Quantum Mechanical Study of CO₂ and CO Hydrogenation on Cu(111) Surfaces Doped with Ga, Mg, and Ti

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Abstract

DFT methods were used to analyze metal (M)-doped Cu(111) surfaces to identify surface alloys that could catalyze the hydrogenation of CO₂. The adsorption of relevant species for CO₂/CO hydrogenation were studied on Cu(111) surfaces doped with Ga, Mg, and Ti. Preferred adsorption sites, geometries, and binding energies for relevant intermediates were determined. A systematic study of the thermochemistry of plausible surface reactions for CO₂/CO hydrogenation on Ga/Cu(111), Mg/Cu(111), and Ti/Cu(111) was performed to postulate reaction mechanisms for the synthesis of formic acid, formaldehyde, and methanol. Our results suggest that Ga/Cu(111) and Mg/Cu(111) surfaces might be promising catalysts for the synthesis of methanol from CO₂ hydrogenation. CO₂ is activated by chemisorption on Mg/Cu(111) and Ti/Cu(111), but the latter surface has a strong interaction with O, which inhibits the last reaction steps and the desorption of the products. Our results demonstrate that the thermochemistry of CO₂ hydrogenation for the synthesis of the different products varies drastically depending on the dopant on Cu(111). Furthermore, our results suggest that the formation energies of HCOO, CH₂O, CH₃O, and HCO are good descriptors for catalyst screening.

Keywords: CO₂, CO hydrogenation; Metal-doped copper surfaces; Density functional theory; Reaction mechanism; Synthesis of methanol, formic acid, formaldehyde

1. Introduction

Fossil fuels are currently the main carbon source in chemical industry. Because these resources are expected to be depleted and their combustion is the major cause of CO₂ emissions to the atmosphere, the need for finding alternative carbon sources has sparked interest in using renewable sources. The conversion of CO₂ into valuable organic compounds promises to be a potential approach to reduce the environmental impact of CO₂ emissions, and to generate alternate sources of energy and feedstock.

Cu-based catalysts (e.g. copper oxides, supported and composite Cu catalysts) have been extensively employed for the synthesis of methanol [1–5] and carbon monoxide [6,7] through the hydrogenation of CO₂. Methanol is industrially produced from CO, H₂ and small amounts of CO₂ using Cu/ZnO/Al₂O₃ as catalyst at high pressures (50-100 bar) [8]. This catalyst, however, has three limitations: it is susceptible to poisons usually present in syngas sources, it has been observed that the methanol productivity is low in the absence of CO [9] and at low pressures, significant amounts of CO are formed through the reverse water-gas shift (RWGS) reaction [10]. The RWGS reaction competes with the methanol synthesis from CO₂ hydrogenation. Experimental and theoretical results indicate that the rate of the RWGS reaction is approximately two to three orders of magnitude faster than the methanol synthesis on Cu nanoparticles, resulting in CO accumulation on the catalyst surface [5]. The RWGS reaction is endothermic, while the hydrogenation of CO₂ to methanol is an exothermic reaction, as described in Table 1 [11]. However, the hydrogenation of CO to methanol is even more exothermic than CO₂ hydrogenation [12]. Consequently, in addition to high pressures, relative low temperatures (>240 °C) are required to favor the hydrogenation of CO₂ to methanol. High reaction temperatures (e.g. 500-873 K) typically favor the formation of undesired products, such as CO, hydrocarbons, and higher alcohols [4].

In an effort to find efficient catalysts for the hydrogenation of CO_2 , different metal dopants or promoters have been previously studied to modify the conventional catalyst used for CO_2 hydrogenation and improve its performance. Toyir and coworkers studied Ga-promoted Cu-based catalysts on SiO_2 and ZnO supports and obtained high activity, selectivity, and stability for Cu-Zn-Ga/ SiO_2 (hydrophobic silica) [13]. Methanol was the main product, with a selectivity of 99% and a conversion of 5.6% at 543 K. They found that Ga increased the activity and selectivity of the catalyst for methanol when compared to Cu/ $\text{ZnO}/\text{Al}_2\text{O}_3$. In another study, Toyir et al. also proved that the addition of Ga onto Cu/ ZnO improved the catalyst stability [14]. In addition, they determined that higher Ga/Cu ratios increased the methanol production [13,14]. Melián-Cabrera and coworkers studied the effect of Pd incorporation on the performance of a CuO–ZnO catalyst for the methanol synthesis [15]. They found that there is a synergetic effect of Pd on the active Cu sites, and that Pd facilitates the H_2 spillover and transport of hydrogen to the active sites while maintaining CuO in a more reduced state. Nerlov et al. investigated the effect of CO in the methanol synthesis from CO_2 hydrogenation on the Cu(100) surface modified by Ni [16]. They reported that the methanol production increased when CO is fed into the reaction system, because CO activates the catalyst by inducing segregation of Ni to the surface. Studt and coworkers tested the catalytic performance of a CuNi alloy supported on silica in the hydrogenation of CO to methanol, obtaining similar turnover frequencies and slightly higher selectivities for methanol, when compared against the commercial Cu/ $\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst [17].

Catalysts based on other metals (e.g., Ni, Ga and Pd) have been also investigated and they have demonstrated to be potential promoters for the hydrogenation of CO_2 [10,18]. Recently, it has been demonstrated that a Ni-Ga intermetallic compound has better catalytic activity to reduce CO_2 and is more selective than Cu/ $\text{ZnO}/\text{Al}_2\text{O}_3$ for methanol [10]. Fujitani et al. studied Pd-based catalysts for methanol production from CO_2 and H_2 and they reported that Pd/ Ga_2O_3 was more active than Cu/ ZnO on the basis of yields and turnover frequencies [18].

Some of these potential catalysts for the hydrogenation of CO_2 have been also investigated with density functional theory (DFT) calculations. The adsorption and activation of CO_2 were theoretically studied on Cu-Ni bimetallic clusters by evaluating distinct metal compositions and geometry configurations in the clusters [19]. The authors found that the cluster with higher composition of Ni ($\text{Cu}_{42}\text{Ni}_{13}$) and the icosahedral conformation exhibited the highest adsorption of CO_2 . Yang et al. investigated the effects of the metal dopants Pd, Au, Pt, Ni and Rh on the catalytic activity of Cu(111) for the methanol synthesis through CO_2 hydrogenation using DFT methods with kinetic Monte Carlo (KMC) simulations [20]. They determined that Ni, Pt, Pd, and Rh promote the CH_3OH synthesis reaction, while Au deactivates the reaction, being Ni/Cu(111) the surface with the best catalytic performance.

Experimental and theoretical observations indicate that CO_2 is chemically adsorbed on Ni(110) under UHV conditions [21]. Dissociative adsorption of CO_2 has been observed on Ni, Al and Mg surfaces [22]. Behrens and coworkers demonstrated, with DFT calculations that Zn substituted into the Cu(211) surface at the step sites increased the catalyst activity because it increased the adsorption strengths of the intermediates and decreased the energy barriers [8]. They proposed that the use of other promoters with the same oxophilicity of Zn might increase the catalytic activity of Cu. They reported that there is a synergistic effect between Cu and Zn, because Cu sites near Zn atoms serve as adsorption sites for oxygen-bound intermediates.

The hydrogenation of CO_2 and CO have been also studied by DFT methods to elucidate the elementary steps in the reaction mechanisms that have not been fully clarified. There are two major routes that have been proposed for the methanol synthesis from CO_2 hydrogenation: the formate (HCOO) pathway [5,8,20,23] and the RWGS reaction followed by CO hydrogenation [20,23], as illustrated in Fig. 1. In the formate pathway, there is a debate on whether dioxymethylene (CH_2O_2) or formic acid (HCOOH) [8,23,24] is the intermediate that leads to the formation of methanol. Most researchers have proposed dioxymethylene as the reaction

intermediate [5,20,25–28]. The hydrogenation of formic acid or dioxymethylene could produce hydroxymethoxy (H_2COOH) [8,23,24,27], which could decompose to form formaldehyde (CH_2O). Formaldehyde could be directly generated from dioxymethylene [28]. Finally, methoxy (CH_3O) or hydroxymethyl (CH_2OH) formed by the hydrogenation of formaldehyde could lead to methanol when either of these intermediates are hydrogenated, being methoxy more stable than hydroxymethyl [23]. In the route of RWGS reaction and CO hydrogenation, the formation of CO has been proposed through the decomposition of CO_2 [23] or carboxyl (COOH) [20,23,27]. Formyl, formaldehyde and methoxy have been established as the main reaction intermediates in this pathway. Works in which the HCOO pathway and the RGSW reaction with CO hydrogenation are considered have reported that the latter is the dominant pathway because it is faster than the formate pathway [20]. However, the dominant pathway depends on the slow steps and in the reaction conditions, as determined in a microkinetic analysis of the methanol synthesis on Cu(111) [23]. For instance, Yang et al. reported that CH_3OH is not produced from CO hydrogenation despite the fast kinetics of the RWGS reaction, because HCO is not a stable intermediate and its dissociation back to $\text{CO}^* + \text{H}^*$ is preferred over the HCO hydrogenation on Cu(111) [5]. Thus, the metal employed as the catalyst and the reaction conditions, ultimately determine the rate-limiting steps of these reaction mechanisms. In the formate pathway, the hydrogenation of formate [5], dioxymethylene [5,20] and methoxy [23,29] have been proposed as the rate-limiting steps in the synthesis of methanol. While in the CO hydrogenation pathway, the reaction is limited by hydrogenation of CO and HCO [5].

In this work, DFT methods were used to analyze heterogeneous catalysts for the conversion of CO_2 into formic acid, formaldehyde, and methanol. Taylor et al. reported that the hydrogenation of formate on Cu(100) most likely produces formaldehyde and/or formic acid instead of methanol [30]. However, to our knowledge, the performance of modified Cu-based catalysts has not been extensively explored for the production of formic acid and formaldehyde. A systematic analysis of the adsorption of relevant species and intermediates involved in

CO₂/CO hydrogenation was performed. Insights into the thermochemistry of plausible elementary steps for the synthesis of formic acid, formaldehyde, and methanol from these hydrogenations were provided to postulate reaction mechanisms on Mg, Ti, and Ga doped Cu surfaces. We also analyzed the hydrogenation of CO to determine how feasible is the RWGS reaction over these doped surfaces and if the formation of the desired products via this reaction is favored over other reaction pathways. The stability of these catalysts was also studied by determining if the adsorption of species, such as carbon, are energetically favorable. Furthermore, the reliability of the descriptors used for the catalyst screening is discussed based on the thermochemistry results.

2. Theoretical Methods

Periodic DFT calculations were used to screen M-doped Cu(111) surfaces with to evaluate the feasibility of employing these materials as catalysts for CO/CO₂ hydrogenation. The details of the methodology used for the screening and the calculations of solution and segregation energies for these M-doped copper surfaces are in the Supplementary Material.

The adsorption of key species and intermediates involved in the hydrogenation of CO and CO₂ has also been studied using periodic DFT calculations. Adsorbed species, such as: H, O, C, CO, CO₂, OH, H₂O, COH, HCO, COOH, HCOO, HCOOH, CH₂O₂, CH₂O, CH₂OH, CH₃O, CH₃O₂ and CH₃OH on M/Cu(111) were thoroughly analyzed to evaluate the performance of these catalysts. For the systematic study of M-doped Cu(111) surfaces, a Cu slab of 36 atoms with dimensions of 3x3x4 and a vacuum layer of 14 Å-thick was used to accommodate coadsorbates and avoid the interaction between them through successive slabs. Surface alloys were simulated with a simple model in which the Cu(111) surface was doped with another metal (M) by substituting two Cu atoms in the top layer of the 3x3x4 Cu(111) slab by the metal dopant, and obtaining a dopant coverage of 2/9 ML in the surface. An adsorbate was placed on the 3x3x4 slab obtaining a surface coverage of 1/9 ML. The top two layers of the slab and the

adsorbates were allowed to relax, while the atoms on the bottom two layers were fixed in their optimized bulk coordinates. The calculated equilibrium lattice constant for bulk Cu was 3.63 Å, which closely agrees with the experimental value of 3.62 Å [31]. The level of theory employed was the Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [32,33] and we also used the DFT-D2 method of Grimme [34] to account for the dispersion effects. For these calculations, plane wave functions with a cutoff energy of 400 eV were used to expand the Kohn-Sham one-electron valence states, while the core electrons were described by projector-augmented wave (PAW) potentials [35,36]. The Gamma centered k-point mesh used for the Brillouin zone sampling was 6x6x1. All these calculations were performed using the Vienna *ab initio* simulation package (VASP) [37,38].

For the M-doped Cu(111) surfaces, the eight high symmetry sites illustrated in Fig. A.1b were explored: fcc1, fcc2, hcp1, hcp2, top1, top2, bridge1 and bridge2. We included an additional bridge, fcc and hcp site between the two dopant atoms denoted with ('), as illustrated in Fig. A.1c. Number 1 denotes sites with Cu atoms only, while number 2 corresponds to mixed sites that have Cu and the dopant. Energies of isolated species (E_A), surface (E_S) and adsorbed species (E_{A-S}) on the different adsorption sites were obtained, and used to calculate the binding energies (E_b) with Equation 1. The preferred binding site for each adsorbate was the one with the lowest binding energy.

$$E_b = E_{A-S} - (E_A + E_S) \quad (1)$$

3. Results and Discussion

Based on the screening results discussed in detail in the Supplementary Material, we have selected the Cu surfaces doped with Ga, Mg, and Ti as potential catalysts for the hydrogenation of CO and CO₂. The PBE energies of plausible reaction intermediates in their preferred adsorption sites together with the energies of the adsorbates in the gas phase and the surface, have been used to calculate reaction energies of elementary steps for the hydrogenations of

CO₂ and CO on the M (e.g., Ga, Mg, or Ti) doped Cu(111) surfaces. This thermochemistry analysis, illustrated in Figs. 4, 8 and 12, enables us to postulate plausible pathways for the synthesis of formic acid, formaldehyde, and methanol on the M/Cu(111) surfaces, and quantify the effect of the dopants Ga, Mg, and Ti on the energetics of reactions. We note that the kinetics of these pathways were not considered in this work, and our conclusions are based on the thermochemistry analysis. Thus, the dominant pathway proposed in this work might change depending on the activation barriers.

3.1 Ga-doped Cu(111) surface as catalyst for CO₂/CO hydrogenation

3.1.1 Adsorption study and binding energies for Ga/Cu(111)

The adsorption of several species involved in the hydrogenation of CO₂ and CO has been studied on the Ga-doped Cu(111) surface. From this analysis, the preferred adsorption sites along with the minimum energy geometries of the analyzed adsorbates have been determined, as shown in Fig. 2 and detailed in Table 2. The geometrical parameters for the configurations illustrated in Fig. 2 have been included on Table A.2 in the Supplementary Material. Most species adsorbed on Ga/Cu(111) adopt monodentate conformations, in which the adsorbate is bonded to the surface through one atom. Few adsorbates, such as HCOO, CH₂O, CH₂O₂, CO₃ and HCO₃, have a bidentate configuration. The binding energies associated with the adsorption of these species at the minimum energy sites on Ga/Cu(111) have been also estimated (see Table 2 and Fig. 3). On the basis of our results, CO₂ is not activated by Ga-doped Cu(111) surface. CO₂ is physically adsorbed on Ga/Cu(111) surface with a binding energy of -0.23 eV (Table 2), and maintains a linear configuration. The average Cu-O bond distance is 3.13 Å (Table A.2). Similar observations have been reported for CO₂ adsorption on pure Cu(111) surface using DFT methods [23]. However, experimental observations indicate that CO₂ is not physically adsorbed on Cu(111) [39,40]. Fig. 3 depicts that CO₂ is the species with the lowest

adsorption strength on Ga/Cu(111). Other species, such as H₂O, HCOOH and CH₃OH also exhibit physical adsorption. The rest of the adsorbates analyzed are chemically adsorbed, and C is the species with the strongest adsorption on Ga/Cu(111) (see Fig. 3). Most adsorbates have adsorption sites with degenerate binding energies, which are described in Table 2 enclosed by parentheses. CO, HCO, and CH₃O are predicted to have two equally stable adsorption sites, which are shown in Fig. 2.

3.1.2 Thermochemistry of possible surface reactions on Ga/Cu(111)

Hydrogenation of CO₂ and CO to formic acid (HCOOH): The thermochemistry of plausible reaction pathways have been evaluated for the synthesis of formic acid via CO₂ hydrogenation over the Ga-doped Cu(111) surface, as depicted in Fig. 4a. These routes are mediated by the formation of formate (HCOO) (pink route in Fig. 4a) and carboxyl (COOH) (green route in Fig. 4a), and the dissociation of CO₂ (brown route). In the formate pathway, formic acid might be produced by either the formate hydrogenation (pink line) or the decomposition of HCOO to formyl (HCO*) and O* followed by the hydrogenation of oxygen and the coupling reaction of formyl and hydroxyl (pink, purple and orange lines). In the carboxyl pathway, two routes have been postulated. The first one is the hydrogenation of carboxyl to formic acid (green line) and the second one is the decomposition of carboxyl to CO* and OH* together with the hydrogenation of CO* to formyl and the coupling of HCO* and OH* (green and orange lines). The formyl intermediate could be also generated after the dissociation of CO₂, as illustrated by the brown and orange routes. We have also evaluated the formation of COH, but this reaction is more endothermic than $\text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + *$ (R22 in Table 3) by 0.33 eV. The hydrogenation of CO to formic acid is slightly more thermodynamically favorable via the formation of carboxyl than the CO₂ dissociation. However, the direct synthesis of formic acid through the formate intermediate is thermodynamically more favorable than the routes with carboxyl as intermediate

or the decomposition of formate. The CO_2 hydrogenation to HCOO is an exothermic reaction, but the hydrogenation is endothermic for the formation of COOH . Moreover, the HCOO decomposition is estimated to require 1.40 eV more than the hydrogenation of HCOO . Fig. 5 illustrates the elementary steps with the lowest reaction energies for the formation of formic acid from CO_2 hydrogenation on Ga-doped Cu(111). Fig. 5 shows the most thermodynamically stable intermediate on that surface involving the formation of formic acid. The total electronic energy of reaction is -0.17 eV.

Hydrogenation of CO_2 and CO to formaldehyde (CH_2O) and methanol (CH_3OH): Because adsorbed formic acid is a possible reaction intermediate for the synthesis of formaldehyde and methanol, the reaction pathway obtained from the previous analysis of formic acid production, involving the formate intermediate, has been proposed for the formation of formaldehyde and methanol (see Fig. 4b). Formate can be hydrogenated to either formic acid (pink line in Fig. 4b) or dioxymethylene (CH_2O_2) (red line), or it might be decomposed to formyl (purple line). Formaldehyde could be produced through the hydroxymethoxy (H_2COOH) intermediate from the hydrogenation of formic acid or dioxymethylene. On the other hand, formaldehyde could be directly generated from the hydrogenation of formyl or by the decomposition of CH_2O_2 . From these pathways, the route that involves the formation of the intermediates HCOO^* , HCOOH^* , and H_2COOH^* (blue and pink lines) has the lowest reaction energies (Fig. 5) because HCOOH^* is more stable than CH_2O_2^* and $\text{HCO}^* + \text{O}^*$ by -0.32 and -1.40 eV, respectively. The total electronic energy for the formaldehyde synthesis from $\text{CO}_{2(\text{g})}$ and $\text{H}_{2(\text{g})}$ has been calculated to be 0.14 eV.

The thermochemistry for the methanol synthesis has been analyzed through formaldehyde and hydroxymethyl (CH_2OH) as reaction intermediates, which are illustrated with the pink and gray lines in Fig. 4b. The reaction $\text{H}_2\text{COOH}^* + * \rightarrow \text{CH}_2\text{O}^* + \text{OH}^*$ (R12) is energetically more favorable than $\text{H}_2\text{COOH}^* + * \rightarrow \text{CH}_2\text{OH}^* + \text{O}^*$ (R13) by -0.30 eV. However, hydroxymethyl could also be produced by the hydrogenation of the oxygen atom of formaldehyde (R15) (pink, yellow

and gray lines), which is almost a thermoneutral step, with an electronic reaction energy of -0.07 eV. If the carbon atom of formaldehyde is hydrogenated to form methoxy (CH₃O) (R14), the reaction is more exothermic than the previous one by -0.85 eV. The formate pathway with HCOOH, H₂COOH, CH₂O, and CH₃O as reaction intermediates (blue and pink lines in Fig. 5) are the reactions with the lowest reaction energies for the formation of methanol from CO₂ hydrogenation on Ga/Cu(111) surface. Methoxy is more stable than hydroxymethyl and the hydrogenation of methoxy is thermoneutral, with an electronic reaction energy of 0.01 eV. The overall electronic energy of reaction for $\text{CO}_{2(g)} + 3\text{H}_{2(g)} \rightarrow \text{CH}_3\text{OH}_{(g)} + \text{H}_2\text{O}_{(g)}$ is estimated to be -1.20 eV.

3.2 Mg-doped Cu(111) surface as catalyst for CO₂/CO hydrogenation

3.2.1 Adsorption study and binding energies for Mg/Cu(111)

The preferred adsorption sites for the atomic and molecular species analyzed on Mg/Cu(111) are illustrated on Fig. 6 and Table 4. Most species adsorb preferentially on mixed adsorption sites, in which the molecule is bonded to Cu and Mg atoms, adopting monodentate, bidentate, or tridentate conformations. This is probably because most adsorbates are adsorbed through oxygen and Mg is oxophilic. On the Mg/Cu(111) surface, the species that do not have oxygen (e.g. H and C) or the ones that are not bonded to the surface through oxygen (e.g. CO and COH) prefer the adsorption sites on Cu atoms.

The calculated binding energies for the adsorption sites shown in Fig. 6 are detailed in Table 4 and Fig. 7. For some of the adsorbed species on Mg/Cu(111), we obtained adsorption sites that have degenerate binding energies, which are described in Table 4 and enclosed by parentheses. Fig. 7 presents the binding energies on Mg/Cu(111) in ascending order, which indicates that water is the species with the lowest binding strength, while carbonate has the strongest adsorption. Water and methanol have been predicted to be weakly adsorbed on the

Mg/Cu(111) surface at the Mg atom with bond distances of 2.12 and 2.11 Å, as shown in Table A.3 in the Supporting Material. The high adsorption strength observed for carbonate is because this species adsorbs with its two oxygen atoms, as illustrated in Fig. A.7b. CO₂ is activated in the Mg/Cu(111) surface adopting two stable configurations (Otop2-Otop2 and Otop2-Ctop1), one bidentate and another tridentate, with a binding energy of -1.15 eV, which are shown in Fig. 6. CO₂ adsorbs on the Otop2-Otop2 site with average O-Mg bond lengths of 1.99 Å and a O-C-O angle of 124°, as illustrated in Fig. A.7c.

3.2.2 Thermochemistry of possible surface reactions on Mg/Cu(111)

Hydrogenation of CO₂ and CO to formic acid (HCOOH): The production of formic acid via the hydrogenation of CO₂ on the Mg-doped Cu(111) surface was evaluated through the formation of formate and carboxyl, and through the hydrogenation of CO, as illustrated on Fig. 8a. As shown in this figure, the formation of HCOO (pink line in Fig. 8a) has a lower reaction energy than the COOH pathway (green line) and the decomposition of CO₂ to CO* and O* (orange line) by -1.04 eV and -0.73, respectively. The formation of adsorbed HCO through the decomposition of HCOO (purple line) is thermodynamically favored over the CO hydrogenation. Thus, the thermochemistry results indicate that the lowest energy route for the synthesis of formic acid from CO₂ hydrogenation on Mg/Cu(111) might be the formate pathway.

Hydrogenation of CO₂ and CO to formaldehyde (CH₂O) and methanol (CH₃OH): Fig. 8b shows the thermochemistry of the different pathways that were analyzed to produce formaldehyde and methanol from CO₂ hydrogenation on Mg/Cu(111). The hydrogenation of HCOO could generate two intermediates, HCOOH or CH₂O₂. The hydrogenation at the C atom to produce CH₂O₂ (red line) has a lower reaction energy than the hydrogenation at the O atom to produce HCOOH (pink line) by -0.42 eV, as shown in Fig. 8b. The next step in the CH₂O₂ pathway could be the C-O bond breaking in CH₂O₂ (R11) or the hydrogenation of CH₂O₂ (R10),

where the former is endothermic by 0.37 eV and the last one is thermoneutral. However, the hydrogenation of O* (R18), which is the next step for CH₂O₂ route, is less endothermic than the C-OH bond breaking in H₂COOH* (R12) for the H₂COOH pathway. For Cu(111), Grabow and Mavrikakis [23] found that the reactions CH₂O₂* + * → CH₂O* + O* (R11) and H₂COOH* + * → CH₂O* + OH* (R12) are spontaneous in the reverse direction, obtaining only thermodynamic barriers for these reactions. This has been also reported by Sakong for the R11 reaction on Cu(110) [41]. If on Mg/Cu(111) the same trends prevail, then the activation energy barriers for the hydrogenation of O (R18) and CH₂O₂ (R10) would dictate the most favorable route in the hydrogenation of CO₂ to formaldehyde. Based on this thermochemistry, we proposed the H₂COOH pathway (red line) as the most favorable route for the synthesis of formaldehyde from CO₂ on Mg/Cu(111) (Fig. 9).

The methanol synthesis on Mg/Cu(111) was also studied through the reaction pathways analyzed for the formaldehyde synthesis, as depicted in Fig. 8b. The H₂COOH pathway followed by the CH₃O pathway (red and green lines in Fig. 8b), is also a plausible route to produce methanol from CO₂ hydrogenation. In addition, we evaluated other route that involves the C-O bond breaking in H₂COOH* to yield CH₂OH* and O* and the hydrogenation of CH₂OH* to methanol (the gray line). This pathway could be competitive for the H₂COOH-CH₃O pathway because the intermediate CH₂O* is more stable than CH₂OH* by only -0.01 eV. Furthermore, the reaction CH₂OH* + H* → CH₃OH* + * (R17) is exothermic with an electronic energy of -0.64 eV, while the reaction CH₃O* + H* → CH₃OH* + * (R16) is endothermic by 0.17 eV. It has been observed in experimental studies with Cu/ZnO and Cu/ZnO/Cr₂O₃ catalysts [29], as well as in a microkinetic analysis with Cu(111) [23] that the hydrogenation of methoxy to methanol is the rate-limiting step in the hydrogenation of CO₂ due to the high energy barrier of this step. A third pathway involves the formation of CH₂OH from the hydrogenation of CH₂O at the O atom instead of the C atom, which connects the red and gray lines. The thermochemical analysis

suggests that the $\text{H}_2\text{COOH-CH}_2\text{OH}$ pathway (red and gray lines in Fig. 9) is the route with the lowest energies of reaction for the hydrogenation of CO_2 to methanol on Mg/Cu(111) .

Carbonate (CO_3) has been proposed as a key intermediate for catalysts in which the dissociation of CO_2 is favorable or the hydrogenation of CO_2 is carried on surfaces treated with oxygen or supported on metal oxides. While for Mg/Cu(111) none of these conditions are met, bicarbonate could be formed if CO_2^* reacts with OH^* (R28) with an almost thermoneutral reaction energy of -0.03 eV. From HCO_3^* , formate might be produced via the following steps: $\text{HCO}_3^* \rightarrow \text{CO}_3^* \rightarrow \text{CO}_2^* + \text{O}^* \rightarrow \text{HCOO}^*$.

Energy barriers are needed to determine which route yields the minimum energy path. However, on the basis of the thermochemistry on Mg/Cu(111) , the pathways with the lowest reaction energies to produce formic acid, formaldehyde, and methanol on Mg/Cu(111) surface involve the formation of formate. As illustrated in Fig. 9, the hydrogenation of CO_2 on Mg-doped Cu(111) surface is downhill in the potential energy on the adsorption steps and uphill in the hydrogenation of the oxygen in formate and on the desorption steps. On this surface, the formaldehyde and methanol formation is thermodynamically favorable, while the formic acid synthesis might not be favored because CH_2O_2 is more stable than HCOOH .

3.3 Ti-doped Cu(111) surface as catalyst for CO_2/CO hydrogenation

3.3.1 Adsorption study and binding energies for Ti/Cu(111)

Fig. 10 and Table 5 show the preferred adsorption sites for some of the adsorbates analyzed on Ti/Cu(111) . Most species preferentially adsorb on sites between Ti atoms, adopting bidentate or tridentate conformations, or on the top site at the Ti atom. The calculated binding energies for these adsorption sites are depicted in Table 5 and Fig. 11. This plot shows that the binding strength on Ti/Cu(111) increases to the right, being H_2O the species with the lowest binding strength and CH_2O_2 the species with the strongest adsorption, preceded by O. CH_2O_2 is

adsorbed on Ti/Cu(111) through the two oxygen atoms on the Ti atoms adopting a bidentate top configuration. Thus, oxygen has a very strong interaction with this surface, which is expected because of the high oxophilicity of Ti.

The structural parameters for the geometries of the adsorbates illustrated on Fig. 10 are detailed in Table A.4 in the Supplementary Material. CO₂ is chemically adsorbed on Ti/Cu(111) with a highly favorable binding energy of -2.40 eV (Table 5) and adopting a bent configuration that is depicted in Fig. A.7a in the Supplementary Material. The O-C-O angle is 122°, the two O atoms are bonded to the Ti atoms at top2 sites with an average bond distance of 1.98 Å, and the C atom is bonded to a Cu atom at the top1 site with a bond length of 2.05 Å (Table A.4). The results in Table A.4 also show that among the atomic species, the adsorption of C causes more deformation in the Ti/Cu(111) surface than O and H. This deformation is caused by increasing the average distance Cu-Cu and Ti-Cu of the atoms in contact with carbon by 0.16 and 0.14 Å, respectively. Adsorbed species, such as CO, CO₂, COH, HCO, COOH, on Ti/Cu(111) cause surface deformations with considerable increments (0.10-0.42 Å) in the average distance between the two Cu atoms at the bridge1' site. However, the adsorption of other molecular species, such as OH, H₂O and HCOO, do not cause a significant change in $d_{\text{Cu-Cu}}$, when compared with the relaxed clean Ti/Cu(111) surface. Upward displacement of 0.02 Å of the Ti atoms in the Cu surface is observed after the adsorption of the species OH, CO, CO₂, HCOO, CH₂O, CH₃O, CH₂O₂ and H₂COOH on Ti/Cu(111), as illustrated in Fig. 10 and detailed in Table A.4.

3.3.2 Thermochemistry of possible surface reactions on Ti/Cu(111)

Hydrogenation of CO₂ and CO to formic acid (HCOOH): The synthesis of formic acid has been studied through the hydrogenations of CO₂ and CO analyzing the thermochemistry of various plausible reaction pathways, as depicted in Fig. 12a. These results indicate that the production of formic acid through CO₂ hydrogenation is thermodynamically more favorable by

the formation of formate than carboxyl (pink and green lines in Fig. 12a, respectively). Formic acid could also be generated from formyl via the decomposition of HCOO (purple line) or the hydrogenation of CO formed by the decomposition of CO₂ (orange line). CO hydrogenation could produce COH intermediate, but this hydrogenation requires 0.92 eV more than the reaction to form HCO. For this reason, the COH intermediate is not considered in the reaction mechanism depicted in Fig. 12a. The HCOO decomposition is thermodynamically more favorable than CO hydrogenation, with reaction energies of -0.15 and 0.35 eV, respectively. However, the decomposition of CO₂ to CO and O is more favorable than any formate route. Thus, the route with the lowest reaction energies to produce formic acid from CO_{2(g)} and H_{2(g)} on Ti/Cu(111) involve the decomposition of CO₂ followed by the hydrogenation of CO (the blue and orange routes).

Hydrogenation of CO₂ and CO to formaldehyde (CH₂O) and methanol (CH₃OH): Fig. 12b shows plausible reaction pathways that were evaluated for the synthesis of formaldehyde and methanol via CO₂ and CO hydrogenation. Formaldehyde could be produced through formic acid and hydroxymethoxy by the routes of COOH (green and pink lines in Fig. 12b) or HCOO (pink line), being the latter more thermodynamically favorable than the former, as discussed in the previous section. However, the reaction to produce dioxymethylene from the hydrogenation of HCOO has a lower reaction energy than the formation of formic acid. A competitive route for the CH₂O₂ pathway (red line) is the decomposition of formate (purple line) followed by the hydrogenation of CO (orange line). These pathways are very similar with electronic energies of reaction -0.18 and -0.15 eV for HCOO* + H* → CH₂O₂* + * (R7) and HCOO* + * → HCO* + O* (R21), respectively. The reaction energies for CH₂O₂* + * → CH₂O* + O* (R11) and HCO* + O* + H* → HCO* + OH* + * (R18) are also similar, with an energy difference of 0.02 eV. The main difference between the CO hydrogenation and CH₂O₂ pathways is that the decomposition of CO₂ is thermodynamically more favorable than the HCOO formation by -0.50 eV. Therefore,

CO₂ decomposition followed by CO hydrogenation is the pathway with the lowest reaction energies for the synthesis of formaldehyde through the hydrogenation of CO₂.

Formaldehyde is a reaction intermediate in the methanol synthesis. Thus, the reactions analyzed on the reaction mechanism for the formation of formaldehyde are also plausible steps for the production of methanol on Ti/Cu(111). In the last steps of the methanol synthesis, formaldehyde can be hydrogenated to two possible intermediates, CH₃O or CH₂OH. As illustrated in Fig. 12b, the hydrogenation of CH₂O to CH₃O (orange line) requires less energy than the hydrogenation to CH₂OH (gray line).

The RWGS reaction might be a competitive reaction for the hydrogenation of CO (R22). The hydrogenation of O* (R18) is slightly more thermodynamically favorable than R22 by 0.18 eV. The hydrogenation of OH* (R19) is less endothermic than the HCOOH* formation (R26) by 0.87 eV. However, the desorption of CO* from Ti/Cu(111) is highly unfavorable, with a reaction energy of 2.44 eV. The adsorbed CO could be oxidized back to CO₂ or hydrogenated to HCO, which is thermodynamically favored over the oxidation by 0.20 eV.

The reaction mechanisms obtained for the synthesis of formic acid, formaldehyde and methanol from CO hydrogenation on the Ti-doped Cu(111) surface have two similarities. The first similarity is the downhill in the potential energy (Region A in Fig. 13) during the adsorption steps and the second one is the uphill region (Region B) in the coupling of HCO* and OH*, the hydrogenation of the oxygen in OH* and CH₃O*, and the desorption steps. This high request of energy in the last steps of the hydrogenation reactions is because of the strong interaction between O and Ti. Thus, the syntheses of formic acid, formaldehyde, and methanol are not thermodynamically favored on Ti/Cu(111).

3.4 Comparison for the M-doped Cu(111) surfaces

The adsorption strength of most of the species adsorbed on Ti/Cu(111) and Ga/Cu(111) surfaces follow similar trends as on Mg/Cu(111). However, a comparison of the charts depicted in Figures 3, 7, and 11 reveals that for Ga/Cu(111) and Mg/Cu(111), CO₂, carbonate, and bicarbonate do not follow similar adsorption strength tendencies. Furthermore, the most favorable adsorption sites, as well as the binding energies are different for most adsorbates on the three M-doped Cu surfaces. For instance, the binding energies of species H₂O, CH₂O, HCOOH, and CH₃OH are, on average, 0.7 eV lower on Ti/Cu(111) than on Mg/Cu(111). Differences in energies are also observed when comparing binding energies of adsorbates at the same mixed site on Ga/Cu(111) with the energies obtained on Cu(111) doped with Ti and Mg. For instance, C and O adsorb preferentially on the same site on Ga/Cu(111) and Ti/Cu(111), but their binding energies on Ti/Cu(111) are lower than on Ga/Cu(111) by 1.6 eV on average. If the surfaces doped with Ga and Mg are compared, the difference between the binding energies of CH₃O is 0.6 eV. For the species adsorbed on Ga and Mg/Cu(111) at sites with only Cu (e.g. CO and COH), there are no significant differences in their binding energies. Therefore, these results indicate that the adsorption strength increases by following this order of the dopant in Cu(111): Ga < Mg < Ti. This is consistent with the order of the binding energy of O, which has been used as descriptor for the catalyst screening, where this energy increases in the same order of dopant: Ga < Mg < Ti.

The thermochemistry of the plausible reaction mechanisms for the hydrogenation of CO₂ to formic acid, formaldehyde, and methanol change with the dopant added on the Cu(111) surface. When the dopant is Ga or Mg, the pathway with the lowest reaction energies is through the formate intermediate, while for the Cu(111) surface doped with Ti, the CO₂ decomposition followed by CO hydrogenation is the most thermodynamically favorable route. For the synthesis of formaldehyde and methanol via the formate pathway, HCOOH is more stable than CH₂O₂ on Ga/Cu(111), which is consistent with the observations of Grabow and Mavrikakis on a pure Cu(111) surface [23]. The opposite trends are observed on Ti and Mg/Cu(111). On the other

hand, CH_3O is proposed as a more stable reaction intermediate than CH_2OH on Ti and Ga/Cu(111), similar to proposed mechanisms for Cu(111) [23,27]. However, CH_2OH might be a key intermediate for the methanol synthesis on Mg/Cu(111) because it is equally stable to CH_2O and its hydrogenation is highly exothermic in contrast with the hydrogenation of CH_3O , which has been considered a rate-limiting step for this reaction in previous studies [23,29]. Thus, the addition of Ga, Ti, or Mg on Cu(111) surface changes drastically the thermochemistry for the hydrogenation of CO_2 .

The thermochemistry analysis suggests that Ti/Cu(111) might not have a good catalytic performance for the hydrogenation of CO (generated from CO_2 decomposition). While this surface activates CO_2 , the last steps in the reaction mechanism have extremely high energy requirements. On the other hand, the Cu(111) surface doped with Ga or Mg might be promising catalysts for the hydrogenation of CO_2 . Based on the thermochemistry, the activation of CO_2 and the formation of the desired products are favorable on Mg/Cu(111). We also note, however, that the hydrogenation catalyzed by Mg/Cu(111) requires more energy than Cu(111) or Ga/Cu(111) for desorption of the products. Ga/Cu(111) does not activate CO_2 , but the hydrogenation of HCOO and the desorption steps are less endothermic on this surface than on Mg/Cu(111), and the hydrogenation of CH_3O is thermoneutral. Both Mg/Cu(111) and Ga/Cu(111) are thus attractive materials for the CO_2 conversion into useful chemical compounds. On both surfaces, the formate route is thermodynamically favored over the RWGS reaction and CO hydrogenation. Moreover, the formation of C from the decomposition of CO is not thermodynamically favorable on these surfaces.

4. Conclusions

In this study, DFT calculations were used to screen metal-doped Cu(111) surfaces for CO_2/CO hydrogenation. The adsorption of relevant species and key intermediates involved in

CO₂/CO hydrogenation and thermochemistry for the synthesis of methanol, formic acid, and formaldehyde on M/Cu(111) with M= Ti, Mg, or Ga were studied.

On the basis of the thermochemistry analysis, a plausible reaction pathway to produce formic acid, formaldehyde, and methanol from CO_{2(g)} and H_{2(g)} on Ti/Cu(111) is via the decomposition of CO₂ followed by the hydrogenation of CO. On Ga/Cu(111), the most thermodynamically favorable route for the synthesis of these products is through the formation of the intermediates: HCOO* → HCOOH* → H₂COOH* → CH₂O* → CH₃O*. For Mg/Cu(111), the following species might be the key intermediates in the reaction mechanism to produce formaldehyde and methanol: HCOO* → CH₂O₂* → H₂COOH* → CH₂O* → CH₂OH*.

The synthesis of formic acid, formaldehyde and methanol is not thermodynamically favorable on Cu(111) doped with Ti because the high energy requirement in the last reaction steps due to the strong interaction between O and Ti. Ga/Cu(111) and Mg/Cu(111) might be promising catalysts for the direct conversion of CO₂ to methanol. However, the desorption of CH₃OH and H₂O from Mg/Cu(111) requires a considerable amount of energy. The stability of these M-doped Cu surfaces was not affected by the carbon accumulation in the surface, because the decomposition of CO was not thermodynamically favorable.

The binding energies of CO₂ and O were good descriptors for the catalyst screening because they predicted that CO₂ can be activated by Ti and Mg/Cu(111) surfaces and that the adsorption strength of species adsorbed by oxygen on mixed sites increases with the following dopant order: Ga < Mg < Ti. Nevertheless, we propose that an effective approach for a catalyst screening is to use as descriptor the reaction energy for the formation of key intermediates in the hydrogenation of CO₂ and CO. Based on our thermochemical results, we have identified these key intermediates as: HCOO, CH₂O and CH₃O and HCO. To our knowledge, Cu surfaces doped Ga, Mg, and Ti have not been studied for the hydrogenation of CO₂ and CO, therefore, these findings provides new insights into the catalytic conversion of CO₂.

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Table 1. Reactions involved in the hydrogenation of CO₂ and CO.

	Reaction	$\Delta H_{\text{rxn}}^\circ$ (kJ/mol)	Ref.
Methanol Synthesis from CO ₂	$\text{CO}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \leftrightarrow \text{CH}_3\text{OH}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	-50	[11,12]
Reverse Water Gas Shift	$\text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})} \leftrightarrow \text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	41	[11]
Methanol Synthesis from CO	$\text{CO}_{(\text{g})} + 2\text{H}_{2(\text{g})} \leftrightarrow \text{CH}_3\text{OH}_{(\text{g})}$	-91	[12]
Formic Acid Synthesis from CO ₂	$\text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})} \leftrightarrow \text{HCOOH}_{(\text{g})}$	15 ^a	
Formaldehyde Synthesis from CO	$\text{CO}_{(\text{g})} + \text{H}_{2(\text{g})} \leftrightarrow \text{CH}_2\text{O}_{(\text{g})}$	-5	[42]
Formaldehyde Synthesis from CO ₂	$\text{CO}_{2(\text{g})} + 2\text{H}_{2(\text{g})} \leftrightarrow \text{CH}_2\text{O}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	36 ^a	

^a Values calculated by using thermodynamic data provided from NIST [43].

Fig. 1. Proposed reaction mechanisms for the hydrogenation of CO₂ and CO.

Fig. 2. Top and side views of the preferred adsorption sites of species on Ga/Cu(111). Table A.1 provides the geometric details for these structures.

Table 3. Preferred adsorption sites with their binding energies for each species adsorbed on Ga/Cu(111).

Adsorbate	Preferred adsorption site	Binding energy (eV)
H	hcp1(fcc1)	-1.75 (-1.74)
O	fcc2 (hcp2')	-4.93 (-4.86)
C	fcc2 (fcc1)	-5.01 (-5.00)
CO	hcp1(fcc1)	-1.00 (-1.00)
OH	fcc1 (hcp1)	-3.10 (-3.05)
CO ₂	physisorption	-0.23
H ₂ O	physisorption	-0.32
COH	fcc1 (hcp1)	-2.99 (-2.94)
HCO	Ctop1 (Cbr1)	-1.48 (-1.48)
COOH	Ctop1-H down (Ctop1-H up) ^a	-2.38 (-2.37)
HCOO	Otop1-Otop1 (Otop2-Otop1)	-3.05 (-2.98)
HCOOH	physisorption	-0.51
CO ₃	Otop2-Obr1 (Otop2-Ofcc2')	-4.34 (-4.28)
HCO ₃	Otop1-Otop1 (Otop2-Otop1)	-2.89 (-2.82)
CH ₂ O	Ctop1-Obr1 (Ctop1-Otop2)	-0.41 (-0.30)
CH ₂ OH	Ctop1	-1.39
CH ₂ O ₂	Obr2-Obr2	-4.47
H ₂ COOH	Obr1 (Obr2)	-2.46 (-2.37)
CH ₃ O	fcc1 (fcc2)	-2.62 (-2.62)
CH ₃ OH	physisorption	-0.49

^a Two stable carboxyl (COOH) binding geometries were found over the top site, but they differ on the orientation of the H atom in the OH group when the species is adsorbed on Ga/Cu(111). H down indicates that H is looking to the downward direction near the surface while H up means that H is oriented away from the surface because is looking to the upward direction.

Fig. 3. Binding energies for species relevant to CO₂/CO hydrogenation at their preferred adsorption site on Ga/Cu(111).

Fig. 4. Thermochemistry of the plausible reaction pathways for the synthesis of: (a) formic acid, (b) formaldehyde and methanol via CO₂/CO hydrogenation on Ga/Cu(111). The reference zero corresponds to the energies of the isolated species in gas phase and the clean relaxed Ga/Cu(111) slab. Gas-phase species are indicated with (g) and adsorbed species are indicated with (*). The spectator H_{2(g)} in the reaction mechanism of formaldehyde and formic acid, and the adsorbed hydrogen (H*) have been omitted from the labels to improve legibility.

Table 4. The elementary steps evaluated in the thermochemistry analysis for the hydrogenation of CO₂ and CO on the M-doped Cu(111) surfaces where M=Ga, Ti, Mg.

Reaction No.	Reaction	ΔE (eV)		
		Ga/Cu(111)	Ti/Cu(111)	Mg/Cu(111)
R1	$H_2 + 2^* \rightarrow 2H^*$	-0.52	-1.23	-0.69
R2	$CO_2 + ^* \rightarrow CO_2^*$	-0.23	-2.40	-1.15
R3	$CO_2^* + ^* \rightarrow CO^* + O^*$	0.60	-0.55	0.29
R4	$CO_2^* + H^* \rightarrow HCOO^* + ^*$	-0.27	-0.05	-0.45
R5	$CO_2^* + H^* \rightarrow COOH^* + ^*$	0.53	1.37	0.59
R6	$HCOO^* + H^* \rightarrow HCOOH^* + ^*$	0.34	1.88	1.02
R7	$HCOO^* + H^* \rightarrow CH_2O_2^* + ^*$	0.65	-0.18	0.60
R8	$COOH^* + H^* \rightarrow HCOOH^* + ^*$	-0.46	0.46	-0.02
R9	$HCOOH^* + H^* \rightarrow H_2COOH^* + ^*$	0.12	-0.79	-0.39
R10	$CH_2O_2^* + H^* \rightarrow H_2COOH^* + ^*$	-0.20	1.27	0.03
R11	$CH_2O_2^* + ^* \rightarrow CH_2O^* + O^*$	0.73	0.21	0.37
R12	$H_2COOH^* + ^* \rightarrow CH_2O^* + OH^*$	0.57	-0.90	0.49
R13	$H_2COOH^* + ^* \rightarrow CH_2OH^* + O^*$	0.87	0.11	0.35
R14	$CH_2O^* + H^* \rightarrow CH_3O^* + ^*$	-0.91	-0.19	-0.80
R15	$CH_2O^* + H^* \rightarrow CH_2OH^* + ^*$	-0.07	1.17	0.01
R16	$CH_3O^* + H^* \rightarrow CH_3OH^* + ^*$	0.01	1.37	0.17
R17	$CH_2OH^* + H^* \rightarrow CH_3OH^* + ^*$	-0.83	0.01	-0.64
R18	$O^* + H^* \rightarrow OH^* + ^*$	-0.36	0.17	0.15
R19	$OH^* + H^* \rightarrow H_2O^* + ^*$	-0.07	1.09	0.13
R20	$COOH^* + ^* \rightarrow CO^* + OH^*$	-0.29	-1.76	-0.16
R21	$HCOO^* + ^* \rightarrow HCO^* + O^*$	1.73	-0.15	1.01
R22	$CO^* + H^* \rightarrow HCO^* + ^*$	0.86	0.35	0.27
R23	$CO^* + H^* \rightarrow COH^* + ^*$	1.19	1.27	1.22
R24	$CO^* + ^* \rightarrow C^* + O^*$	2.71	0.95	1.12
R25	$HCO^* + H^* \rightarrow CH_2O^* + ^*$	-0.35	0.18	-0.03
R26	$HCO^* + OH^* \rightarrow HCOOH^* + ^*$	-1.03	1.87	-0.14
R27	$CO_2^* + O^* \rightarrow CO_3^* + ^*$	0.18	-	0.26

R28	$CO_2^* + OH^* \rightarrow HCO_3^* + ^*$	-0.33	-	-0.03
R29	$CO_3^* + H^* \rightarrow HCO_3^* + ^*$	-0.87	-	-0.14
R30	$HCO_3^* + ^* \rightarrow COOH^* + O^*$	1.22	-	0.47
R31	$HCOOH^* \rightarrow HCOOH_{(g)} + ^*$	0.51	1.62	1.09
R32	$CH_2O^* \rightarrow CH_2O_{(g)} + ^*$	0.41	2.54	0.99
R33	$CH_3OH^* \rightarrow CH_3OH_{(g)} + ^*$	0.49	1.25	0.97
R34	$H_2O^* \rightarrow H_2O_{(g)} + ^*$	0.32	1.21	0.86
R35	$CO^* \rightarrow CO_{(g)} + ^*$	1.00	2.44	1.14

Fig. 5. Pathways with the lowest reaction energies for the synthesis of formic acid, formaldehyde, and methanol via CO₂ hydrogenation on Ga/Cu(111). The reference zero corresponds to the energies of the isolated species in gas phase and the clean relaxed Ga/Cu(111) slab. Gas-phase species are indicated with (g) and adsorbed species are indicated with (*). The spectator molecules of H_{2(g)} in the reaction mechanism of formic acid and formaldehyde, and the adsorbed hydrogen (H*) have been omitted from the labels to improve legibility.

Fig. 6. Top and side views of the preferred adsorption sites on the Mg/Cu(111) surface for the studied species. For CO₂, configuration (a) is Otop2-Otop2 and (b) is Otop2-Ctop1. For CH₂O₂, configuration (a) is Otop2-Ofcc2' and (b) is Otop2-Ohcp2'. Table A.3 provides the geometric details for these structures.

Table 6. Preferred adsorption sites with their binding energies for each species adsorbed on Mg/Cu(111).

Adsorbate	Preferred adsorption site	Binding energy (eV)
H	br1' (hcp1)	-2.61 (-2.57)
O	br1' ^a	-6.03
C	br1'	-5.65
CO	fcc1	-1.14
OH	fcc2 (hcp2)	-3.77 (-3.74)
CO ₂	Otop2-Otop2 (Otop2-Ctop1 ^b)	-1.15 (-1.15)
H ₂ O	physisorption	-0.86
COH	fcc1 (Cbr1'-Otop2)	-3.18 (-3.15)
HCO	Otop2-Cbr1 (Otop2-Cbr1')	-2.29 (-2.26)
COOH	Ctop1-H up ^c (Otop2-Ctop1 ^d)	-2.88 (-2.82)
HCOO	Otop2-Otop2	-4.23
HCOOH	top2-H down	-1.09
CO ₃	Otop2-Ofcc2'	-6.27
HCO ₃	Otop2-Otop2	-4.17
CH ₂ O	Otop2-Ctop1 (Otop2)	-0.99 (-0.88)
CH ₂ OH	Ctop1	-1.98
CH ₂ O ₂	Otop2-Ofcc2' (Otop2-Ohcp2')	-5.78 (-5.78)
H ₂ COOH	Otop2	-3.63
CH ₃ O	fcc2 (hcp2)	-3.17 (-3.15)
CH ₃ OH	physisorption	-0.97

^a Indicates that this species is adsorbed through four metal atoms (two Cu and two Mg) on Mg/Cu(111).

^b Indicates that two oxygen atoms of the species are respectively adsorbed on two metal atoms at the top site, forming a tridentate configuration because other atom (C or O) is also bonded to the surface at the preferred site specified.

^c Indicates that COOH is adsorbed with the H atom oriented away from the Mg/Cu(111) surface because it is looking to the upward direction.

^d Indicates that COOH is adsorbed with the H atom looking to the downward direction near the Mg/Cu(111) surface.

Fig. 7. Binding energies for species relevant to CO₂/CO hydrogenation at their preferred adsorption site on Mg/Cu(111). For CO₂, configuration (a) is Otop2-Otop2 and (b) is Otop2-Ctop1. For CH₂O₂, configuration (a) is Otop2-Ofcc2' and (b) is Otop2-Ohcp2'.

Fig. 8. Thermochemistry of the plausible reaction pathways for the synthesis of: (a) formic acid, (b) formaldehyde and methanol via CO_2/CO hydrogenation on $\text{Mg}/\text{Cu}(111)$. The reference zero corresponds to the energies of the isolated species in gas phase and the clean relaxed $\text{Mg}/\text{Cu}(111)$ slab. Gas-phase species are indicated with (g) and adsorbed species are indicated with (*). The spectator $\text{H}_{2(g)}$ in the reaction mechanism of formaldehyde and formic acid, and the adsorbed hydrogen (H^*) have been omitted from the labels to improve legibility.

Fig. 9. Pathways with the lowest reaction energies for the synthesis of formic acid, formaldehyde, and methanol via CO₂ hydrogenation on Mg/Cu(111). The reference zero corresponds to the energies of the isolated species in gas phase and the clean relaxed Mg/Cu(111) slab. Gas-phase species are indicated with (g) and adsorbed species are indicated with (*). The spectator molecules of H₂(g) in the reaction mechanism of formic acid and formaldehyde, and the adsorbed hydrogen (H*) have been omitted from the labels to improve legibility.

Fig. 10. Top and side views of the preferred adsorption sites on the Ti/Cu(111) surface for the studied species. For CO₂, configuration (a) is Otop2-Ctop1 and (b) is Otop2-Cbr1'. Table A.2 provides the geometric details for these structures.

Table 5. Preferred adsorption sites with their binding energies for each species adsorbed on Ti/Cu(111).

Adsorbate	Preferred adsorption site	Binding energy (eV)
H	br1 (br1')	-2.88 (-2.76)
O	fcc2 (fcc2')	-6.81 (-6.73)
C	fcc2 (hcp2)	-6.33 (-6.24)
CO	Otop2-Cfcc2'	-2.44
OH	top2	-4.81
CO ₂	Otop2-Ctop1 ^a (Otop2-Cbr1' ^a)	-2.40 (-2.40)
H ₂ O	top2	-1.21
COH	Cfcc2'	-4.71
HCO	Cfcc2'-Otop2	-3.79
COOH	Otop2-Cbr1' ^b (Otop2-Ctop1 ^c)	-3.62 (-3.54)
HCOO	Otop2-Ctop1 ^a (Otop2-Otop2)	-5.35 (-5.27)
HCOOH	top2-H down	-1.62
CH ₂ O	Otop2-Ctop1 (Otop2)	-2.54 (-2.49)
CH ₂ OH	Otop2-Ctop1 (Otop2)	-2.63 (-2.59)
CH ₂ O ₂	Otop2-Otop2	-7.96
H ₂ COOH	Otop2	-4.83
CH ₃ O	top2	-4.38
CH ₃ OH	top2	-1.25

^a Indicates that two oxygen atoms of the species are respectively adsorbed on two metal atoms at the preferred site specified, forming a tridentate configuration because the C atom is also bonded to the surface at the preferred site specified.

^b Indicates that COOH is adsorbed with the H atom oriented away from the Ti/Cu(111) surface because it is looking to the upward direction.

^c Indicates that COOH is adsorbed with the H atom looking to the downward direction near the Ti/Cu(111) surface.

Fig. 11. Binding energies for species relevant to CO₂/CO hydrogenation at their preferred adsorption site on Ti/Cu(111). For CO₂, configuration (a) is Otop2-Ctop1 and (b) is Otop2-Cbr1¹.

Fig. 12. Thermochemistry of the plausible reaction pathways for the synthesis of: (a) formic acid, (b) formaldehyde and methanol via CO_2/CO hydrogenation on Ti/Cu(111). The reference zero corresponds to the energies of the isolated species in gas phase and the clean relaxed Ti/Cu(111) slab. Gas-phase species are indicated with (g) and adsorbed species are indicated with (*). The spectator $\text{H}_{2(\text{g})}$ in the reaction mechanism of formaldehyde and formic acid, and the adsorbed hydrogen (H^*) have been omitted from the labels to improve legibility.

Fig. 13. Pathways with the lowest reaction energies for the synthesis of formic acid, formaldehyde and methanol via CO_2/CO hydrogenation on Ti/Cu(111). The reference zero corresponds to the energies of the isolated species in gas phase and the clean relaxed Ti/Cu(111) slab. Gas-phase species are indicated with (g) and adsorbed species are indicated with (*). The spectator molecules of $\text{H}_{2(g)}$ in the reaction mechanism of formic acid and formaldehyde, and the adsorbed hydrogen (H^*) have been omitted from the labels to improve legibility.