (VASP-PAW-rPBE)	Carboxyl (COOH)	CO ₂ * + H* → trans-COOH* + * or cis-COOH*	Li and Ho [21]
Ga ₃ Ni ₅ (111)	DFT (GGA-VASP-PBE) and Microkinetic model	Carboxyl (COOH)	H* + OH* → H ₂ O	Tang, et al. [17]
In ₂ O ₃ (111)	DFT (GGA-VASP-PBE) and Microkinetic model	Formate (HCOO)	CH ₂ O* + H* → CH ₃ O* + *	Frei, et al. [10]
InZr ₃ (110)	DFT (GGA-PBE)	RWGS+CO-hydrogenation	HCO* + H* → H ₂ CO* + *	Zhang, et al. [22]
Mo ₆ S ₈	DFT (GGA-PBE)	RWGS+CO-hydrogenation	CO* + H* → HCO* + *	Ye, et al. [11]
Pt(111)	DFT (GGA) and Microkinetic model	Carboxyl (COOH)	COOH* + * → CO ₂ * + H*	Grabow, et al. [23]

PdCu ₃	DFT (GGA-PW91)	Carboxyl (COOH)	$\text{HCOH}^* + \text{H}^* \rightarrow \text{H}_2\text{COH}^* + ^*$	Liu, et al. [24]
Pd ₄ /In ₂ O ₃	DFT (VASP-GGA-PAW-PBE) and Microkinetic model	Formate (HCOO)	$\text{H}_2\text{COO}^* + \text{H}^* \rightarrow \text{H}_2\text{CO}^* + \text{OH}^*$	Ye, et al. [11]
Pt nanoparticle	DFT (VASP-GGA-PW91)	Formate (HCOO)	$\text{HCOO}^* + \text{H}^* \rightarrow \text{H}_2\text{COO}^*$	Kattel, et al. [15]
Rh ₃ Cu ₆ (111)	DFT (DMol ³ -GGA-PW91)	RWGS+CO-hydrogenation	$\text{CO}_2^* + \text{H}^* \rightarrow \text{trans-COOH}^* + ^*$	Liu, et al. [24]

References

- [1] Y. Li, S. H. Chan, and Q. Sun, "Heterogeneous catalytic conversion of CO₂: A comprehensive theoretical review," *Nanoscale*, vol. 7, pp. 8663-8683, 2015. Available at: <https://doi.org/10.1039/c5nr00092k>.
- [2] S. Kattel, P. J. Ramírez, J. G. Chen, J. A. Rodriguez, and P. Liu, "Active sites for CO₂ hydrogenation to methanol on Cu/ZnO catalysts," *Science*, vol. 355, pp. 1296-1299, 2017. Available at: <https://doi.org/10.1126/science.aal3573>.
- [3] D. Kopač, M. Huš, M. Ogrizek, and B. Likozar, "Kinetic Monte Carlo simulations of methanol synthesis from carbon dioxide and hydrogen on Cu (111) catalysts: Statistical uncertainty study," *The Journal of Physical Chemistry C*, vol. 121, pp. 17941-17949, 2017. Available at: <https://doi.org/10.1021/acs.jpcc.7b04985>.
- [4] Z.-M. Hu, K. Takahashi, and H. Nakatsuji, "Mechanism of the hydrogenation of CO₂ to methanol on a Cu (100) surface: Dipped adcluster model study," *Surface science*, vol. 442, pp. 90-106, 1999. Available at: [https://doi.org/10.1016/s0039-6028\(99\)00900-0](https://doi.org/10.1016/s0039-6028(99)00900-0).
- [5] T. Kakumoto and T. Watanabe, "A theoretical study for methanol synthesis by CO₂ hydrogenation," *Catalysis Today*, vol. 36, pp. 39-44, 1997. Available at: [https://doi.org/10.1016/s0920-5861\(96\)00194-0](https://doi.org/10.1016/s0920-5861(96)00194-0).
- [6] Q.-J. Hong and Z.-P. Liu, "Mechanism of CO₂ hydrogenation over Cu/ZrO₂ (212) interface from first-principles kinetics Monte Carlo simulations," *Surface Science*, vol. 604, pp. 1869-1876, 2010. Available at: <https://doi.org/10.1016/j.susc.2010.07.018>.
- [7] Q.-L. Tang, Q.-J. Hong, and Z.-P. Liu, "CO₂ fixation into methanol at Cu/ZrO₂ interface from first principles kinetic Monte Carlo," *Journal of Catalysis*, vol. 263, pp. 114-122, 2009. Available at: <https://doi.org/10.1016/j.jcat.2009.01.017>.
- [8] S. A. French, A. A. Sokol, S. T. Bromley, C. R. A. Catlow, S. C. Rogers, F. King, and P. Sherwood, "From CO₂ to methanol by hybrid QM/MM embedding," *Angewandte Chemie International Edition*, vol. 40, pp. 4437-4440, 2001.
- [9] M. Huš, V. D. Dasireddy, N. S. Štefančič, and B. Likozar, "Mechanism, kinetics and thermodynamics of carbon dioxide hydrogenation to methanol on Cu/ZnAl₂O₄ spinel-type heterogeneous catalysts," *Applied Catalysis B: Environmental*, vol. 207, pp. 267-278, 2017. Available at: <https://doi.org/10.1016/j.apcatb.2017.01.077>.
- [10] M. S. Frei, M. Capdevila-Cortada, R. García-Muelas, C. Mondelli, N. López, J. A. Stewart, D. C. Ferré, and J. Pérez-Ramírez, "Mechanism and microkinetics of methanol synthesis via CO₂ hydrogenation on indium oxide," *Journal of Catalysis*, vol. 361, pp. 313-321, 2018. Available at: <https://doi.org/10.1016/j.jcat.2018.03.014>.
- [11] J. Ye, C. J. Liu, D. Mei, and Q. Ge, "Methanol synthesis from CO₂ hydrogenation over a Pd₄/In₂O₃ model catalyst: A combined DFT and kinetic study," *Journal of Catalysis*, vol. 317 pp. 44-53, 2014. Available at: <https://doi.org/10.1016/j.jcat.2014.06.002>.
- [12] Y. Yang, J. Evans, J. A. Rodriguez, M. G. White, and P. Liu, "Fundamental studies of methanol synthesis from CO₂ hydrogenation on Cu (111), Cu clusters, and Cu/ZnO (0001 [combining macron])," *Physical Chemistry Chemical Physics*, vol. 12, pp. 9909-9917, 2010. Available at: <https://doi.org/10.1039/c001484b>.
- [13] W. Wang, S. Wang, X. Ma, and J. Gong, "Recent advances in catalytic hydrogenation of carbon dioxide," *Chemical Society Reviews*, vol. 40, pp. 3703-3727, 2011. Available at: <https://doi.org/10.1039/c1cs15008a>.
- [14] Y. Yang, M. G. White, and P. Liu, "Theoretical study of methanol synthesis from CO₂ hydrogenation on metal-doped Cu (111) surfaces," *The Journal of Physical Chemistry C*, vol. 116, pp. 248-256, 2012. Available at: <https://doi.org/10.1021/jp208448c>.
- [15] S. Kattel, B. Yan, J. G. Chen, and P. Liu, "CO₂ hydrogenation on Pt, Pt/SiO₂ and Pt/TiO₂: Importance of synergy between Pt and oxide support," *Journal of Catalysis*, vol. 343, pp. 115-126, 2016. Available at: <https://doi.org/10.1016/j.jcat.2015.12.019>.
- [16] Y.-F. Zhao, Y. Yang, C. Mims, C. H. Peden, J. Li, and D. Mei, "Insight into methanol synthesis from CO₂ hydrogenation on Cu (1 1 1): Complex reaction network and the effects of H₂O," *Journal of Catalysis*, vol. 281, pp. 199-211, 2011. Available at: <https://doi.org/10.1016/j.jcat.2011.04.012>.
- [17] Q. Tang, Z. Shen, C. K. Russell, and M. Fan, "Thermodynamic and kinetic study on carbon dioxide hydrogenation to methanol over a Ga₃Ni₅ (111) surface: The effects of step edge," *The Journal of Physical Chemistry C*, vol. 122, pp. 315-330, 2018. Available at: <https://doi.org/10.1021/acs.jpcc.7b08232>.
- [18] Y. Ji and Y. Luo, "New mechanism for photocatalytic reduction of CO₂ on the anatase TiO₂ (101) surface: The essential role of oxygen vacancy," *Journal of the American Chemical Society*, vol. 138, pp. 15896-15902, 2016. Available at: <https://doi.org/10.1021/jacs.6b05695>.
- [19] L. Grabow and M. Mavrikakis, "Mechanism of methanol synthesis on Cu through CO₂ and CO hydrogenation," *Acs Catalysis*, vol. 1, pp. 365-384, 2011. Available at: <https://doi.org/10.1021/cs200055d>.
- [20] M. Hus, D. Kopac, and B. Likozar, "Catalytic hydrogenation of carbon dioxide to methanol: Synergistic effect of bifunctional Cu/perovskite catalysts," *Acs Catalysis*, vol. 9, pp. 105-116, 2018. Available at: <https://doi.org/10.1021/acscatal.8b03810>.
- [21] H.-J. Li and J.-J. Ho, "Density functional calculations on the hydrogenation of carbon dioxide on Fe (111) and W (111) surfaces," *The Journal of Physical Chemistry C*, vol. 114, pp. 1194-1200, 2010. Available at: <https://doi.org/10.1021/jp909428r>.
- [22] M. Zhang, M. Dou, and Y. Yu, "DFT study of CO₂ conversion on InZr₃ (110) surface," *Physical Chemistry Chemical Physics*, vol. 19, pp. 28917-28927, 2017. Available at: <https://doi.org/10.1039/c7cp03859c>.
- [23] L. C. Grabow, A. A. Gokhale, S. T. Evans, J. A. Dumesic, and M. Mavrikakis, "Mechanism of the water gas shift reaction on Pt: First principles, experiments, and microkinetic modeling," *The Journal of Physical Chemistry C*, vol. 112, pp. 4608-4617, 2008. Available at: <https://doi.org/10.1021/jp7099702>.
- [24] L. Liu, F. Fan, M. Bai, F. Xue, X. Ma, Z. Jiang, and T. Fang, "Mechanistic study of methanol synthesis from CO₂ hydrogenation on Rh-doped Cu (111) surfaces," *Molecular Catalysis*, vol. 466, pp. 26-36, 2019. Available at: <https://doi.org/10.1016/j.mcat.2019.01.009>.