CO₂ hydrogenation to formic acid on Ni(111)

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**Abstract:** Periodic, self-consistent, density functional theory (DFT) calculations are employed to study CO₂ hydrogenation on Ni(111). CO₂ hydrogenation with H adsorbed on the surface and with H absorbed in the subsurface is investigated systematically and the respective microscopic reaction mechanisms are elucidated. We show that on Ni(111), CO₂ hydrogenation to formate intermediate is more favorable than to carboxyl intermediate. The hydrogenation to formate goes through the unidentate structure that rapidly transforms into the bidentate structure. Further hydrogenation from formate to formic acid is energetically more difficult than formate formation. Formation of adsorbed formic acid from adsorbed CO₂ and surface hydrogen is an endothermic reaction. Because subsurface H in Ni(111) is substantially less stable compared to surface H, its reaction with adsorbed CO₂ to adsorbed formic acid is an exothermic one. Our results may have significant implications for the synthesis of liquid fuels from CO₂ and for catalytic hydrogenation reactions in general.
1. Introduction

Using CO₂ as a carbon source to synthesize useful chemicals is of great interest.¹,² It is an abundant and inexpensive feedstock whose removal from industrial emissions is highly desirable to mitigate the greenhouse effect. One example of CO₂ conversion to a useful liquid hydrocarbon is hydrogenation of CO₂ to formic acid (HCOOH). Formic acid is an important chemical used in making animal feeds, in tanning and dyeing leather and textile, and as a food preservative. Currently, formic acid synthesis is mainly performed through a two-step process: (1) the carbonylation of methanol to methyl formate (HCOOCH₃) using high-pressures of toxic CO as the feedstock, and (2) the hydrolysis of HCOOCH₃ to formic acid and methanol. Producing formic acid by direct hydrogenation of CO₂ is a promising alternate route in terms of economy, ecology, and safety. Thus a detailed microscopic understanding on the reaction mechanism for CO₂ hydrogenation is of great importance.

Recently, Mavrikakis and co-workers studied CO₂ hydrogenation on Cu(111) and Pt(111) in the framework of their studies of the water gas shift (WGS) and its reverse reaction.³,⁴ They found that formate, an intermediate involved in formic acid production, is a spectator species for the WGS reaction. The energy barriers for adding an adsorbed H atom to physisorbed CO₂ to form formate are 1.02 and 1.39 eV on Cu(111) and Pt(111), respectively. Using a mixture of CO₂, H₂, and CO over Cu/ZnO/Al₂O₃ catalysts, Chorkendorff and co-workers showed that Ni and Co significantly promote the rate of methanol production.⁵,⁶ Because in the absence of the methanol synthesis gas phase environment and at typical reaction temperatures, Ni and Co would tend to segregate to the interior of Cu nanoparticles, the increase in activity was ascribed to a promotion through adsorbate-induced surface segregation of Ni and Co. Independently, Ni has been found to be a good catalyst for hydrogenation of hydrocarbons, whereby the presence of bulk and/or subsurface hydrogen played a special role in the observed reactivity.⁷⁻¹⁰ In particular, it has been suggested that bulk and/or subsurface H exhibits unique reactivity in the heterogeneously catalyzed hydrogenation of hydrocarbons, such as methyl, ethylene and acetylene, on Ni(111).⁷⁻¹⁴ For example, in seminal work by Ceyer et al.,⁷ it was unambiguously
demonstrated that subsurface H is the reactant for hydrogenation of methyl radical to methane on Ni(111), whereas surface H is unreactive. The effect of subsurface species on the reactivity of transition metal surfaces was also found in other systems. For example, it has been shown that subsurface O increases the reactivity of Ag(111) towards dissociation of H$_2$, O$_2$, and NO,$^{15}$ and oxidation of methanol.$^{16}$

Very recently, it was reported that under ultrahigh vacuum (UHV) conditions, CO$_2$ can be hydrogenated to formate (HCOO) on Ni(110).$^{17}$ Further hydrogenation of HCOO to formic acid, however, was not observed. Under the UHV conditions applied in the work described in Ref. 17, only surface H exists on Ni. The absence of subsurface H under these experimental conditions may be the reason for the lack of formic acid production.

Here, we systematically study CO$_2$ hydrogenation with H adsorbed on the surface and with H absorbed in the subsurface on Ni(111). We explore the detailed reaction mechanism and derive the potential energy surface for CO$_2$ hydrogenation to formate and further to formic acid with surface H and subsurface H. We compare the competitive hydrogenation processes via formate and carboxyl intermediates. We then discuss the role of subsurface H either as a spectator or as a reactant in CO$_2$ hydrogenation. Our results shed light on the microscopic reaction mechanism for CO$_2$ hydrogenation on Ni(111) in the absence and presence of subsurface H and may have significant implications for producing useful chemicals from CO$_2$.

2. Computational Methods

All calculations were performed using the Vienna ab-initio Simulation Package (VASP) code$^{18,19}$ based on spin-polarized density functional theory. The projector augmented wave (PAW) potentials$^{20,21}$ were used for electron-ion interactions and the generalized gradient approximation (GGA–PW91)$^{22}$ was used to describe the exchange-correlation functional. The electron wave function was expanded using plane waves with an energy cutoff of 400 eV. The Ni(111) surface was modeled by a five-layer slab with a (3×3) surface unit cell separated from its image in the z-direction by a vacuum equivalent of six
atomic layers. The Brillouin zone of the Ni(111)-(3×3) surface was sampled using a (4×4×1) k-point mesh based on the Monkhorst-Pack scheme. The two bottom-most Ni(111) layers were fixed during relaxation. All structures were fully relaxed until the Hellmann-Feynman forces acting on the atoms were smaller than 0.05 eV/Å. Convergence with respect to energy cutoff, k-point set, and number of metal layers is confirmed. The climbing image nudged elastic band (CI-NEB) method was used to calculate the activation energy barriers for the various elementary steps considered. Transition states were verified by calculating the Hessian matrix with the finite difference approach and identifying a single imaginary frequency. The binding energy (BE) is defined as 
\[ \text{BE} = E_{\text{ads}} - E_{\text{clean}} - E_{\text{gas}}, \]
where \( E_{\text{ads}} \), \( E_{\text{clean}} \), and \( E_{\text{gas}} \) are the calculated total energies of the slab with adsorbate, the clean slab, and the adsorbate species in the gas phase, respectively. All calculations were performed with spin polarization and a ferromagnetic phase was adopted for Ni(111), with a remaining magnetic moment of 0.67 μB per atom of the clean slab. The calculated Ni lattice constant is 3.52 Å, in good agreement with the experimental value of 3.524 Å.

3. Results and Discussion

A. Adsorption and co-adsorption of H and CO₂. We first studied the adsorption and co-adsorption of atomic hydrogen (H) and CO₂ on Ni(111). The fcc hollow site is the most stable site (calculated binding energy of -2.83 eV) of a hydrogen atom adsorbed in an ordered (3×3) overlayer with a coverage of 1/9 monolayer (ML). The hcp hollow site is slightly less stable (by -0.01 eV), whereas the bridge and top sites are much less favorable, with binding energies of -2.69 and -2.22 eV, respectively. The calculated trends in binding of H on Ni(111) are in good agreement with results of earlier studies. For CO₂ adsorption on Ni(111) at 1/9 ML coverage, we found that CO₂ is nearly parallel to the surface and the C—O bond length is 1.18 Å which is nearly unchanged with respect to that in the gas phase CO₂ molecule. The \( z \)-distance of CO₂ to the surface is ca. 3.5 Å. This adsorption geometry together with the weak calculated binding energy of -0.06 eV implies that CO₂ is weakly physisorbed on the surface, similar to what was found for CO₂ adsorption on Cu(111) and Pt(111). The presence of 1/9 ML...
surface H at the *fcc* site of Ni(111) leaves the CO$_2$ adsorption geometry and binding energy practically unchanged. This is expected because CO$_2$ is far away from the surface and the interaction with the adsorbed H is negligible.

**B. CO$_2$ hydrogenation with surface H.** Having analyzed the adsorption and co-adsorption of H and CO$_2$, we then studied CO$_2$ hydrogenation on Ni(111). For CO$_2$ hydrogenation with H adsorbed on the surface (H$_s$), two different routes exist: CO$_2$ can be hydrogenated either at its carbon atom to lead to formate (HCOO) formation, or at its oxygen atom to lead to carboxyl (COOH) formation, an intermediate that was proposed to be key for the low-temperature WGS reaction on Cu(111) and Pt(111). On Ni(111), our calculations suggest that formate in its most stable bidentate structure (HCOO$^{**}$(bi), with two O atoms bound to two Ni atoms at atop sites) is more stable than carboxyl (COOH) in its most stable *trans*-configuration (with H pointing towards the surface) by 0.32 eV. This is in contrast to the gas phase structures of these species, where COOH is more stable than HCOO by ~0.4 eV. We first examine CO$_2$ hydrogenation to formate. Shown in Figure 1 is the calculated potential energy surface (PES) for CO$_2$ hydrogenation to HCOOH via the formate intermediate. We found that before reacting with the adsorbed surface H to form formate, the physisorbed CO$_2$ moved close to the surface and settled in a metastable state characterized by a bent CO$_2$ geometry. In this metastable state, designated as (H$_s^* +$ CO$_2^*$) in Figure 1, the C—O bond lengths are 1.21 and 1.26 Å, and the longer C—O bond is nearly parallel to a Ni—Ni bond. The O—C—O bond angle in that state is 138°. This metastable state is 0.36 eV less stable than the weakly physisorbed state and has been suggested as an intermediate state for CO oxidation on oxygen-predosed Ni(111) and Pt(111). The activation energy barrier of transforming the physisorbed state into the metastable state is 0.41 eV. In the transition state (see TS1 in Figure 1), the C—O bond lengths are 1.19 and 1.21 Å, and the O—C—O bond angle is 160°. After CO$_2$ reaches that state on the surface, it is ready to react with the pre-adsorbed H and form formate. The minimum energy path involves the approach of H to C en route to forming a H—C bond. The distance between H and C at the transition state (TS2 shown in inset of Figure 1) is 1.29 Å, which is only 0.18 Å larger than the H—C bond length in the preferred adsorbed state of
formate. After that, the molecule flips and ends up with formate in a unidentate structure with one of its O atoms positioned at an \textit{fcc} site (state denoted as (HCOO*(uni), thereafter). The activation energy \textit{barrier for this reaction is 0.62 eV}. \textit{Notice that the unidentate formate is 0.59 eV less stable than the bidentate structure, which has both its O atoms bonded to two Ni atoms at atop sites. A similar unidentate formate was found to be stable on Cu(111)\textsuperscript{3} but not on Pt(111).\textsuperscript{4} The transformation from the unidentate to the bidentate formate is almost spontaneous, with a very small barrier of 0.06 eV. This is similar to the respective formate structural transformation on Cu(111).\textsuperscript{3} We also analyzed the minimum energy path for hydrogenation from the co-adsorbed CO\textsubscript{2} and surface H state directly to the bidentate formate, without passing through the unidentate structure. Compared with the two-step process path (via the unidentate formate) which needs an overall energy barrier of 0.62 eV, the direct path, not shown in Fig. 1, is characterized by an energy barrier of 0.78 eV and, is, therefore, less favorable.
Figure 1. Potential energy surface (PES) of CO₂ hydrogenation to formate (HCOO) and formic acid (HCOOH) with H adsorbed (Hs*) on Ni(111). The dashed gray line shows the PES for CO₂ hydrogenation to carboxyl (COOH) intermediate. The atomic structures of reactants, intermediates, transition states, and products are schematically illustrated in the respective insets. Blue, black, red, and grey spheres indicate H, C, O, and Ni atoms, respectively. * denotes an adsorbed state. Two species within the same parenthesis signify a coadsorbed state. TS represent transition states. Symbol ∞ denotes that adsorbed states at infinite separation from each other (no interaction energy).

We now consider the other route for CO₂ hydrogenation on Ni(111) that adds the H atom to one of the two oxygen atoms of CO₂ and leads to the carboxyl (COOH) intermediate. Similarly to the microscopic findings for formate formation, we found that for carboxyl formation, first the physisorbed CO₂ state transforms to the metastable CO₂ state discussed above. The resulting CO₂ state reacts with the co-adsorbed surface H atom to form carboxyl in its most stable trans-configuration. The relevant energetics is shown with the gray dashed line in Figure 1. The activation energy barrier to form carboxyl is 0.83 eV, which is 0.21 eV higher than the barrier to form formate. The inferior thermochemical stability of carboxyl relative to formate and the higher activation energy barrier associated with carboxyl formation
suggest that the hydrogenation route via formate is clearly favored on Ni(111). Therefore, we will not consider the carboxyl route further for the purpose of this study.

We then turn our attention to adding a surface H atom to formate to produce a formic acid molecule on the Ni(111) surface. First, we find that there is a repulsive interaction (~0.2eV) between coadsorbed HCOO(bi) and H (see Table I). For the adsorption of the final product formic acid on Ni(111), we found that the most stable site is the atop site, with O of the carbonyl bonding with an atop Ni atom and the OH being above a bridge site. The PES of the second hydrogenation to form formic acid is also provided in Figure 1. The respective reaction coordinate involves HCOO rotation towards H and diffusion of H from the fcc site to the neighboring bridge site for the final H—O bond making event. At the transition state (TS4 shown in Figure 1), the O—H distance is 1.49 Å. After the TS, H moves vertically towards O (of C=O) and settles with HCOOH in the atop molecular structure. As shown, an activation energy barrier of 0.83 eV is associated with this second hydrogen addition step. This barrier is larger than that of the first hydrogen addition step (0.62 eV), indicating that the second hydrogenation step might be the rate-determining step for formic acid production.

C. CO$_2$ hydrogenation with subsurface H. As discussed above, subsurface and bulk hydrogen in metals, such as Ni, have been shown to possess substantially different reactivity than surface-adsorbed hydrogen in the catalytic hydrogenation of hydrocarbons.$^{11,12}$ Subsurface and bulk H could act as spectators modifying the electronic structure of the metal surface and thus its catalytic activity,$^{31}$ or act as a direct reactant in the hydrogenation reaction.$^7$ Compared to surface H, subsurface H in the octahedral site ($O_h$) of Ni(111) —directly underneath a surface fcc site—is metastable, with a binding energy of -2.19 eV. This metastable subsurface H can be prepared at low temperatures by exposure of the surface to atomic hydrogen followed by collision-induced recombinative desorption to remove the surface bound H under UHV conditions.$^{32-34}$ To explore the role of subsurface H (H$_b$) in CO$_2$ hydrogenation on Ni(111), we first studied CO$_2$ hydrogenation with surface H in the presence of subsurface H as a spectator. We then studied CO$_2$ hydrogenation with subsurface H as a reactant at a low coverage (2/9 ML) and a full ML coverage.
Figure 2. Potential energy surface of CO$_2$ hydrogenation to formate (HCOO) and formic acid (HCOOH) with surface H (Hs*) at 2/9ML initial coverage on Ni(111) and in the presence of 1/9ML subsurface H (Hb*) as a spectator species. The detailed structures of reactants, transition states, intermediates, and products are schematically illustrated in insets. For further symbol definitions see caption of Fig. 1.

Table I. Binding energy (in eV) of CO$_2$, HCOO, and HCOOH on clean Ni(111), Ni(111) with a 1/9 monolayer (ML) surface H (Hs), a 1/9 ML and a 1 ML subsurface H (Hb). Binding energies refer to the respective adsorbates in the gas phase.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Site</th>
<th>Clean</th>
<th>1/9 ML H$_s$</th>
<th>1/9 ML H$_b$</th>
<th>1 ML H$_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>physisorbed</td>
<td>-0.06</td>
<td>-0.06</td>
<td>-0.06</td>
<td>-0.06</td>
</tr>
<tr>
<td></td>
<td>metastable state</td>
<td>+0.19</td>
<td>+0.30</td>
<td>+0.27</td>
<td>+0.21</td>
</tr>
<tr>
<td>HCOO</td>
<td>unidentate</td>
<td>-2.45</td>
<td>-</td>
<td>-2.46</td>
<td>-2.30$^a$</td>
</tr>
<tr>
<td></td>
<td>bidentate</td>
<td>-3.03</td>
<td>-2.84</td>
<td>-3.13</td>
<td>-3.00$^a$</td>
</tr>
<tr>
<td>HCOOH</td>
<td>atop</td>
<td>-0.43</td>
<td>-</td>
<td>-0.48</td>
<td>-0.48$^b$</td>
</tr>
</tbody>
</table>
The coverage of H\textsubscript{b} is 8/9 ML. The coverage of H\textsubscript{b} is 7/9 ML.

In the study of CO\textsubscript{2} hydrogenation with surface H in the presence of subsurface H as a spectator species, one H atom is pre-absorbed at an \(O_h\) site in the first subsurface layer of Ni(111), corresponding to a H\textsubscript{b} coverage of 1/9 ML. The elementary steps of the reaction along the path shown in Figure 1 were all recalculated and the results are shown in Figure 2. By comparing Figure 1 with Figure 2, we conclude that within the accuracy of our calculations, subsurface H as a spectator species does not change the PES of CO\textsubscript{2} hydrogenation with surface H. Hence, the effect of subsurface H as a spectator on the reactivity of the Ni(111) surface towards CO\textsubscript{2} hydrogenation is small and can be neglected.

Next, we investigated CO\textsubscript{2} hydrogenation with subsurface H in Ni(111) as a reactant. We started with the initial structure with a subsurface H at an \(O_h\) site and a CO\textsubscript{2} physisorbed at the surface. The PES we found for CO\textsubscript{2} hydrogenation using the subsurface H as a reactant is shown in Figure 3. The presence of the pre-absorbed subsurface H has negligible effect on CO\textsubscript{2} adsorption. The calculated binding energy of physisorbed CO\textsubscript{2} is essentially unchanged (see Table I). For the reaction between subsurface H and physisorbed CO\textsubscript{2} to happen, subsurface H has to emerge onto the surface and physisorbed CO\textsubscript{2} has to move closer the surface. Our CI-NEB calculations using the structure with subsurface H at an \(O_h\) site and physisorbed CO\textsubscript{2} as the initial state and a final state comprised of an H atom at an \(fcc\) site and a CO\textsubscript{2} molecule in its metastable surface state discussed above showed that the subsurface H emergence onto the surface occurs before the transformation of the physisorbed CO\textsubscript{2} into its surface metastable state. The emergence of subsurface H is characterized by an activation energy barrier of 0.1 eV. At the transition state of H emergence, the interatomic distance between the surface Ni atoms surrounding the emerging H atom is ca. 5% larger than the equilibrium distance in Ni(111) and the H atom is nearly at the same height as its neighboring Ni atoms. After the emergence of subsurface H to the surface, the reaction paths of the transformation from physisorbed CO\textsubscript{2} to the metastable state of surface CO\textsubscript{2} and
the first hydrogenation to formate using the emerged H as a reactant are exactly the same as in the corresponding steps of CO\textsubscript{2} hydrogenation with surface H (see earlier discussion).

By introducing a second subsurface H co-adsorbed with a HCOO in its bidentate state, we studied the second hydrogenation leading from formate to formic acid. The presence of the subsurface H slightly stabilizes the adsorbed formate. As seen in Table I, the binding energy of the bidentate formate is -3.13 eV, whereas it is -3.03 eV on the clean Ni(111). Our CI-NEB calculations suggest that before reacting with the formate, the subsurface H emerges onto the surface, with an energy barrier of 0.13 eV. After emergence of the subsurface H atom, the pathway for the hydrogenation of formate to formic acid is the same with that described above (0.83 eV activation energy barrier).

We notice that the metastable subsurface H changes the thermochemistry of the overall reaction $2\text{H}^*+\text{CO}_2^* \rightarrow \text{HCOOH}^*$. As shown in Figures 1 and 3, the reaction $2\text{H}_b^*+\text{CO}_2^* \rightarrow \text{HCOOH}^*$ is endothermic by 0.56 eV; whereas the reaction $2\text{H}_b^*+\text{CO}_2^* \rightarrow \text{HCOOH}^*$ is exothermic by 0.71 eV. This difference reflects the energy difference between two surface and two subsurface H atoms on/in Ni(111). Unfortunately, the methods used in this work do not allow directly probing reactivity of the emerging H atom with the metastable CO\textsubscript{2} surface state before the emerging H atom has equilibrated with the surface and become a surface bound H atom. We are currently exploring that reactivity by utilizing the appropriate force-fields based Born-Oppenheimer molecular dynamics calculations.
Finally, we studied CO$_2$ hydrogenation on Ni(111) with a full ML of H absorbed in the first subsurface layer, which is the model system representing reactivity of Ni(111) loaded with subsurface H by using the collision-induced recombinative desorption strategy.\textsuperscript{7,32-34} The most stable configuration has all $O_h$ sites in the subsurface populated with H. At a full ML coverage, the calculated binding energy is -2.27 eV per subsurface H, which is slightly larger (by 0.08 eV) in magnitude than that in a low coverage limit discussed earlier. This indicates that the interaction between absorbed subsurface H is attractive. To explore the hydrogenation process on Ni(111) with a full ML H$_b$, we first calculated the adsorption of a CO$_2$ molecule on the surface. As on clean Ni(111), we found that CO$_2$ is weakly physisorbed on the surface and the presence of H$_b$ does not change its binding strength. The overall PES for CO$_2$ hydrogenation on Ni(111) with 1 ML subsurface H is shown in Figure 4.

**Figure 3.** Potential energy surface of CO$_2$ hydrogenation to formate (HCOO) and formic acid (HCOOH) on Ni(111) with 2/9 monolayer subsurface H as the initial reactant. The atomic structures of reactants, transition states, intermediates, and products are schematically illustrated in insets. For symbol definitions, see Fig. 1.
Figure 4. Potential energy surface of CO$_2$ hydrogenation to formate (HCOO) and formic acid (HCOOH) on Ni(111) with a full monolayer of subsurface H. The atomic structures of reactants, transition states, intermediates, and products are schematically illustrated in insets. Pink solid arrows in insets denote the subsurface H ($n_0$, $n_1$, and $n_2$) which eventually emerge to the surface. See text for details and Fig. 1 for symbol definitions.

Similarly to CO$_2$ hydrogenation with H$_b$ as a reactant at low coverage, we found that the interaction of newly emerged H$_b$ with adsorbed CO$_2$ results in movement of CO$_2$ closer to the surface, leading to the metastable (Hs* + CO$_2$*) state. The emergence of the Hb from site $n_2$ (see inset in Figure 4) to the corresponding surface fcc site is characterized by a 0.18 eV activation energy barrier. Following the emergence of H$_b$, the weakly physisorbed CO$_2$ comes close to the surface and goes to its metastable state with an energy barrier of 0.43 eV. Subsequently, the first hydrogenation step H$_s^*$ + CO$_2^*$ $\rightarrow$ HCOO$^*$ (uni) is characterized by a 0.8 eV energy barrier, which is 0.18 eV larger than that the corresponding barrier on the clean Ni(111). The subsequent transformation HCOO$^*$(uni)$\rightarrow$
HCOO**(bi) takes place almost spontaneously. To study the second hydrogenation from HCOO**(bi) to formic acid HCOOH*, we considered two pathways using two different Hb at the nearest Hb at site $n_0$ and the next nearest Hb at site $n_1$, as indicated by the pink arrows in the atomic structure of HCOO**(bi) shown in the inset of Figure 4. The first path for the second hydrogenation includes two steps: (1) the emergence of Hb at $n_0$ to the above fcc site ($f_0$), which has the same energy barrier (0.18 eV) as the first Hb emergence, and (2) the reaction between H at $f_0$ and HCOO**(bi), which requires an energy barrier of 0.84 eV, similar to the respective process at low Hb coverage. The second path for the hydrogenation to formic acid consists of three steps: (1) the emergence of Hb at $n_1$ to the fcc site right above ($f_1$), with an energy barrier of 0.17 eV, (2) the diffusion of H at $f_1$ to the neighboring hcp site $h_1$ with an energy barrier of 0.27 eV, and (3) the reaction of H at $h_1$ and HCOO**(bi) with an energy barrier of 0.80 eV. Overall, the hydrogenation from CO$_2$* to HCOOH* on Ni(111) with 1 ML Hb absorbed is exothermic with an reaction energy of -0.46 eV. The energy barriers for the first and second hydrogenation steps are comparable ($\sim$ 0.8 eV).

4. Conclusions

In summary, we presented a periodic, self-consistent DFT study of CO$_2$ hydrogenation on Ni(111) surfaces. We systematically studied CO$_2$ hydrogenation with H adsorbed on the surface and with H absorbed in the subsurface. Our results showed that CO$_2$ hydrogenation to formate intermediate is more favorable than to carboxyl intermediate. The first hydrogenation to formate goes through the unidentate structure with a barrier of $\sim$ 0.6 eV, whose structure then transforms to the more stable bidentate structure easily. The second hydrogenation process from formate to formic acid is energetically more difficult than the first hydrogenation (barrier of $\sim$ 0.8 eV). Furthermore, we studied the role of subsurface H either as a spectator or as a reactant in CO$_2$ hydrogenation on Ni(111). We showed that subsurface H as a spectator essentially has no effect on the hydrogenation process. In contrast, subsurface H as a reactant by emerging out onto the surface changes the thermodynamics of CO$_2$ hydrogenation to adsorbed HCOOH from endothermic to exothermic, due to the excess energy
possessed by the less stable subsurface H. Our studies have probed surface chemistry with H
equilibrated on the Ni(111) surface upon its emergence from subsurface. Current studies explore the
analogous chemistry on Ni(110) and other more direct reactive paths, where the transient non-
equilibrated H species reacts with adsorbed CO₂ as it emerges from the subsurface.

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