

Article

Thermodynamic and Kinetic Study of Carbon Dioxide Hydrogenation on the Metal-Terminated Tantalum-Carbide (111) Surface: A DFT Calculation

Saeedeh Sarabadani Tafreshi ^{1,*}, S. Fatemeh. K. S. Panahi ², Narges Taghizade ², Maryam Jamaati ², Mahkameh Ranjbar ¹ and Nora H. de Leeuw ^{3,4,*}

¹ Department of Chemistry, Amirkabir University of Technology (Tehran Polytechnic), No. 350, Hafez Avenue, Tehran 15916-34311, Iran

² Department of Physics, Iran University of Science and Technology, Narmak, Tehran 16846-13114, Iran

³ School of Chemistry, University of Leeds, Leeds LT2 9JT, UK

⁴ Department of Earth Sciences, Utrecht University, 3584 CB Utrecht, The Netherlands

* Correspondence: s.s.tafreshi@aut.ac.ir (S.S.T.); n.h.deleeuw@leeds.ac.uk (N.H.d.L.)

Abstract: The need to reduce our reliance on fossil fuels and lessen the environmentally harmful effects of CO₂ have encouraged investigations into CO₂ hydrogenation to produce useful products. Transition metal carbides exhibit a high propensity towards CO₂ activation, which makes them promising candidates as suitable catalysts for CO₂ hydrogenation. Here, we have employed calculations based on the density-functional theory to investigate the reaction network for CO₂ hydrogenation to product molecules on the tantalum-terminated TaC (111) surface, including two routes from either HCOOH* or HOCOH* intermediates. Detailed calculations of the reaction energies and energy barriers along multiple potential catalytic pathways, along with the exploration of all intermediates, have shown that CH₄ is the predominant product yielded through a mechanism involving HCOOH, with a total exothermic reaction energy of −4.24 eV, and energy barriers between intermediates ranging from 0.126 eV to 2.224 eV. Other favorable products are CO and CH₃OH, which are also produced via the HCOOH pathway, with total overall reaction energies of −2.55 and −2.10 eV, respectively. Our calculated thermodynamic and kinetic mechanisms that have identified these three predominant products of the CO₂ hydrogenation catalyzed by the TaC (111) surface explain our experimental findings, in which methane, carbon monoxide, and methanol have been observed as the major reaction products.

Keywords: carbon dioxide; hydrogenation; catalyst; tantalum carbide; DFT

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1. Introduction

The Earth's expanding population continues to lead to an increase in the world's energy consumption. However, it is now clear that CO₂ emissions from burning fossil fuels [1] are responsible, to a great extent, for climate change and the resulting environmental consequences. Hence, developments in the production of renewable resources and useful products from CO₂ hydrogenation is a fascinating research area [2–4].

Since fossil fuel reserves are finite, hydrogen production and storage as an alternative energy source to balance diminishing oil and gas resources could be feasible in a methanol economy [4,5]. Methanol, an important chemical raw materials, is already in significant demand due to its wide application in power generation and electricity, and it is an excellent alternative fuel [4,6]. Similarly, formic acid is another promising hydrogen storage material, and it is of considerable importance in the chemical and energy industries [2]. Apart from the traditional role of methane (CH₄) for power production and

heating, this gas is also valuable for industrial processes and for use in the production of important chemicals, e.g., in its conversion to methanol [1,7]. In addition, the low cost, high purity, versatility, and variety of chemical reactions for formaldehyde make it a good candidate for use in various industrial applications, especially in the production of resins [8]. It is also considered as a chemical intermediate in many chemical reactions due to its high reactivity [8], and it is one of the final products in carbon dioxide hydrogenation. Carbon monoxide, another product of CO₂ hydrogenation, has also attracted much attention in both academic and industrial settings [9].

As previously mentioned, the conversion of CO₂ into a range of useful products is important, both to achieve sustainable energy and to mitigate its global harmful effects [3,10,11]. Clearly, the design of new efficient, active, and low-cost catalysts to capture, activate, and utilize CO₂ is a major area of research [12,13].

Tantalum carbide, TaC, one of the family of transition metal carbides (TMCs), possesses many of the common characteristics of TMCs, such as extreme hardness, chemical stability, high melting point, and high corrosion resistance [14–17]. Even among the various carbides, TaC is stable at very high temperatures [18,19]. The extraordinary physical and chemical properties of TMCs are attributed to their chemical bond features, which make them a combination of covalent solids and ionic crystals, but with transition metal behavior [20,21]. Although Pt-group metals are valued as highly effective catalysts, their high cost makes them impractical for catalytic processes. Here, it is worth mentioning that TMCs display similar performance to the Pt-group metals, and owing to their low cost, high durability, and high activity, along with their interesting catalytic properties towards many reactions, TMCs are receiving increasing attention [22,23], as originally highlighted by the study by Levy and Boudart in 1973 [24].

Recent experimental and computational studies have confirmed that TMCs can be appealing materials to achieve CO₂ activation [21,22,25–29] and conversion into CO [25], CH₄ [30], CH₃OH [26], as well as other hydrocarbons [31,32]. TMCs show good performance in the reaction of CO₂ conversion, and studies based on the density-functional theory (DFT) have shown that early transition metal carbides (TMCs) such as TiC, ZrC, WC, NbC, TaC, and δ -MoC are able to strongly trap and activate CO₂ [22]. In addition, there is experimental and/or computational evidence that δ -MoC(001), β -Mo₂C(001), α -Mo₂C, WC, metal-terminated NbC(111), and NbC(001) surfaces present high selectivity toward CO₂ conversion [12,25,29,33,34]. In other works, adsorption energies of the CO₂ molecule on the low Miller index (001), (011), and (111) surfaces of TiC and ZrC have been explored, and it was found that CO₂ molecules reduce more easily on the (111) surface than on other facets [35,36].

According to the literature, fcc (111) surfaces of TMCs are less stable and generally more reactive, which is related to the existence of more surface states near the Fermi level than is the case in other low-index surfaces [27,37–39]. The (111) surfaces of TaC have been found to be unreconstructed and terminated by the transition metal after heating and ion or electron bombardment under low-temperature and low pressure conditions [40,41]. Other experimental characterizations of transition metal carbide surfaces have also indicated that the topmost layer of the clean (111) surface consists of metal atoms [14,42]. According to the study by Kitchin et al., TM-terminated carbide surfaces were found to be more reactive than the corresponding pure metal or carbon-terminated carbide surfaces. The surface atoms of the TM-terminated carbide surfaces are under-coordinated compared to the surface atoms of the pure metals, which could explain why atoms and small molecules are adsorbed more strongly, whereas the subsurface carbon atoms are expected to attenuate this effect [15,43]. As such, we have focused our study on the TM-terminated (111) surface, and even though many studies have explored TMC surfaces, there is no comprehensive DFT study regarding CO₂ hydrogenation on the TaC (111) surface. For these reasons, this paper is devoted to the investigation of the physical properties and chemical reactions relevant to the conversion of CO₂ to products on the

TaC (111) surface. We have employed calculations based on the density-functional theory to obtain a comprehensive overview of the CO₂ surface chemistry on TaC.

2. Computational Details

2.1. Method

The computational results are obtained using the Vienna Ab initio simulation package (VASP) [44,45], with the exchange-correlation functional developed by Perdew-Burke-Ernzerhof [46] and used within the generalized gradient approximation (GGA). Moreover, in order to improve the energy description of each system, we have included the DFT-D3 dispersion correction, as proposed by Grimme [47], with a plane wave cut-off energy of 600 eV. We have used a Monkhorst-Pack k-point mesh of 11×11×11 and 4×4×1 for the TaC bulk and (111) surface, respectively. The lattice parameter was calculated at $a_0 = 4.450$ Å, which is in excellent agreement with the experimental data ($a_0 = 4.454$ Å) from the inorganic crystal structure database (ICSD) [48] and other DFT studies using different exchange-correlation functionals (4.485 and 4.436 Å) [14]. The convergence force between atoms is set to be smaller than 0.01 eV/Å, and the maximum energy of each atom is converged to 10^{−5} eV. In order to avoid the interaction between neighboring unit cells, a vacuum space of more than 20 Å is introduced to create the surface slabs. Transition states were found using the IDM method [49,50], and frequency calculations were carried out to ensure that we have obtained the correct initial, transition, and final states.

2.2. Model

The TaC (111) surface and the molecules to be adsorbed at the surface are shown in Figure 1. Two possible planes, terminated by tantalum or carbon atoms, exist for the face-centered cubic (fcc) structure of the TaC (111) surface. In this study the tantalum-terminated TaC (111) surface (see Figure 1a) is investigated. To provide an adequate description of the surface relaxations, the TaC (111) surface is constructed of seven layers, with four bottom layers fixed to mimic the bulk crystal. The simulation cell contains 112 atoms and is the same as the slab used in the study by Vojvodic et al. for the adsorption of atoms and molecules on TMC (111) surfaces [51]. Each adsorbed molecule is located in different initial positions on the surface to calculate the favorable adsorption geometries. We have calculated the adsorption energies of the intermediates relative to CO₂ and four H₂ molecules in the gas phase [52]:

$$E_{ads} = E_{C_xO_yH_z}^{surf} + (1-x)E_C^{surf} + (2-y)E_O^{surf} + (8-z)E_H^{surf} - E^{surf} - E_{CO_2}^{gas} - 4 * E_{H_2}^{gas} \quad (1)$$

where $E_{C_xO_y}^{surf}$ is the total energy of the C_xO_y intermediates adsorbed on a relaxed TaC (111) surface, and E_C^{surf} , E_H^{surf} , and E_O^{surf} are the energies of isolated carbon, hydrogen, and oxygen atoms, respectively, adsorbed at a distance elsewhere on the relaxed surface. E^{surf} , $E_{CO_2}^{gas}$, and $E_{H_2}^{gas}$ are the energies of the naked TaC (111) slab, isolated gas-phase carbon dioxide, and hydrogen molecules, respectively. Within this definition, a negative E_{ads} value means a release of energy during an exothermic adsorption.

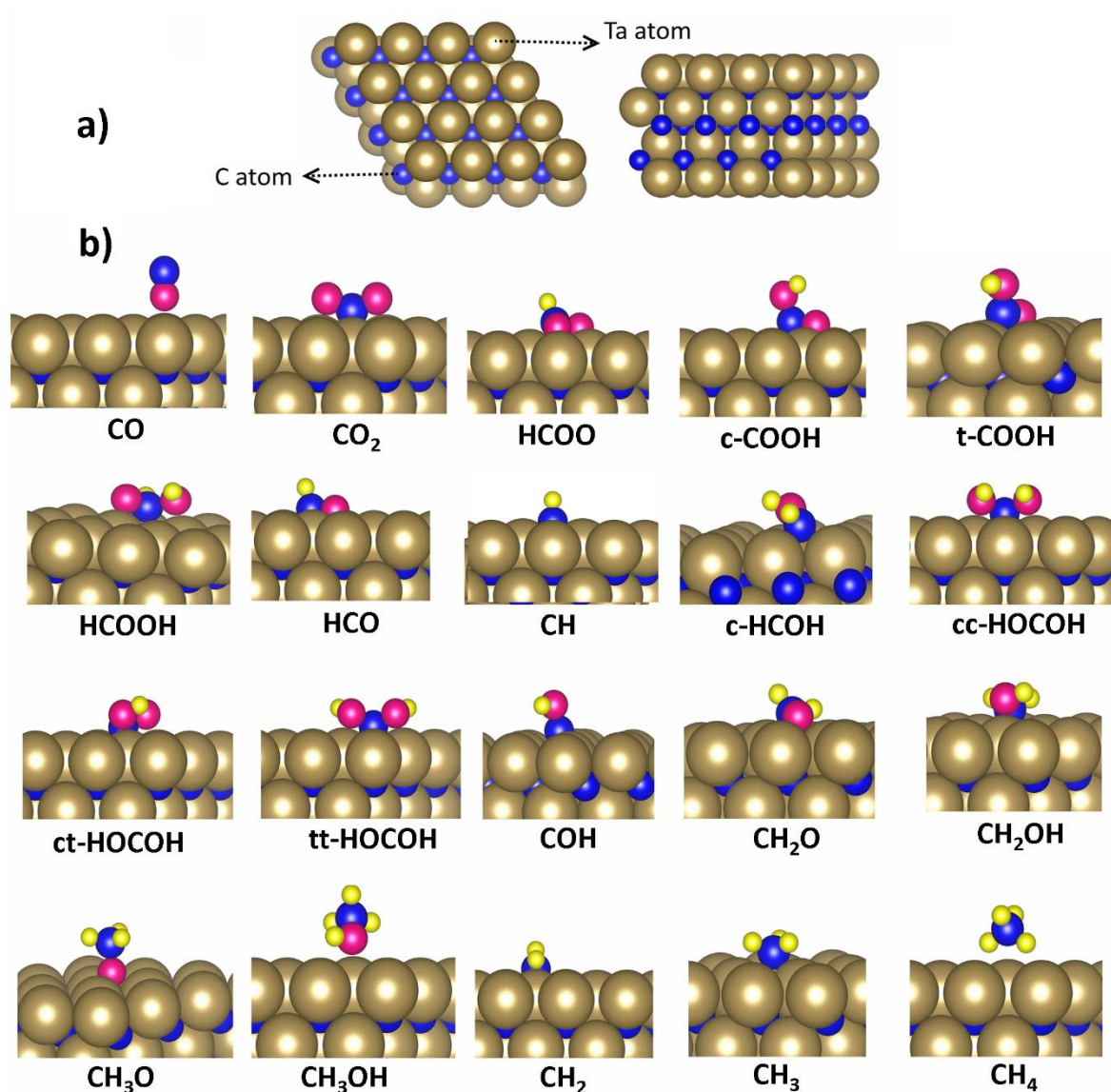


Figure 1. (a) TaC (111) surface, (b) the adsorbed geometries of the studied species during CO₂ hydrogenation on the TaC (111) surface. Carbon atoms are shown in dark blue, oxygen atoms in magenta, titanium atoms in gold, and hydrogen atoms in yellow spheres.

3. Results and Discussion

3.1. Adsorption Configurations and Energies on TaC (111) Surface

In this section, the CO₂ hydrogenation processes at the TaC (111) surface and the stable adsorption of all possible intermediates are calculated. First, by constructing several initial configurations, the most favorable locations were selected after complete geometric optimization of the TaC (111) surface and adsorbates. The preferred adsorption positions for all intermediates at the TaC (111) surface are presented in Figure 1b, with geometric information and adsorption energies provided in Table 1.

CO binds to the TaC (111) surface through its O atom, which is located exactly on top of a surface Ta atom, with a bond length of 2.27 Å and an adsorption energy of −0.226 eV. In the adsorbed CO₂ molecule, two oxygen atoms bond strongly to the surface Ta atoms, while its carbon atom does not bind to the surface atoms; the Ta–O bond lengths are 2.21 Å to both oxygen atoms. Adsorption of the CO₂ molecule results in an alteration in the initial structure of the molecule, where the C–O bond length shortens from 1.177 Å to 1.27 Å. Besides the bond lengths, the O–C–O bond angle decreases from 180° to 132° after

adsorption of the molecule, which indicates that the molecule has become activated. These geometric changes have been seen in other studies [53]. For example, the adsorption of CO₂ on the TaC (111) surface without cleavage of the C–O bond agrees with the DFT study of the chemisorption of a CO₂ molecule on the MoC surface, without cleavage of the C–O bonds when the Mo/C ratio is equal to one [54]. The CO₂ adsorption energy (−0.1.891 eV) is also very close to the values found by Kunkel et al. [22,55] for transition metal carbide (001) surfaces.

The adsorption energy of HCOO is −0.477 eV, with a C–O chemical bond of 1.41 Å. Both cis-COOH and trans-COOH approach the surface from their O side, with the oxygen becoming located between the Ta atoms, creating Ta–O bonds of 2.22 and 2.23 Å in c-COOH and 2.21 and 2.22 Å in t-COOH. The adsorption energies of c-COOH and t-COOH are −0.620 eV and −0.702 eV, respectively.

Each oxygen atom of HCOOH bonds to one Ta atom on the surface, with bond lengths of 2.22 Å and 2.23 Å and an adsorption energy of −0.711 eV. The C–O bonds in the HCOOH molecule lengthen by about 9.6% and 11.5% due to adsorption. In the HCO molecule, the oxygen atom is located between three surface Ta atoms, to which it is bound with Ta–O bond lengths of 2.18 Å, 2.18 Å, and 4.18 Å, respectively, causing an adsorption energy of −0.330 eV. Similarly, the O atom of cis-HCOH tends to form a Ta–O bond with a surface Ta atom, with a bond length of 2.21 Å. The c-HCOH molecule is adsorbed immediately above one of the Ta atoms in the surface, with an adsorption energy of −0.458 eV. It is worth mentioning that trans-HCOH on the surface converts to c-HCOH.

Moreover, in the dihydroxycarbene (HOCO) molecule, the C atom of molecule is located between two surface Ta atoms, but it does not form a bond, whereas two oxygen atoms are bonded with surface Ta atoms with Ta–O bond lengths of 2.29 Å, 2.27 Å, and 2.25 Å and adsorption energies of −0.589, −0.739, and −0.850 eV for cc-HOCO, ct-HOCO, and tt-HOCO, respectively.

The COH molecule approaches the surface by its carbon atom, but the carbon does not bind to the Ta atoms on the surface. The distance between the carbon atom of the CH₂O molecule and a surface Ta atom is 2.05 Å, but it adsorbs via its O atom, with a bond length of 2.20 Å and an adsorption energy of −0.335 eV.

CH₂OH adsorbs on top of a surface Ta site at the TaC (111) through its O atom, with an adsorption energy of −0.752 eV, forming a Ta–O bond length of 2.23 Å and causing the initial C–O bond length to increase by about 10.9%. CH₃O also approaches the surface through its O atom, where the oxygen atom bonds to three surface Ta atoms with equal Ta–O bond lengths of 2.24 Å and an adsorption energy of −0.645 eV. The oxygen atom of CH₃OH adsorbs above a surface Ta atom, with an adsorption energy of just −0.141 eV, forming a Ta–O bond with a bond length of 2.26 Å.

It should be noted that CH₂ prefers to be sited between two surface Ta atoms, but without forming a bond to the TaC (111) surface via its carbon atom. The shortest distance between the C atom and the surface Ta atoms is 2.23 Å, with an adsorption energy of −0.615 eV. CH₃ adsorbs close to the surface in the hollow site of Ta, where it behaves similarly to the CH₂ molecule, at the shortest distance of 2.42 Å between the C atom and the surface Ta atoms and a calculated adsorption energy of −0.998 eV. The CH₄ molecule approaches the surface through its C atom, at a minimum distance of about 2.80 Å and an adsorption energy of −0.095 eV.

Table 1. The preferred adsorption geometric information and adsorption energies for all intermediates on the TaC (111) surface during CO₂ hydrogenation on the TaC (111) surface.

Species	E _{ads} (eV)	Bond Length (Å)	Species	E _{ads} (eV)	Bond Length (Å)
CO	−0.226	d [*] _{Ta-C} = 2.27, d _{O-C} = 1.15	c-HCOH	−0.458	d [*] _{Ta-O} = 2.21, d _{O-C} = 1.51
CO ₂	−1.891	d [*] _{Ta-O} = 2.21, d _{Ta-C} = 2.27	cc-HOCO	−0.589	d [*] _{Ta-O} = 2.29, d _{O-C} = 1.45

HCOO	−0.477	$d_{\text{Ta-O}}^* = 2.14,$ $d_{\text{Ta-O}}^* = 2.27,$ $d_{\text{O-C}} = 1.41$	ct-HOCO	−0.739	$d_{\text{Ta-O}}^* = 2.27,$ $d_{\text{O-C}} = 1.46$
c-COOH	−0.620	$d_{\text{Ta-O}}^* = 2.23,$ $d_{\text{Ta-O}}^* = 2.22,$ $d_{\text{O-C}} = 1.37,$ $d_{\text{O-C}} = 1.34$	tt-HOCO	−0.850	$d_{\text{Ta-O}}^* = 2.25,$ $d_{\text{O-C}} = 1.46$
t-COOH	−0.702	$d_{\text{Ta-O}}^* = 2.21,$ $d_{\text{Ta-O}}^* = 2.22,$ $d_{\text{O-C}} = 1.37,$ $d_{\text{O-C}} = 1.34$	COH	−0.233	$d_{\text{Ta-C}}^* = 2.05,$ $d_{\text{O-C}} = 1.36$
HCOOH	−0.711	$d_{\text{Ta-O}}^* = 2.06,$ $d_{\text{O-C}} = 1.49,$ $d_{\text{O-C}} = 1.35$	CH ₂ O	−0.335	$d_{\text{Ta-O}}^* = 2.20,$ $d_{\text{O-C}} = 1.42$
HCO	−0.330	$d_{\text{Ta-O}}^* = 2.18,$ $d_{\text{Ta-O}}^* = 2.18,$ $d_{\text{Ta-O}}^* = 4.18,$ $d_{\text{O-C}} = 1.43$	CH ₂ OH	−0.752	$d_{\text{Ta-O}}^* = 2.23,$ $d_{\text{O-C}} = 1.15$
CH ₂	−0.615	$d_{\text{Ta-C}}^* = 2.23$	CH ₃ O	−0.645	$d_{\text{Ta-O}}^* = 2.24,$ $d_{\text{O-C}} = 1.45$
CH ₃	−0.998	$d_{\text{Ta-C}}^* = 2.42,$ $d_{\text{H-C}} = 1.13$	CH ₃ OH	−0.141	$d_{\text{Ta-O}}^* = 2.26,$ $d_{\text{O-C}} = 1.45$
CH ₄	−0.095	$d_{\text{Ta-C}} = 2.80$			

It should be noted that the bond between the molecules and the surface is indicated by the symbol *, while the chemical bonds in each molecule after adsorption are shown without any sign.

3.2. Reaction Networks of CO₂ Hydrogenation

Next, we present a detailed investigation of the reaction networks for all possible intermediates involved in the processes of CO₂ hydrogenation at the Ta-terminated TaC (111) surface. It is known that the TaC (111) surface is able to catalyze the following reactions:

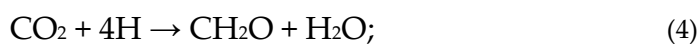
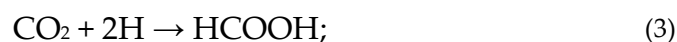
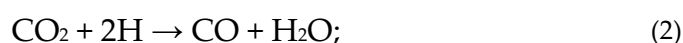


Figure 2 explores a range of specific elementary steps for the reaction map of CO₂ hydrogenation to CO, HCOOH, CH₂O, CH₃OH, and CH₄ at the Ta-terminated TaC (111) surface, where the reaction networks include pathways either from HCOO or from (c,t)-COOH.



Figure 2. The possible reaction networks of CO₂ hydrogenation to CO, HCOOH, CH₂O, CH₃OH, and CH₄ at the TaC (111) surface. It should be noted that the adsorbed intermediates on the surface are indicated by the symbol *.

3.3. Chemical Reactions

In this section, we discuss the feasible reactions underpinning the mechanism of CO₂ hydrogenation on the TaC (111) surface. The calculated reaction energies of all intermediates, including the processes of CO₂ hydrogenation at the TaC (111) surface, are shown in Table 2. The initial step associated with CO₂ hydrogenation is either the formation of a formate (HCOO*) or the generation of a carboxyl species (t-COOH* and/or c-COOH*). The former takes place when hydrogen attacks the carbon atom of CO₂ through $\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^*$, which requires an energy of 0.198 eV. Similarly, the reactions $\text{CO}_2^* + \text{H}^* \rightarrow (\text{c,t})\text{-COOH}^*$ occur when H atoms attach to the O atoms of the CO₂ molecule; these are endothermic processes, with energies of 1.056 eV and 0.974 eV for the cis and trans conformer products, respectively. Thus, the first hydrogen atom prefers to attack the carbon atom rather than the oxygen atoms of CO₂ to form HCOO*, which agrees with the results of CO₂ hydrogenation on the bimetallic MoTiC₂ MXenes [56]. Formic acid (HCOOH) is generated from the hydrogenation of HCOO* via the reaction $\text{HCOO}^* + \text{H}^* \rightarrow \text{HCOOH}^*$, which is also an endothermic process requiring an energy of 1.580 eV. Moreover, further hydrogenation of the carboxyl species can also result in the formation of HCOOH*. These reactions $(\text{c,t})\text{-COOH}^* + \text{H}^* \rightarrow \text{HCOOH}^*$ are also endothermic processes, with energies of 0.723 eV and 0.805 for the c-COOH* and t-COOH* reactant

species, respectively. In conclusion, the formation of HCOOH^* via the carboxyl species is more favorable than via the formate intermediate as a result of the lower reaction energy.

The carboxyl species may further hydrogenate to produce dihydroxycarbene (cc-HOCO^* , ct-HOCO^* , and tt-HOCO^*) through the reaction $(\text{c,t})\text{-COOH}^* + \text{H}^* \rightarrow (\text{ct, cc, tt})\text{-HOCO}^*$. As is clear from Table 2, all of the above reactions are endothermic processes, although the transformation of $(\text{cc,ct})\text{-HOCO}^*$ to tt-HOCO^* is exothermic, with reaction energies of -0.261 eV and -0.111 eV, respectively. Therefore, the reaction pathways for CO_2 hydrogenation at the TaC (111) surface include two routes, either from the HCOOH^* or HOCO^* intermediates, which can be followed to achieve the formation of other products. Figure 3. Shows the reaction profile for the hydrogenation of CO_2 and subsequent reactions of intermediates to HCOOH , CO , CH_2O , CH_3OH , and CH_4 via HCOOH , and HOCO^* at the TaC (111) surface. In the next section, these reaction pathways are studied in detail.

Table 2. The possible reactions and their corresponding energies in the hydrogenation of intermediates to form CO , HCOOH , CH_2O , CH_3OH , and CH_4 . It should be noted that the adsorbed intermediates on the surface are indicated by the symbol * .

Elementary Reactions	$\Delta E(\text{eV})$	Elementary Reactions	$\Delta E(\text{eV})$
$\text{CO}_2(\text{g}) \rightarrow \text{CO}_2^*$	-1.891	$\text{c-COOH}^* + \text{H}^* \rightarrow \text{cc-HOCO}^*$	1.845
$\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^*$	0.198	$\text{t-COOH}^* + \text{H}^* \rightarrow \text{tt-HOCO}^*$	1.666
$\text{CO}_2^* + \text{H}^* \rightarrow \text{c-COOH}^*$	1.056	$\text{c-COOH}^* + \text{H}^* \rightarrow \text{ct-HOCO}^*$	1.695
$\text{CO}_2^* + \text{H}^* \rightarrow \text{t-COOH}^*$	0.974	$\text{t-COOH}^* + \text{H}^* \rightarrow \text{ct-HOCO}^*$	1.777
$\text{c-COOH}^* \rightarrow \text{t-COOH}^*$	-0.082	$\text{cc-HOCO}^* + \text{H}^* \rightarrow \text{tt-HOCO}^*$	-0.261
$\text{HCOO}^* + \text{H}^* \rightarrow \text{HCOOH}^*$	1.580	$\text{ct-HOCO}^* + \text{H}^* \rightarrow \text{tt-HOCO}^*$	-0.111
$\text{c-COOH}^* \rightarrow \text{CO}^* + \text{OH}^*$	0.702	$\text{tt-HOCO}^* \rightarrow \text{COH}^* + \text{OH}^*$	-1.375
$\text{t-COOH}^* \rightarrow \text{CO}^* + \text{OH}^*$	0.784	$\text{ct-HOCO}^* \rightarrow \text{COH}^* + \text{OH}^*$	-1.486
$\text{c-COOH}^* + \text{H}^* \rightarrow \text{HCOOH}^*$	0.723	$\text{cc-HOCO}^* \rightarrow \text{COH}^* + \text{OH}^*$	-1.636
$\text{t-COOH}^* + \text{H}^* \rightarrow \text{HCOOH}^*$	0.805	$\text{COH}^* \rightarrow \text{CO}^* + \text{H}^*$	0.493
$\text{HCOOH}^* \rightarrow \text{HCO}^* + \text{OH}^*$	-1.611	$\text{COH}^* + \text{H}^* \rightarrow \text{c-HCOH}^*$	0.589
$\text{HCOOH}^* \rightarrow \text{HCOOH}(\text{g})$	2.320	$\text{c-HCOH}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^*$	0.520
$\text{HCO}^* + \text{H}^* \rightarrow \text{c-HCOH}^*$	1.687	$\text{CH}_2\text{OH}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^*$	1.424
$\text{HCO}^* \rightarrow \text{CO}^* + \text{H}^*$	1.590	$\text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^* + \text{OH}^*$	-1.855
$\text{CO}^* \rightarrow \text{CO}(\text{g})$	0.263	$\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^*$	0.431
$\text{HCO}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^*$	0.809	$\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4^*$	1.818
$\text{CH}_2\text{O}^* \rightarrow \text{CH}_2\text{O}(\text{g})$	2.834	$\text{CH}_4^* \rightarrow \text{CH}_4(\text{g})$	0.240
$\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}^*$	0.504	$\text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{OH}(\text{g})$	1.037
$\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^*$	1.398	$\text{H}_2\text{O}^* \rightarrow \text{H}_2\text{O}(\text{g})$	0.894
$\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^*$	2.318		

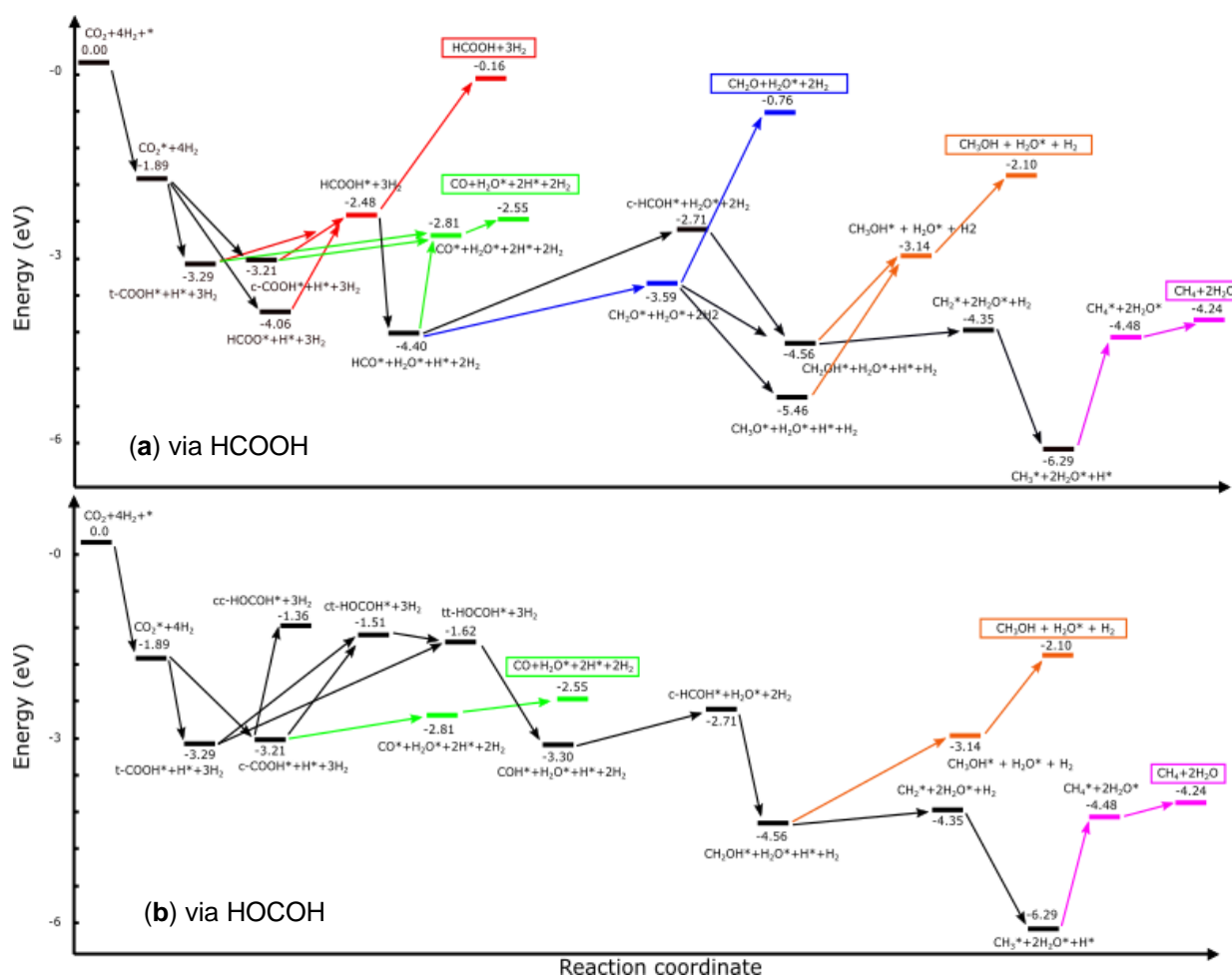


Figure 3. Reaction profile for the hydrogenation of CO₂ and subsequent reactions of intermediates to HCOOH, CO, CH₂O, CH₃OH, and CH₄ via (a) HCOOH and (b) HOCO at the TaC (111) surface.

3.3.1. Reaction Pathways of CO₂ to Possible Products through HCOOH

The Reaction Mechanisms for CO₂ Hydrogenation to HCOOH

As discussed above, CO₂ hydrogenation can lead to the formation of HCOO* or the generation of t-COOH* and/or c-COOH*. These species can further react with hydrogen to yield the HCOOH product. Although all these reactions are endothermic processes, the formation of HCOOH* via a carboxyl species appears to be more favorable than via the HCOO* intermediate because of its lower reaction energy.

The Reaction Paths for CO₂ Hydrogenation to CO via HCOOH

There are two paths to CO production: a direct path through the decomposition of (t,c)-COOH* via the reaction (c,t)-COOH* → CO* + OH*, where the reaction is endothermic by 0.702 eV and 0.784 eV for the cis and trans conformers, respectively. Another path is through the decomposition of the HCOOH* intermediate, which leads to the formation of HCO*, with further decomposition of HCO* yielding CO*. The calculated reaction energy of −1.611 eV shows that the decomposition of HCOOH* via HCOOH* → HCO* + OH* is an exothermic process, while the subsequent decomposition of HCO* through HCO* → CO* + H* is an endothermic reaction requiring an energy of 1.590 eV.

The Reaction Paths for the CO₂ Hydrogenation to CH₂O via HCOOH

After formation of HCO*, it can further react with an H atom to form either formaldehyde (CH₂O*) or c-HCOH*. As such, the only pathway to obtain the CH₂O

molecule from CO₂ takes place through the $\text{HCO}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^*$ reaction, with an endothermic energy of 0.809 eV.

The Reaction Paths for CO₂ Hydrogenation to CH₃OH via HCOOH

The pathway to CH₃OH includes either CH₂O* or c-HCOH*, and these routes are explained separately. As mentioned previously, HCO* hydrogenation can result in the formation of c-HCOH* through $\text{HCO}^* + \text{H}^* \rightarrow \text{c-HCOH}^*$, with a reaction energy of 1.687 eV. Next, c-HCOH* attaches a hydrogen via $\text{c-HCOH}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^*$, with an energy of 0.520 eV, to form CH₂OH*. Further hydrogenation of CH₂OH* leads to CH₃OH* ($\text{CH}_2\text{OH}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^*$) which is an endothermic process at an energy of 1.424 eV. The other pathway to CH₃OH is through the hydrogenation of formaldehyde via $\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^*$, which is an endothermic reaction requiring an energy of 1.398 eV. For the subsequent reaction, the CH₂OH* can further react with another H atom to produce CH₃OH*, which reaction is endothermic by 1.424 eV. Besides CH₂OH*, further hydrogenation of CH₂O* may result in the formation of methoxy (CH₃O*) via the $\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}^*$ reaction, which process is endothermic and requires 0.504 eV. Once the formed CH₃O* intermediate reacts further with another H atom, CH₃OH* will be produced, with the reaction $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^*$ requiring 2.318 eV.

The Reaction Paths for CO₂ Hydrogenation to CH₄ via HCOOH

The route to CH₄* formation involves the dissociation of CH₂OH* ($\text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^* + \text{OH}^*$), which leads to CH₂*. This reaction is exothermic at −1.855 eV. Next, CH₃* and CH₄* are produced through the subsequent hydrogenation of CH₂* and CH₃* via $\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^*$ and $\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4^*$. Both these reactions are endothermic processes, with reaction energies of 0.431 eV and 1.818 eV, respectively.

3.3.2. Reaction Pathways of CO₂ to Possible Products through HOCOH

As mentioned previously, another route to CO, CH₃OH, and CH₄ products is via the HOCOH* pathway, where HOCOH* conformers form through the hydrogenation of c,t-COOH* via $(\text{c,t})\text{-COOH}^* + \text{H}^* \rightarrow (\text{ct, cc, tt})\text{-HOCOH}^*$. The tt-HOCOH* conformer is favored, as conversion of cc-HOCOH* and ct-HOCOH* to tt-HOCOH* ($(\text{cc,ct})\text{-HOCOH}^* + \text{H}^* \rightarrow \text{tt-HOCOH}^*$) is exothermic, with energies of −0.261 eV and −0.111 eV, respectively, and tt-HOCOH* is therefore a likely intermediate.

The Reaction Paths for CO₂ Hydrogenation to CO via HOCOH

There are two pathways to CO, directly from (c,t)-COOH* decomposition, where (c,t)-COOH* decomposes to CO* and OH* via the $(\text{c,t})\text{-COOH}^* \rightarrow \text{CO}^* + \text{OH}^*$ reaction. Both processes are endothermic, with energies of 0.702 eV and 0.784 eV for the cis and trans conformers, respectively. Another pathway involves the decomposition of tt-HOCOH* to COH* and OH* through $\text{tt-HOCOH}^* \rightarrow \text{COH}^* + \text{OH}^*$, which is an exothermic reaction by −1.375 eV. Next, CO* will form via further decomposition of COH* via the $\text{COH}^* \rightarrow \text{CO}^* + \text{H}^*$ reaction, which requires 0.493 eV of energy.

The Reaction Paths for CO₂ Hydrogenation to CH₃OH via HOCOH

Once the formed COH* intermediate reacts further with another hydrogen, c-HCOH* will form through the $\text{COH}^* + \text{H}^* \rightarrow \text{c-HCOH}^*$ reaction, with an endothermic energy of 0.589 eV. Subsequent hydrogenation of c-HCOH* will produce CH₂OH* through $\text{c-HCOH}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^*$, which reaction is an endothermic process at 0.520 eV. If CH₂OH* attaches another hydrogen, CH₃OH* will finally be produced through the $\text{CH}_2\text{OH}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^*$ reaction, with an endothermic energy of 1.424 eV.

The Reaction Paths for CO₂ Hydrogenation to CH₄ via HOCO⁺

The dissociation of CH₂OH* results in CH₂*, which process takes place through the CH₂OH* → CH₂* + OH* reaction with an exothermic reaction energy of −1.855 eV. Further hydrogenation of CH₂* will produce CH₃* via CH₂* + H* → CH₃*, with an energy of 0.431 eV. Finally, subsequent hydrogenation of CH₃* leads to CH₄* via CH₃* + H* → CH₄*, which is also endothermic, at 1.818 eV.

3.4. Activation Energies

In order to gain further insight, activation barriers of a number of selected elementary reactions (listed in Table 3) in the CO₂ hydrogenation process over the TaC (111) surface have been calculated and compared, using the $E_b = E_{TS} - E_{IS}$ relationship, where E_{IS} and E_{TS} represent the total energy of the initial and transition states, respectively. The calculated activation barriers for the selected steps are summarized in Table 3, and in the following section, we will discuss these reactions in more detail, with the initial, transition and final states of the reactions depicted in Figure 4.

Table 3. The selected reactions and their corresponding activation barrier energies. It should be noted that the adsorbed intermediates on the surface are indicated by the symbol *.

Elementary Reactions	E _b (eV)	Elementary Reactions	E _b (eV)
CO ₂ * + H* → HCOO*	0.808	CH ₂ O* + H* → CH ₃ O*	1.282
HCOO* + H* → HCOOH*	1.828	CH ₃ O* + H* → CH ₃ OH*	1.429
HCOOH* → HCO* + OH*	0.264	CH ₂ OH* → CH ₂ * + OH*	0.126
HCO* → CO* + H*	0.614	CH ₂ * + H* → CH ₃ *	1.210
HCO* + H* → CH ₂ O*	1.304	CH ₃ * + H* → CH ₄ *	2.224
CH ₂ O* + H* → CH ₂ OH*	1.480		

As previously mentioned, in the formation of HCOO (CO₂* + H* → HCOO*) H approaches the C atom of CO₂ to form a C–H bond, where the distance between the C and H atoms decreases from 3.29 Å in the initial state (IS) to 1.95 Å in the transition state (TS), and then to 1.10 Å in the final state (FS). The calculated activation barrier is 0.808 eV. The generation of formic acid through formate hydrogenation (HCOO* + H* → HCOOH*) must overcome an activation barrier of 1.828 eV, where H bonds with the O of formate to form an O–H bond, which shortens from an initial distance of 2.55 Å to 1.27 Å and finally, to 0.98 Å in the IS, TS, and FS, respectively. The dissociation of HCOOH* via HCOOH* → HCO* + OH* has a rather small activation barrier of 0.264 eV, which is therefore kinetically favorable. The increase in the C–O bond length in HCOOH* weakens the C–O bond, resulting in the decomposition of HCOOH* to HCO* and OH*, with the C–O bond lengthening from 1.49 Å to 1.91 Å and finally, to 3.2 Å in the IS, TS, and FS, respectively. HCO* can further hydrogenate to formaldehyde or dissociate to carbon monoxide. In the former reaction (HCO* + H* → CH₂O*), formaldehyde can be produced when the distance between the H* and C atom of HCO* decreases from 1.61 Å in the TS to 1.15 Å in the FS to form an H–C bond. This reaction must overcome an activation barrier of 1.304 eV. The latter reaction (HCO* → CO* + H*) takes place over an energy barrier of 0.614 eV, which shows that kinetic CO formation occurs preferentially. The hydrogenation of CH₂O* generates either CH₂OH* through CH₂O* + H* → CH₂OH* or CH₃O* via CH₂O* + H* → CH₃O*. The formation of CH₃O* (1.282 eV) is slightly more favorable than CH₂OH* production (1.480 eV), owing to the lower energy barrier.

In the next step, CH₃OH* can be produced via CH₃O* hydrogenation (CH₃O* + H* → CH₃OH*), with an energy barrier of $E_b = 1.429$ eV. The H atom approaches the O atom of the methoxide, leading to O–H bond formation. In the IS, the distance between H and O is 3.8 Å, decreasing to 1.88 Å and 0.98 Å in the TS and FS, respectively. However, hydroxymethyl (CH₂OH) can dissociate to CH₂* (CH₂OH* → CH₂* + OH*), with a small activation barrier of 0.126 eV that is kinetically favorable. The C–O bond in CH₂OH

weakens as the bond length increases, from a C-O distance of 1.52 Å to 1.81 Å and 3.18 Å in the IS, TS, and FS, respectively.

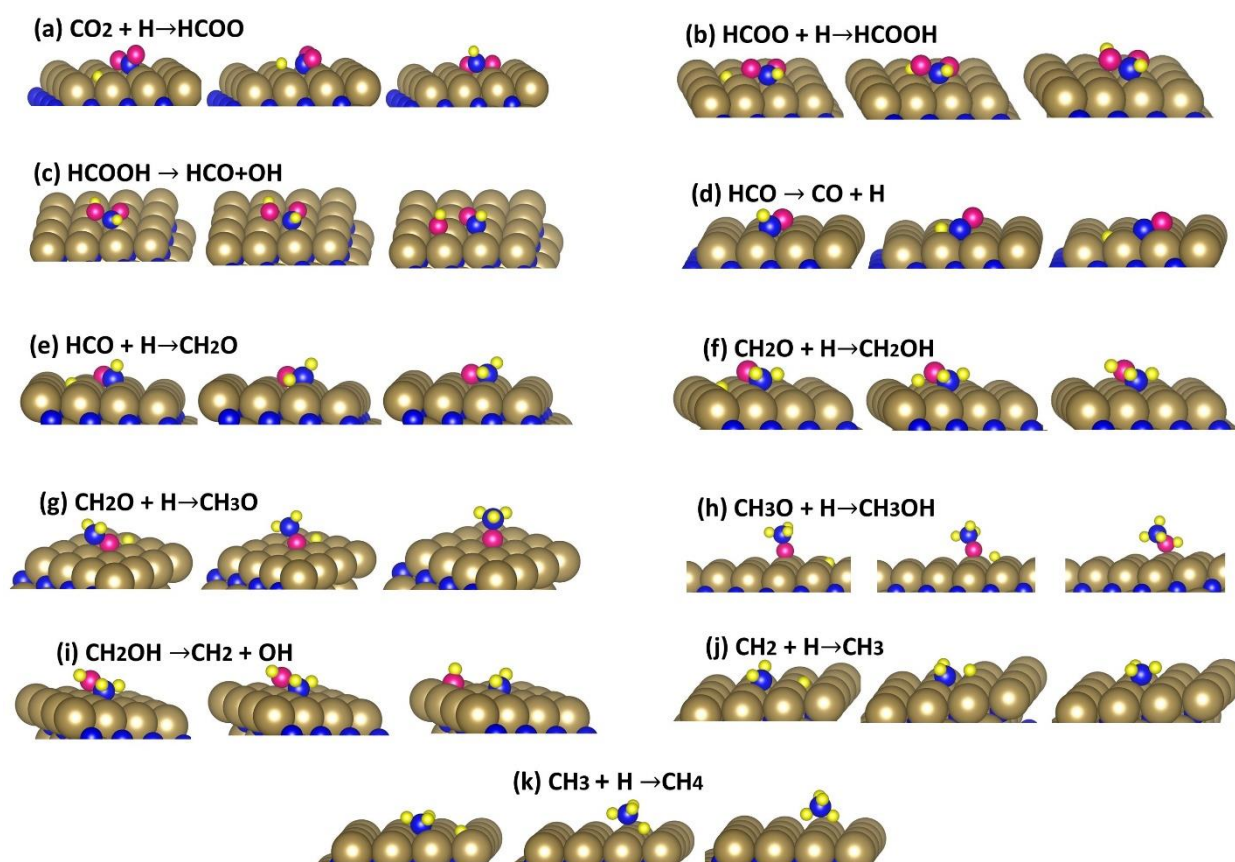


Figure 4. The selected reactions with their corresponding transition states at the TaC (111) surface.

As discussed above, CH_2 can be produced from $\text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^* + \text{OH}^*$ and then can react further with adsorbed hydrogen to produce CH_4 within two continuous reaction steps. A first pathway to CH_3^* ($\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^*$) has an activation barrier of 1.210 eV, whereas in the subsequent reaction, the adsorbed CH_3 can further react with another H atom to produce CH_4 , but with a much higher activation barrier of 2.224 eV. The formed CH_4 species can be assumed to bind only weakly with the surface, from which it may easily desorb.

From the above detailed insight, we can conclude that the mechanism of $\text{CO}_2^* \rightarrow \text{HCOO}^* \rightarrow \text{HCOOH}^* \rightarrow \text{HCO}^* \rightarrow \text{CH}_2\text{O}^* \rightarrow \text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^* \rightarrow \text{CH}_3^* \rightarrow \text{CH}_4^*$ is the preferred overall exothermic pathway, passing thorough HCOO^* and HCOOH^* species, which releases a total energy of 4.24 eV (Figure 3), indicating that CH_4 is the predominant product of CO_2 hydrogenation over the TaC (111) surface. These results agree well with other studies, showing that all TMCs form CH_4 as the primary product, except for WC and NbC, which produce a significant amount of CO [12]. The rate-determining step (RDS) in this pathway is the hydrogenation reaction of CH_3 to CH_4 , with a barrier of 2.224 eV and the largest endothermic reaction energy of 1.818 eV. The smallest barrier, at 0.126 eV, belongs to the reaction of $\text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^* + \text{OH}^*$, with the largest exothermic reaction energy of −1.855 eV. The present mechanism resulting in CH_4 formation is also similar to that in the DFT study by Qi et al. [57] on CO hydrogenation over molybdenum carbide, in which they found the same mechanism for the favorable pathway with the reaction of CH_3 to CH_4 as in the RDS reaction. The preferred reaction mechanism is also consistent with previous work studying CO hydrogenation over MoS_2 , where the reaction product is CH_4 , progressing through the intermediate of CH_2OH prior to C–O bond breaking [58].

The reaction pathway of $\text{CO}_2^* \rightarrow \text{HCOO}^* \rightarrow \text{HCOOH}^* \rightarrow \text{HCO}^* \rightarrow \text{CO}^*$ producing CO as the second favored product releases a total energy of 2.55 eV overall. CH_3OH as the next product was formed by the reaction series $\text{CO}_2^* \rightarrow \text{HCOO}^* \rightarrow \text{HCOOH}^* \rightarrow \text{HCO}^* \rightarrow \text{CH}_2\text{O}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_3\text{OH}^*$, with a total exothermic energy of −2.10 eV. The RDS for the reaction mechanisms resulting in CO and CH_3OH is the hydrogenation step of HCOO^* , with a barrier of 1.828 eV, while the reaction of $\text{HCOOH}^* \rightarrow \text{HCO}^* + \text{OH}^*$ contains the smallest barrier of 0.264 eV.

4. Conclusions

We have performed a series of DFT calculations to shed light on the reaction network of CO_2 hydrogenation to CO, HCOOH , H_2CO , CH_4 , and CH_3OH products over the Ta-terminated TaC (111) surface, first identifying the optimal adsorption sites for all of the reactants, intermediates, and products on the TaC (111) surface. The adsorption of the CO_2 molecule results in its activation, shown by the alteration of the initial structure, where the C–O bond lengths increase from 1.17 to 1.27 Å and the O–C–O bond angle decreases to 132°. The two oxygen atoms of the CO_2 molecule strongly bond to the Ta atoms on the surface.

The results from the reaction energy calculations of the hydrogenation reaction sequences showed that the largest exothermic reaction energy value of −1.891 eV is related to the adsorption of CO_2^* , which could therefore release sufficient energy to overcome some of the energy barriers in the hydrogenation reactions. The range of exothermic reactions is wide, with the smallest energy of only −0.111 eV, produced during the conversion of ct- HOCO^* to tt- HOCO^* . The sequence of reactions, in order of the largest exothermic reaction energies to the least energetically favorable, is as follows:

$\text{CO}_2(\text{g}) \rightarrow \text{CO}_2^*$, $\text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^* + \text{OH}^*$, cc- $\text{HOCO}^* \rightarrow \text{COH}^* + \text{OH}^*$, $\text{HCOOH}^* \rightarrow \text{HCO}^* + \text{OH}^*$, ct- $\text{HOCO}^* \rightarrow \text{COH}^* + \text{OH}^*$, tt- $\text{HOCO}^* \rightarrow \text{COH}^* + \text{OH}^*$, cc- $\text{HOCO}^* + \text{H}^* \rightarrow \text{tt-} \text{HOCO}^*$, ct- $\text{HOCO}^* + \text{H}^* \rightarrow \text{tt-} \text{HOCO}^*$

The results revealed that the thermodynamically preferred CO_2 hydrogenation mechanism, including two routes from either HCOOH^* or HOCO^* intermediates, progresses via $\text{CO}_2^* \rightarrow \text{HCOO}^* \rightarrow \text{HCOOH}^* \rightarrow \text{HCO}^*$, which results in CH_4 , CO, and CH_3OH formation.

The results from the energy barrier and reaction energy calculations show that the mechanism of $\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^*$, $\text{HCOO}^* + \text{H}^* \rightarrow \text{HCOOH}^*$, $\text{HCOOH}^* \rightarrow \text{HCO}^* + \text{OH}^*$, $\text{HCO}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^*$, $\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_2\text{OH}^*$, $\text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^* + \text{OH}^*$, $\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^*$, and $\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4^*$ resulting in methane production is the most exothermic mechanism, releasing a total energy of 4.24 eV, indicating that CH_4 will be the predominant product, which is in good agreement with the results in the available literature. The RDS along this pathway is the hydrogenation reaction of $\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4^*$, with a barrier of 2.224 eV and the largest endothermic reaction energy of 1.818 eV, while the dissociation reaction of $\text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^* + \text{OH}^*$ has the smallest barrier and largest exothermic reaction energies of 0.126 eV and −1.855 eV, respectively.

Carbon monoxide is the second-most favored product from CO_2 hydrogenation, both thermodynamically and kinetically, through reaction sequences of $\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^*$, $\text{HCOO}^* + \text{H}^* \rightarrow \text{HCOOH}^*$, $\text{HCOOH}^* \rightarrow \text{HCO}^* + \text{OH}^*$, and $\text{HCO}^* \rightarrow \text{CO}^* + \text{H}^*$ and releasing 2.55 eV via the preferred mechanism for CO production. The mentioned mechanism results in CO formation, where $\text{HCOO}^* + \text{H}^* \rightarrow \text{HCOOH}^*$ and $\text{HCOOH}^* \rightarrow \text{HCO}^* + \text{OH}^*$ have the largest and smallest barriers of 1.828 and 0.264 eV, respectively, and the dissociation reactions of $\text{HCOOH}^* \rightarrow \text{HCO}^* + \text{OH}^*$ and $\text{HCO}^* \rightarrow \text{CO}^* + \text{H}^*$ have the largest exothermic and endothermic reaction energies of −1.611 and 1.590 eV, respectively.

Methanol production as the third-preferred product occurs via the reactions of $\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^*$, $\text{HCOO}^* + \text{H}^* \rightarrow \text{HCOOH}^*$, $\text{HCOOH}^* \rightarrow \text{HCO}^* + \text{OH}^*$, $\text{HCO}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^*$, $\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}^*$, and $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^*$ by releasing a total exothermic reaction energy of 2.10 eV. Along this pathway, HCOO^* hydrogenation and HCOOH^* dissociation require the largest and smallest barriers of 1.828 and 0.264 eV, respectively,

to be overcome, whereas HCOOH^* dissociation and CH_3O^* hydrogenation have the largest exothermic and endothermic reaction energies of -1.611 eV and 2.318 eV, respectively.

The chemical picture and molecular level insights derived from this work suggest that TaC (111) surfaces should have high activity towards CO_2 activation, which along with their other favorable properties, makes them promising candidates for the catalytic hydrogenation of CO_2 to beneficial products.

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