



CO₂ hydrogenation to formic acid on Ni(110)

Guowen Peng^a, S.J. Sibener^b, George C. Schatz^c, Manos Mavrikakis^{a,*}

^a Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

^b Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, IL 60637, USA

^c Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

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ABSTRACT

Hydrogen (H) in the subsurface of transition-metal surfaces exhibits unique reactivity for heterogeneously catalyzed hydrogenation reactions. Here, we explore the potential of subsurface H for hydrogenating carbon dioxide (CO₂) on Ni(110). The energetics of surface and subsurface H reacting with surface CO₂ to form formate, carboxyl, and formic acid on Ni(110) is systematically studied using self-consistent, spin-polarized, periodic density functional theory (DFT-GGA-PW91) calculations. We show that on Ni(110), CO₂ can be hydrogenated to formate by surface H. However, further hydrogenation of formate to formic acid by surface H is hindered by a larger activation energy barrier. The relative energetics of hydrogenation barriers is reversed for the carboxyl-mediated route to formic acid. We suggest that the energetics of subsurface H emerging to the surface is suitable for providing the extra energy needed to overcome the barrier to formate hydrogenation. CO₂ hydrogenation to formic acid could take place on Ni(110) when subsurface H is available to react with CO₂. Additional electronic-structure based dynamic calculations would be needed to elucidate the detailed reaction paths for these transformations.

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1. Introduction

Bulk or subsurface hydrogen (H) embedded in transition metal (e.g., Nickel) single crystals has been suggested to have distinctly different reactivity than surface-adsorbed H for catalytic hydrogenation of hydrocarbons.^{1,2} Subsurface and bulk H could act as spectator species modifying the electronic structure of catalytic metal surfaces and thus the reactivity of those surfaces, or act as direct reactants for the hydrogenation reactions. However, until bulk and subsurface H was synthesized under well-controlled ultrahigh vacuum (UHV) conditions, the role of these H states was not well understood.^{3–9} In the seminal work by Ceyer et al.,^{3,6,8} it was shown that subsurface H is the reactant for the catalytic hydrogenation of surface adsorbed hydrocarbons such as methyl, ethylene, and acetylene. Subsurface species have also been suggested to affect the reactivity of transition

metal surfaces for other catalytic systems. For example, subsurface O has been implicated in ethylene epoxidation catalyzed by Ag,¹⁰ and it has been shown that it increases the reactivity of Ag(111) towards dissociation of H₂, O₂, and NO,¹¹ and towards oxidation of methanol.¹²

CO₂ hydrogenation to useful chemical products, such as formic acid (HCOOH) and methanol (MeOH), is of great interest for practical processes because CO₂ is an inexpensive and abundant carbon source, and because removal of CO₂ from industrial emissions can reduce its greenhouse effect.^{13,14} Currently, HCOOH synthesis, the main focus of this study, is mainly performed through a two-step process: (1) the carbonylation of methanol to methyl formate (HCOOCH₃) using high-pressure CO as the feedstock, which is toxic, and (2) the hydrolysis of HCOOCH₃ to HCOOH and methanol. Producing formic acid by direct hydrogenation of CO₂ would be a promising alternate route from financial, ecological, and safety perspectives. Therefore, a detailed microscopic understanding of the reaction mechanism and its associated energetics for CO₂ hydrogenation to HCOOH is of great importance.

Recently, our group studied the reaction mechanism and energetics for CO₂ hydrogenation to formate (HCOO) and carboxyl (COOH) on Cu(111) and Pt(111), as elementary steps playing a role in the water

* Corresponding author. Tel./fax: +1 608 262 9053.

E-mail address: manos@engr.wisc.edu (M. Mavrikakis).

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gas shift (WGS) reaction.^{15,16} Both HCOO and COOH are possible intermediates in the HCOOH production reaction. It was found that for the WGS reaction, HCOO is a spectator species, whereas COOH is responsible for turning over the rates. Very recently, Vesselli et al. reported that under UHV conditions, CO₂ can be hydrogenated to the HCOO intermediate on Ni(110).¹⁷ Further hydrogenation of HCOO to HCOOH, however, was not observed. Under the UHV conditions applied in Ref.,¹⁷ only surface H exists on the Ni surfaces, and the absence of subsurface H may have been the reason for the lack of HCOOH production.

In this contribution, we systematically study the reaction mechanism and energetics of CO₂ hydrogenation to formate, carboxyl, and formic acid, where H is (i) adsorbed on the surface (H_s) or (ii) absorbed in the subsurface (H_b) of Ni(110). We show that on Ni(110), CO₂ can be hydrogenated by H_s to HCOO, but further hydrogenation of HCOO to HCOOH by H_s is hindered by a larger activation energy barrier. The opposite is true for the carboxyl-mediated path, where first H addition to adsorbed CO₂ is much more activated than the second H addition to make HCOOH. We find that H_b as a spectator species has no significant effect on CO₂ hydrogenation energetics. On the contrary, as a reactant, the transiently energetic H_b may be able to overcome the energy barrier to HCOOH formation and therefore we suggest that CO₂ hydrogenation to HCOOH could take place on Ni(110) under well-controlled UHV conditions, provided that H_b is available. Our results may have broader potential implications for producing useful chemicals by using subsurface species as reactants in catalytic processes.

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 Ni(110) surface was modeled by a (2×3) surface unit cell in a seven-layer slab, separated from its successive images in the z-direction by a vacuum region ~12 Å thick. The electron wave function was expanded using plane waves with an energy cutoff of 400 eV. The Brillouin zone of the Ni(110) – (2×3) surface was sampled with a (4×3×1) k-point mesh based on the Monkhorst–Pack scheme.²³ The climbing image nudged elastic band (CI-NEB) method²⁴ was used to calculate the activation energy barrier and the detailed reaction coordinate for each elementary step considered. The three bottom-most Ni(110) layers were fixed during energy minimization; all other layers and the adsorbates were allowed to relax. Structures were fully relaxed until the Hellmann–Feynman forces acting on the atoms were smaller than 0.05 eV/Å. Transition states were verified by calculating the Hessian matrix with the finite difference approach and by identifying a single imaginary frequency. The binding energy is defined as $BE = E_{\text{ads}} - E_{\text{clean}} - E_{\text{gas}}$, where E_{ads} , E_{clean} , and E_{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 spin-polarized; the ferromagnetic phase was adopted for Ni(110). The calculated Ni

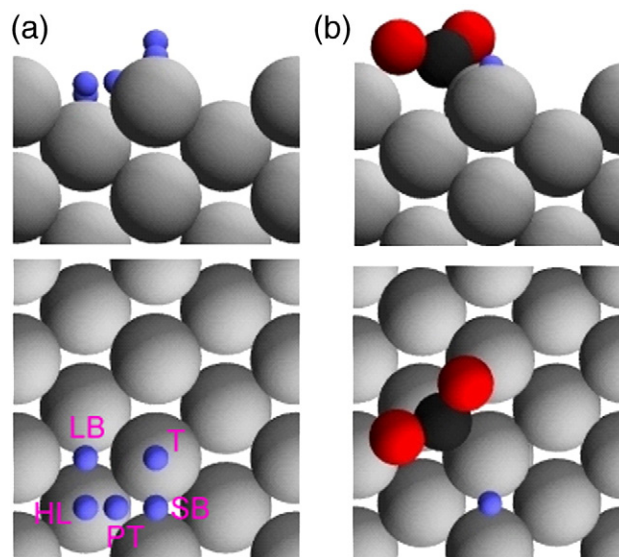


Fig. 1. (a) Side and top views of different high symmetry sites for H adsorption on Ni(110). PT: pseudo-three-fold site, SB: short bridge site, LB: long bridge site, T: top site, HL: hollow site. (b) Side and top views of the atomic structure of the most stable V-shaped CO₂^{δ-} configuration, coadsorbed with H at the SB site, on Ni(110). Blue, black, red, and grey spheres indicate H, C, O, and Ni atoms, respectively.

lattice constant is 3.52 Å, in good agreement with the experimental value of 3.524 Å.²⁵

3. Results and discussion

3.1. Adsorption and co-adsorption of H and CO₂ on Ni(110)

We first studied adsorption and co-adsorption of H and CO₂ on Ni(110). For H adsorption, different high symmetry adsorption sites, as schematically illustrated in Fig. 1a, were considered. The calculated binding energy of H at the pseudo-three-fold (PT), short bridge (SB), long bridge (LB), hollow (HL), and top (T) sites are −2.73, −2.71, −2.66, −2.51, and −2.24 eV, respectively, in good agreement with results from previous studies.^{17,26} For CO₂ adsorption, we found that the V-shaped CO₂^{δ-} structure (see Fig. 1b) is most stable, a result consistent with previous literature.^{17,27} As illustrated in Fig. 1b, in this V-shaped CO₂^{δ-} configuration, the C–O bond length is 1.28 Å and the C–O–C bond angle is 126°. The C–Ni bond length is 1.91 Å, and the two O–Ni distances are 1.95 and 1.98 Å. The calculated CO₂ binding energy for that state is −0.47 eV. A Bader analysis²⁸ revealed that a Bader charge of −0.8e is on CO₂, indicating that electrons are transferred from the surface to the molecule. For H and CO₂ co-adsorption, the most stable structure is the structure with CO₂ in the V-shaped configuration and H at the neighboring SB site (see Fig. 1b), where the interaction between the two adsorbed species is mildly attractive with an energy gain of 0.04 eV.

3.2. CO₂ hydrogenation to formate, carboxyl, and formic acid with surface H

Having identified the best co-adsorption structure, we first investigated the detailed reaction coordinate of CO₂ hydrogenation to formate (HCOO) and further to formic acid (HCOOH) with surface H. Fig. 2 shows the overall potential energy surface (PES) for CO₂

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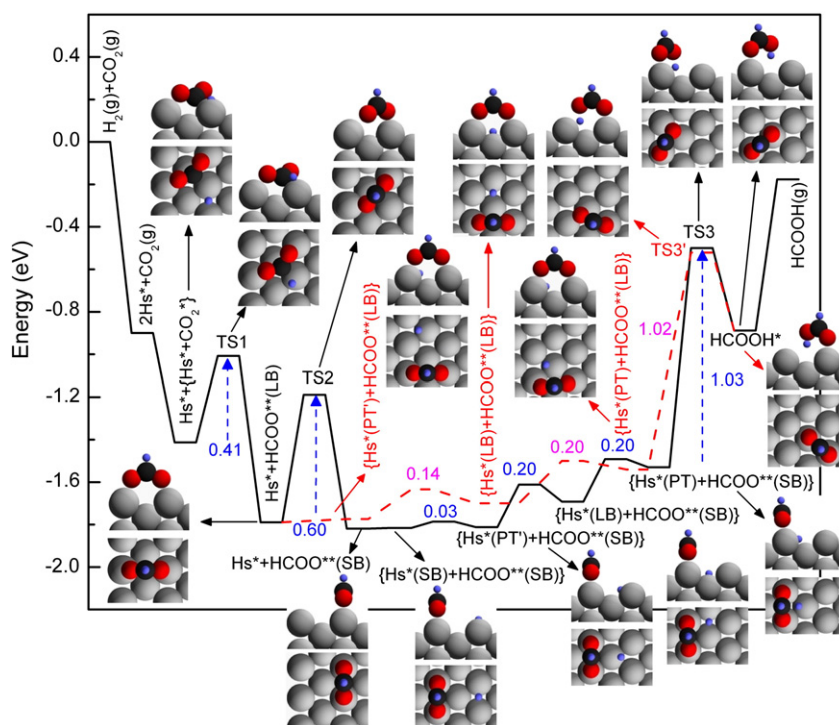


Fig. 2. Potential energy surface (PES) of CO_2 hydrogenation to formate (HCOO) and formic acid (HCOOH) with surface H adsorbed on $\text{Ni}(110)$. Black solid and red dashed red lines are the PES of CO_2 hydrogenation to formic acid via formate at the short bridge (SB) site and long bridge (LB) site, respectively. The atomic structures of reactants, intermediates, transition states, and products are schematically shown in the respective insets, comprised of a cross section and a top view of each state right next to each other in each inset's column. Blue, black, red, and grey spheres indicate H, C, O, and Ni atoms, respectively. * denotes an adsorbed state. Two species contained within the same curly brackets signify a coadsorbed state. TS represents transition states.

hydrogenation with surface H on $\text{Ni}(110)$: the first hydrogenation to HCOO at the LB site is characterized by an activation energy barrier of 0.41 eV. The path involves the approach of H to CO_2 for making an H—C bond, followed by a $\sim 90^\circ$ rotation of the HCOO intermediate. At the transition state (see TS1 in Fig. 2), H is at the off-top site, and the H—C distance is 1.47 Å. The binding energy of formate on $\text{Ni}(110)$ at the LB site and the SB site is -3.66 and -3.69 eV, respectively. The LB state of formate can transform to the slightly more stable SB state, with an activation energy barrier of 0.60 eV.

We then considered further hydrogenation of adsorbed HCOO to HCOOH . For this second hydrogenation step, two different paths starting from HCOO at the SB site and from HCOO at the LB site were studied. We first calculated the minimum energy path starting from HCOO at the most stable SB site. The best co-adsorbed state for HCOO and H has H at the SB site in the adjacent row (see inset in Fig. 2), with the interaction between HCOO and H being negligible. The reaction coordinate consists of a series of H diffusion steps ($\text{H}_s^*(\text{SB}) \rightarrow \text{H}_s^*(\text{PT}) \rightarrow \text{H}_s^*(\text{LB}) \rightarrow \text{H}_s^*(\text{PT})$, see black line in Fig. 2), with diffusion barriers typically on the order of 0.2 eV. The addition of H to HCOO takes place after H diffuses to the neighboring PT site, next to the adsorbed HCOO . The hydrogenation involves the rotation of HCOO around one O atom bonded to the surface. At the transition state (see TS3 in Fig. 2), the HCOO is rotated by $\sim 32^\circ$ towards H, and the H—O distance is 1.38 Å. This H-addition step is characterized by an activation energy barrier of 1.03 eV, which is ~ 2.5 times the respective energy barrier calculated for making HCOO from CO_2 and H co-adsorbed. We also studied the alternative path for HCOO to HCOOH , starting from formate at the LB site and without passing through the slightly more stable HCOO state at the SB site. The results are shown by the red dashed line in Fig. 2 for comparison. As shown, this alternative path is similar to the path starting from the HCOO at the SB site and consists of several H diffusion steps. The activation energy barrier for the actual bond-making step forming HCOOH is 1.02 eV, nearly identical to the one just discussed above.

We subsequently studied an alternative route for the hydrogenation of CO_2 to formic acid through the carboxyl intermediate (COOH), a key intermediate for the low-temperature WGS reaction.^{15,16} We note that carboxyl and formate are two isomeric intermediates, the former having its H bonded to an oxygen atom and the latter to its carbon atom. According to our calculations, on $\text{Ni}(110)$, COOH prefers an SB site in the *trans*-configuration (with its H pointing towards the surface). This most stable adsorbed COOH state, however, is 0.62 eV less stable than the most stable adsorbed state of HCOO (SB site). Shown in Fig. 3 is the calculated potential energy surface of CO_2 hydrogenation to formic acid via the carboxyl intermediate. The calculated activation energy barrier for hydrogenating CO_2 to carboxyl is 1.16 eV, which is close to three times the respective barrier for making its isomeric formate on $\text{Ni}(110)$.

The second hydrogenation from carboxyl to formic acid starts with a facile hydrogen diffusion step, ($\text{H}_s^*(\text{PT}) \rightarrow \text{H}_s^*(\text{LB})$), with a small energy barrier of 0.18 eV, see Fig. 3), followed by the reaction of $\text{H}_s^*(\text{LB})$ with the coadsorbed COOH^* to form a *cis*- $\text{HCOOH}_{\text{II}}^*$ adsorbed on the surface in the parallel configuration. This bond-making event has an activation energy barrier of 0.58 eV. The molecule in the *cis*- $\text{HCOOH}_{\text{II}}^*$ configuration can transform to the slightly more stable *trans*- $\text{HCOOH}_{\text{II}}^*$ configuration with an energy barrier of 0.27 eV. The *trans*- $\text{HCOOH}_{\text{II}}^*$ configuration can then easily rotate to settle into the most stable HCOOH^* structure in the perpendicular configuration, with a small energy barrier of 0.15 eV.

In addition, we investigated the decomposition of COOH^* to $^*\text{CO}$ and $^*\text{OH}$, because this could be a viable route for consuming COOH , competing with its further hydrogenation to HCOOH , the other route for consuming COOH . The calculated PES for COOH decomposition to CO and OH is shown by the red dashed line in Fig. 3. This elementary step is highly activated, with an energy barrier of 1.06 eV. This finding suggests that, once COOH is formed on $\text{Ni}(110)$, it is likely to proceed to form HCOOH (with a barrier of 0.58 eV) rather than to decompose to CO and OH (with a barrier of 1.06 eV).

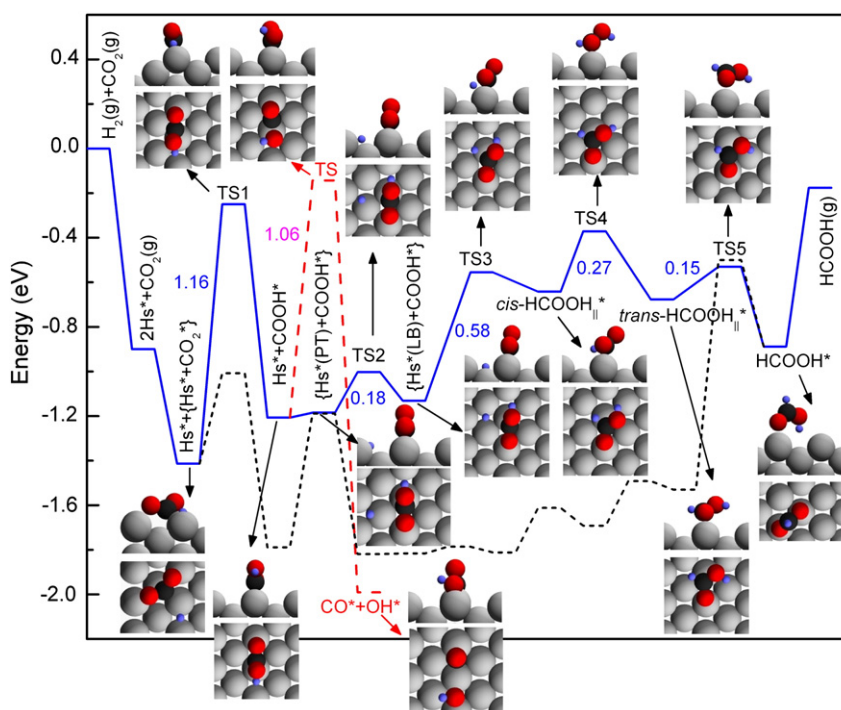


Fig. 3. Potential energy surface (PES, blue line) of CO_2 hydrogenation to carboxyl (COOH) and formic acid (HCOOH) with surface H adsorbed on Ni(110). The red dashed line gives the PES of COOH decomposition to CO and OH. For comparison, the PES of CO_2 hydrogenation via the formate route (black line in Fig. 2) is also shown with the dashed black line. The atomic structures of reactants, intermediates, transition states, and products are schematically shown in the respective insets. For detailed symbol definitions, see the caption of Fig. 2.

In summary, on Ni(110), the first hydrogenation of CO_2 to formate with surface H is characterized by a 0.41 eV energy barrier; whereas the second hydrogenation from formate to formic acid is characterized by a much larger barrier (1.03 eV). By comparison, the alternative route of CO_2 hydrogenation with surface H to formic acid via the carboxyl intermediate is characterized by a larger energy barrier (1.16 eV) for the first hydrogenation step (from CO_2 to carboxyl) and a smaller energy barrier (0.58 eV) for the second hydrogenation step (from carboxyl to formic acid). Therefore, in terms of calculated energy barriers, the formate and carboxyl routes for CO_2 hydrogenation to formic acid could be competitive. However, because formate is more stable than carboxyl by ~ 0.6 eV, one might argue that formate may be partially poisoning the surface with a substantial presence, whereas carboxyl might be responsible for turning-over the HCOOH production rates (see Fig. 3). Yet, this assessment might be quite different under various experimental conditions, and to gain further insight into which route might be dominant under certain experimental conditions of temperature, pressure, and feed composition, detailed microkinetic modeling is necessary. This task goes beyond the scope of the present study. In what follows, we focus on the study of the effect of subsurface H on CO_2 hydrogenation via the formate route.

Apparently, under the UHV conditions used in Ref.,¹⁷ the barrier for the first hydrogenation via formate intermediate could be surmounted, but the barrier for the second hydrogenation from formate to formic acid could not. To allow for the second hydrogenation step from formate to formic acid to take place, one could consider utilizing the extra energy stored in subsurface H. To explore this possibility, we discuss CO_2 hydrogenation via formate on Ni(110) with subsurface H.

3.3. CO_2 hydrogenation to formate and formic acid with subsurface H

For H absorption in the first subsurface layer of Ni(110), denoted with H_b , we found that the most stable site is the octahedral site (O_h) with a binding energy of -2.12 eV, followed by the tetrahedral site (T_d) with a binding energy of -1.98 eV. As mentioned earlier,

subsurface H could either work as a spectator by modifying the electronic structure of the surface and thus changing the reactivity of the surface, or work as a reactant to participate in the reaction directly. To explore these two possibilities, we considered H_b either as a spectator or as a reactant for CO_2 hydrogenation on Ni(110).

We first studied the role of H_b as a spectator in CO_2 hydrogenation on Ni(110). For this purpose, one H_b was pre-adsorbed in an O_h site (the preferred site for H_b), corresponding to a coverage of $1/6$ monolayer (ML). As summarized in Table 1, we found that the binding of CO_2 , HCOO, and HCOOH is slightly enhanced in the presence of H_b . To examine the role of the spectator H_b in CO_2 hydrogenation on Ni(110), we recalculated the PES shown in the black line in Fig. 2 in the presence of a $1/6$ ML H_b at an O_h site. The results are shown in Fig. 4. By comparing Figs. 2 and 4, we notice that the presence of a $1/6$ ML H_b leaves the PES practically invariant. For example, the activation energy barriers for the first and second hydrogenation steps are 0.43 and 1.03 eV in Fig. 4, as opposed to 0.41 and 1.03 eV, respectively, in Fig. 2. This suggests that, at least for the coverage regime examined, H_b as a spectator essentially has no effect on CO_2 hydrogenation to formate and formic acid on Ni(110).

We then studied the role of H_b as a reactant in CO_2 hydrogenation on Ni(110). Fig. 5 shows the entire PES of CO_2 hydrogenation to formate and formic acid with H_b as a reactant. We started with CO_2 adsorbed on Ni(110) with an H_b co-adsorbed at an O_h site, as illustrated in the corresponding structure in the inset of Fig. 5. To react with the

Table 1

Binding energy (in eV) of CO_2 , HCOO, and HCOOH on clean Ni(110), and on Ni(110) pre-adsorbed with a $1/6$ monolayer (ML) subsurface H (H_b).

Adsorbate	Site	Clean	$1/6$ ML H_b
CO_2	V-shaped	-0.47	-0.48
HCOO	LB	-3.66	-3.72
	SB	-3.69	-3.80
HCOOH	Atop	-0.71	-0.77

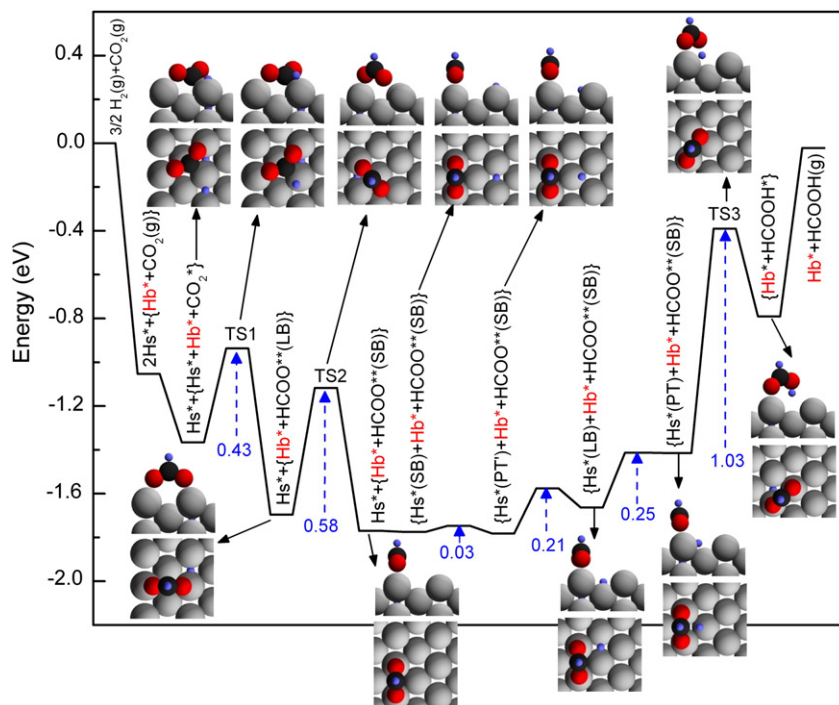


Fig. 4. Potential energy surface for CO₂ hydrogenation to formate (HCOO) and formic acid (HCOOH) with surface H on Ni(110) in the presence of 1/6 monolayer subsurface H (H_b) as a spectator. The atomic structures of reactants, intermediates, transition states, and products are schematically illustrated in the respective insets. For further symbol definitions, see the caption of Fig. 2.

adsorbed CO₂, the H_b needs to emerge onto the surface. The calculated activation energy barrier for the emergence of H_b to the Ni(110) surface (from the O_h site to the PT site right above that) is 0.14 eV, which is nearly identical to the respective barrier in the absence of co-adsorbed CO₂. At the transition state (TS1 in Fig. 5), the H atom is nearly at the same plane as the three neighboring Ni atoms. The H atom at the PT surface site then diffuses to a neighboring SB site with a negligible barrier and reacts with the co-adsorbed CO₂ to form formate at an LB site, with an activation energy barrier of 0.41 eV. The formate at the LB site

can diffuse to the slightly more stable SB site with an activation energy barrier of 0.60 eV, identical to the corresponding barrier shown in Fig. 2.

By introducing a second H_b at the O_h site underneath the HCOO adsorbed at the SB site, we studied the second hydrogenation step (formate to formic acid) using this H_b as a reactant. As shown in Fig. 5, the barrier of the emergence of this second H_b is slightly larger (by 0.05 eV) than the barrier for the emergence of the first H_b. Once the second H_b emerges onto the surface, it then reacts with the adsorbed HCOO, with an activation energy barrier of 1.03 eV. We

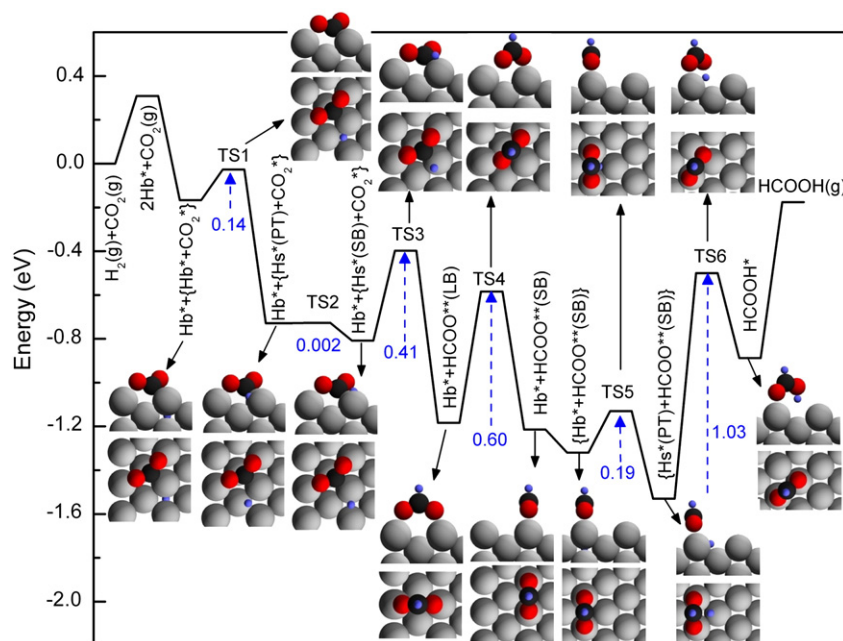


Fig. 5. Potential energy surface of CO₂ hydrogenation to formate (HCOO) and formic acid (HCOOH) on Ni(110) with 1/3 monolayer subsurface H as a reactant. The atomic structures of reactants, intermediates, transition states, and products are schematically illustrated in insets. For further symbol definitions, see the caption of Fig. 2.

note here that we were unable to find a direct pathway for H_b to react with $HCOO$, which was also true of the first H_b reaction with CO_2 towards the $HCOO$ intermediate.

Interestingly, by comparing the PES shown in Figs. 2 and 5, we notice that even though H_b as a reactant does not change the reaction barriers of the individual elementary steps, it does drastically change the thermochemistry of the reaction transforming adsorbed reactants to adsorbed products. The reaction energy of $2H_s^* + CO_2^* \rightarrow HCOOH^*$ in Fig. 2 is endothermic by 0.53 eV, while the reaction energy of $2H_b^* + CO_2^* \rightarrow HCOOH^*$ in Fig. 5 is exothermic by -0.72 eV. This change in reaction energy directly reflects the energy difference of the two H-states (H_s versus H_b , at their most stable configurations, respectively). As seen in Fig. 2, with surface H only, the transition state highest in energy along the whole reaction path (between adsorbed reactants and adsorbed products) is at TS3, i.e., the transition state of the second hydrogenation step for making formic acid. Contrary to that, with H_b as the reactant (see Fig. 5), the transition state highest in energy along the entire reaction path (between adsorbed reactants and adsorbed products) is at TS1, i.e., the transition state for the first H_b emergence onto the surface. For the case of H_b being the reactant (Fig. 5), the transition state TS6 for making the adsorbed formic acid is 0.47 eV lower in energy than TS1. This suggests that, in principle, one could use the transiently energetic subsurface H (TS1) to overcome the barrier for making $HCOOH$. Thereby, the direct hydrogenation of CO_2 by using subsurface hydrogen could be a promising avenue for catalytic $HCOOH$ synthesis. Molecular dynamics studies are currently under way for exploring the details of a direct CO_2 hydrogenation path involving emerging subsurface H, prior to H's equilibration to the Ni(110) surface.

We also considered the effect of subsurface H on CO_2 hydrogenation to formic acid via the carboxyl route. For H_b as a spectator, our calculations showed that H_b has no effect on CO_2 hydrogenation, similar to what we found for the formate route. Further, for the carboxyl route, our calculations showed that H_b as a reactant changes the thermochemistry of the reaction, transforming adsorbed reactants to adsorbed products from endothermic to exothermic, in complete analogy with our results for the formate-mediated route to $HCOOH$.

Finally, we briefly compare the energetics of CO_2 hydrogenation on Ni(110) presented here with the respective results we got on Ni(111) recently.²⁹ On Ni(111), CO_2 is only weakly physisorbed, whereas on Ni(110), CO_2 binds much more strongly (-0.47 eV) suggesting that hydrogenation reaction rates might be enhanced on (110), based on reactant surface concentration arguments alone. Further, the first surface H addition to CO_2 on Ni(111) is characterized by a 0.62 eV activation energy barrier, whereas formate formation on Ni(110) is characterized by a smaller activation energy barrier (0.41 eV). Yet, hydrogenation of formate with surface H to $HCOOH$ is energetically somewhat easier on Ni(111) than on Ni(110), with

0.83 eV and 1.03 eV activation energy barriers, respectively. On both Ni(111) and Ni(110) surfaces, H_b as a spectator species has essentially no effect on the energetics of CO_2 hydrogenation. In addition, for both Ni(111) and Ni(110), H_b is significantly less stable than H_s , and as a result, the thermochemistry of the reaction between H_b and adsorbed CO_2 to adsorbed $HCOOH$ becomes exothermic, whereas the reaction between H_s and adsorbed CO_2 to adsorbed $HCOOH$ is endothermic. Therefore, on both surfaces the reaction with transient energetic bulk H emerging to the surface might be more driven than the respective reaction with surface H.

4. Conclusions

A systematic spin-polarized, self-consistent, planewave density functional theory (DFT-PW91) study of CO_2 hydrogenation to formate, carboxyl, and formic acid on Ni(110) has been presented. Surface adsorbed hydrogen is more stable than subsurface adsorbed hydrogen by ~ 0.6 eV. The existence of subsurface H as a spectator species has practically no effect on the energetics of CO_2 hydrogenation, when the reactant is surface H. CO_2 can be hydrogenated to formate with surface H, but further hydrogenation of formate to formic acid by surface H is hindered by a larger barrier. For the carboxyl-mediated route to $HCOOH$, the first H addition to CO_2 presents a barrier much larger than the second hydrogen addition. Because of the excess energy possessed by the subsurface H, we suggest that transiently energetic subsurface H emerging onto the Ni(110) surface can lead to hydrogenation of formate to formic acid. Additional electronic-structure based dynamic calculations would be needed to elucidate the detailed reaction paths for these transformations. Our results provide useful insights into the possible role of subsurface H in CO_2 hydrogenation on Ni(110), and may have potential implications for other catalytic reactions involving bulk/subsurface hydrogen.

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