Hydrogenation of CO to Methanol on Ni(110) through Subsurface Hydrogen

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ABSTRACT: We present a combined theoretical and experimental study of CO hydrogenation on a Ni(110) surface, including studies of the role of gas-phase atomic hydrogen, surface hydrogen, and subsurface hydrogen reacting with adsorbed CO. Reaction mechanisms leading both to methane and methanol are considered. In the reaction involving surface or subsurface hydrogen, we investigate four possible pathways, using density functional theory to characterize the relative energetics of each intermediate, including the importance of further hydrogenation versus C−O bond breaking, where the latter may lead to methane production. The most energetically favorable outcome is the production of methanol along a pathway involving the sequential hydrogenation of CO to a H₂CO* intermediate, followed by a final hydrogenation to give methanol. In addition, we find that subsurface hydrogen noticeably alters reaction barriers, both passively and through the energy released by diffusion to the surface. Indeed, the effective reaction barriers are even lower than for CO methanolation on Cu(211) and Cu(111) than for Ni(110). In studies of gas-phase H atoms impinging on a CO−adsorbed Ni(110) surface, Born−Oppenheimer molecular dynamics simulations show that direct impact of H is unlikely to result in hydrogenation of CO. This means that Eley−Rideal or hot-atom mechanisms are not important; thus, thermal reactions involving subsurface hydrogen are the primary reaction mechanisms leading to methanol. Finally, we demonstrate experimentally for the first time the production of methanol and formaldehyde from CO hydrogenation on Ni(110) and confirm the role of subsurface hydrogen in the mechanism of this reaction.

1. INTRODUCTION

The hydrogenation of CO is an extremely important reaction in many contexts, and it has attracted considerable recent interest. This process can, in various conditions, produce methanol, formaldehyde, and methane, in addition to other hydrocarbons. CO hydrogenation is a vital process in industrial synthesis of synthetic hydrocarbons, which is mainly composed of CO and H₂, by hydrogenating CO to produce alkanes.5,6 Syngas itself can be produced via the dry reforming reaction, in which CO₂ and methane (or some other hydrocarbon) are the primary reactants, turning two greenhouse gases into synthetically useful chemicals.5 In this context, hydrogenation of CO is a subsequent reaction that can occur between the reactant H₂ gas and the product CO gas. Either methane or methanol can be a desirable outcome of CO hydrogenation in this scenario. Thus, the reaction of CO with H₂ is very important, both industrially and environmentally, and control of the ratio between the production of methane, methanol, and formaldehyde is of great interest.

Commonly used catalyst surfaces for CO hydrogenation include Cu, Co, and Ni. Methanol production is highly favored by Cu catalysts, as the key step in the methanation process, C−O bond breaking, is highly unfavorable.10 In contrast, Co catalysts strongly favor methane production, as barriers for methanol production are much higher than on Cu surfaces, and C−O dissociation occurs far more readily. Between these two catalysts is Ni, which occupies a middle ground.11 Previous experimental studies have shown Ni to be an active catalyst for CO methanation,10,11,12 but theoretical studies have suggested that methanol production is a strong possibility on Ni surfaces as well.12,13 While the Ni(111) surface is the most well-studied, Ni step-edges and other coordinatively unsaturated sites are significantly more reactive, and the Ni(110) surface is a fair approximation to what is present in these unsaturated sites.13,14 The most direct experimental study thus far of CO hydrogenation on Ni(110) is a recent study by Roiaz et al.,15 which

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demonstrates the presence of two intermediates of the CO methanation process present on the Ni surface.

While the hydrogenation reactions of CO and CO₂ have been studied in great detail, few theoretical studies have explicitly considered the role of subsurface hydrogen. The importance of subsurface hydrogen to the hydrogenation of hydrocarbons adsorbed onto surfaces was initially demonstrated by Johnson et al. in 1992. Subsurface hydrogen, and bulk hydrogen when it is present more than one layer below the surface, can typically be formed in a material through two mechanisms: (i) impact of individual H atoms on the surface with sufficient energy to overcome a significant barrier (roughly 1 eV on a Ni(111) surface) to entering the subsurface and (ii) collision of an inert gas atom or molecule with a H atom adsorbed on the surface with sufficient energy to pound it into the subsurface. Subsurface hydrogen atoms must overcome an energy barrier to return to the surface and undergo reaction. However, once this barrier is overcome the H atom will have a significant amount of kinetic energy (about 0.6 eV on a Ni(110) surface), greatly increasing its reactivity and helping the system to overcome further energetic barriers.

In addition to this kinetic effect, the presence of subsurface hydrogen as a spectator in a surface reaction rather than a direct participant can significantly alter the energetics of that reaction. Subsurface hydrogen has been shown in many cases to increase the adsorption energy of surface adsorbates. This occurs through both altering the electronic structure of the surface as well as distortion of the surface structure. The role of subsurface hydrogen in altering the energetics for the hydrogenation of CO₂ on Ni(110) and Ni(111) surfaces was first shown by Peng et al., who calculated reaction barriers for CO₂ hydrogenation to formic acid. These studies found very little impact of subsurface hydrogen on reaction barriers when acting as a spectator. However, when subsurface hydrogen atoms emerged to the surface as reactants, hydrogenation of CO₂ to formic acid became exothermic, while it was endothermic in the absence of subsurface hydrogen. This work was expanded recently with similar calculations which studied hydrogenation of CO₂ to give CO + H₂O with and without subsurface hydrogen on a Ni(110) surface, and it was found that even as a spectator, subsurface hydrogen alters reaction barriers enough to be considered a significant factor.

In the present work, we apply a methodology similar to our previous works, turning our focus now to hydrogenation (starting from adsorbed, subsurface, and gas-phase atomic hydrogen) of CO to give methane, methanol, and/or formaldehyde. We study the effects of subsurface hydrogen both as a participant and as a spectator to the relevant reaction steps. We also build upon the work of Faji et al., who studied reactions of CO with surface hydrogen on Ni(110). However, in our study, in addition to considering the effects of subsurface hydrogen, we explore a greater number of potential reaction steps and pathways than previously considered, and we do so using a larger unit cell. We also show results from Born–Oppenheimer molecular dynamics (BOMD) simulations of hot H atoms impinging on a CO−adsorbed Ni(110) surface. This aspect of our study is intended to assess the importance of the Eley–Rideal or hot-atom mechanisms, as might contribute to plasma-enhanced dry reforming, since plasma sources containing CH₄ are expected to yield significant amounts of gaseous atomic H. Finally, to tie our modeling to experiment, we present temperature-programmed desorption (TPD) results for formaldehyde and methanol on Ni(110) pretreated with either D atoms or D₂ molecules and then exposed to CO and with the roles of D and CO reversed.

2. METHODS

2.1. Computational Methods. All calculations in this study were performed with spin–polarized density functional theory (DFT) with periodic boundary conditions as implemented in the Vienna Ab initio Simulation Package (VASP), version 5.3.2,25 The Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional was used to model exchange and correlation interactions, while electron–ion interactions were modeled using projector-augmented wave (PAW) potentials. Structural relaxation calculations were performed using the conjugate gradient method, while transition states and reaction barriers were calculated using the climbing image nudged elastic band (CI-NEB) method.26 The CI-NEB method involves relaxing the structures of a series of images that lie along the reaction coordinate between the initial and final reaction states, which have already been relaxed to energy minima. During this relaxation, a potential is applied along the reaction coordinate, allowing the images to converge to what would normally be nonstationary states. Transition states were verified using vibrational frequency calculations.

The Ni(110) surface used in this study is a 2 × 2 × 1 unit cell with 6 Ni atoms per layer and 7 layers. The bottom three layers were constrained to maintain the bulk Ni structure, while the top 4 layers were allowed to relax. The unit cell also contained about 12 Å of vacuum between the uppermost Ni layer and the upper boundary (in the positive z direction) to avoid electronic interactions between vertically neighboring cells. A 4 × 3 × 1 Monkhorst–Pack mesh was used for k-sampling of the Brillouin zone.

In our studies of subsurface atomic hydrogen, which we denote H₂ₗ, these atoms are modeled as a monolayer of atoms on octahedral (O₆) sites just below the surface, as our previous work has shown that H₂ₗ is most stable on O₆ sites.22 A full monolayer consists of six H₂ₗ atoms, as there are six O₆ sites available just below the surface of Ni(110) in the 2 × 3 unit cell used here.

The same system and level of theory were then used for BOMD simulations of hydrogen impinging on CO-adsorbed on a Ni(110) surface. In these simulations the coverage of CO is a half monolayer (three CO molecules adsorbed on the surface on which there are six metal atoms). The kinetic energy of the impinging H was set to 1473 K to mimic the condition in present TPD experiments and the rest of the system was set to 100 K. In total, 100 trajectories were run with the initial H atom randomly distributed in a unit cell that is 4 Å above the CO. The BOMD simulations were performed in a constant energy and volume (NVE) ensemble with a 1 fs time step. All trajectories are 2.5 ps in length, after which the hydrogen atom is mostly thermalized on the surface.

2.2. Experimental Methods. All experiments were performed in a three-level, stainless-steel ultrahigh vacuum (UHV) chamber (2 × 10⁻¹⁰ Torr base pressure) equipped with Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) capabilities, as described previously. AES was performed with a PHI 15–255G double-pass CMA. LEED was performed with a PHI 15–120 LEED optics. TPD experiments were performed with the sample in line-of-sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer with the shield nozzle located 1 mm from the sample. The heating rate was 3 K/s.

The Ni (110) crystal (8 mm square, ±0.5° orientation) was cleaned using 1.5 keV Ar⁺ ion sputtering and annealing cycles at 1100 K. Additional oxygen treatments at P(O₂) = 4 × 10⁻⁸ Torr with the sample at 1000 K were used to eliminate residual carbon. Hydrogen treatments at P(H₂) = 4 × 10⁻⁸ Torr with the sample at 1000 K were used to eliminate residual oxygen. The surface order and periodicity was verified with LEED, and the surface cleanliness was checked with AES. Surface cleanliness was also evaluated with the position and shape of the D₂ desorption peaks in TPD, which are sensitive to surface contamination.
D atoms were produced in a resistively heated, U-shaped Pt tube, similar to a design described by Engel and Rieder.25 The temperature of the Pt tube source was monitored by an optical pyrometer (OS 3708) and was kept at 1473 K. The deuterium gas (Praxair, 99.999%) was introduced into the Pt dissociation tube via a leak valve after passing through a liquid-nitrogen-cooled trap. CO (Praxair, 99.9%) was dosed through backfilling the chamber. Surface coverages θ are given in monolayers (ML), where 1 ML corresponds to the surface Ni atom density of Ni(110) (1.14 × 10^15 atoms/cm^2). Deuterium coverage was determined using TPD. We assume surface saturation of 1.5 ML when produced from dissociative adsorption of D_2 at 100 K.34

3. RESULTS

We first consider reaction pathways for CO hydrogenation with surface adsorbed hydrogen, including calculations with and without subsurface hydrogen (H_{sub}) on the Ni(110) surface. Subsequently, we present BOMD calculations of gas-phase atomic hydrogen with CO/Ni(110), and then, we consider the experimental results. Note that surface adsorbed atoms and molecules are denoted by *, as in H* or CO*, to distinguish them from gas-phase species (H and CO). We will not use the * notation when referring to species that are fragments of an adsorbed molecule (such as the O atom in CO*).

3.1. Adsorption Energies. The adsorption energies of CO*, H*, and the various intermediates along the pathways discussed in this study are shown in Table 1. The preferred binding site of CO* on a Ni(110) is found, both with and without subsurface hydrogen, to be the short-bridge site. A detailed analysis of five possible binding sites of CO* is presented in section S1 of Supporting Information. In addition, we have previously shown that the most stable binding site for a hydrogen atom, again both with and without subsurface hydrogen, is the pseudo-three-fold site.

Notably, we find that the presence of subsurface hydrogen increases (as in, makes more negative) the adsorption energy in all cases. This passive effect is in agreement with our previous work where we considered species important in the H + CO reaction.21 The presence of H_{sub} alters the electronic structure of the metal surface through shifting of the d-band, leading to stabilization of all of the adsorbates considered here. However, the fractional stabilization (E%), defined as E% = (E_{ads,sub} - E_{ads})/E_{ads} is not uniform, ranging from ~5% for HCOH* to ~21% for H_2CO* (Table 1). One important factor here may be distortion of the Ni(110) surface by H_{sub} atoms, which could alter adsorption energy depending on the shape and binding behavior of the adsorbate.

It should be noted that other than CO* none of the reported adsorption energies with subsurface hydrogen are calculated with a full monolayer of six H_{sub} atoms. Rather, as the reaction pathways proceed, H_{sub} atoms are taken out of the subsurface monolayer and participate in reactions on the surface. This simplifies the energetic analysis (as the number of each kind of atom stays constant), but it does cause the H_{sub} monolayer to become depopulated as the reaction progresses. While this does decrease the impact of H_{sub} on the system as a whole, in all cases there remains at least one H_{sub} atom directly below the adsorbate. Previous work has shown the H_{sub} atoms just below an adsorbate to have the dominant impact on adsorption energy.21

3.2. Reaction Pathways. The various reaction pathways in this study can be thought of as pathways toward the production of methanol via hydrogenation of C and O in which each intermediate can also undergo C−O bond breaking. If the C−O bond is broken, then the resulting C- and O-based species can undergo hydrogenation to give methane and water. In accordance with this picture, we consider four main pathways to methanol production:

\begin{align*}
\text{CO}^* & \rightarrow \text{HCO}^* \rightarrow \text{H}_2\text{CO}^* \rightarrow \text{H}_3\text{CO}^* \rightarrow \text{H}_4\text{CO}^* \\
\text{CO}^* & \rightarrow \text{HCO}^* \rightarrow \text{H}_2\text{CO}^* \rightarrow \text{H}_3\text{CO}^* \rightarrow \text{H}_4\text{CO}^* \\
\text{CO}^* & \rightarrow \text{HCO}^* \rightarrow \text{HCOH}^* \rightarrow \text{H}_2\text{COH}^* \rightarrow \text{H}_3\text{COH}^* \\
\text{CO}^* & \rightarrow \text{COH}^* \rightarrow \text{HCOH}^* \rightarrow \text{H}_2\text{COH}^* \rightarrow \text{H}_3\text{COH}^*
\end{align*}

These pathways share some steps with one another, but they differ in the ordering of C− and O-hydrogenation steps. We consider methane production in the context of these four pathways, where each intermediate can either undergo further hydrogenation toward methanol production or C−O bond breaking resulting in methane production. It should be noted that the hydrogenation reactions of C and O to CH_4 and H_2O on a Ni(110) surface have been previously studied.22 As these reactions themselves are not of particular interest, we do not detail them in this study. In our model we assume that C−O bond breaking leads to methane formation.

To compare the energetics of hydrogenation and C−O bond breaking for each intermediate in each pathway, both with and without subsurface hydrogen, presents several significant challenges in presentation, requiring a number of simplifications and adjustments. The most significant of these is in the case of multibarrier steps, for which we show only the highest-energy barrier. Furthermore, in our calculations involving only H*, each reactant H* is added to the surface just before it reacts, i.e., in all four pathway calculations involving H*, only one H* is bound on surface at a time. The simplifications made to the pathways shown in this paper are explained in detail in section S2 of the Supporting Information.

We will discuss pathway 1 (the most favorable path) here, and the other three pathways are presented in section S3 of the Supporting Information. For all pathways, the relative energetics of each intermediate for hydrogenation or C−O bond breaking is considered, both with and without subsurface hydrogen. As a convenient reference, the reaction barriers and energies for each reaction step in pathway 1 are also shown in Table 2.

Table 1. Adsorption Energies for the Intermediates along the Reaction Pathways on Bare Ni(110) (E_{ads}) and for Ni(110) with 1 ML of H_{sub} (E_{ads,sub})

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>E_{ads} (eV)</th>
<th>E_{ads,sub} (eV)</th>
<th>E%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>−1.91</td>
<td>−2.12</td>
<td>11.0%</td>
</tr>
<tr>
<td>HCO</td>
<td>−2.60</td>
<td>−2.91</td>
<td>11.9%</td>
</tr>
<tr>
<td>COH</td>
<td>−4.01</td>
<td>−4.27</td>
<td>6.5%</td>
</tr>
<tr>
<td>HCOH (trans)</td>
<td>−3.25</td>
<td>−3.42</td>
<td>5.2%</td>
</tr>
<tr>
<td>HCOH (cis)</td>
<td>−3.51</td>
<td>−3.69</td>
<td>5.1%</td>
</tr>
<tr>
<td>H_2CO</td>
<td>−1.25</td>
<td>−1.51</td>
<td>20.8%</td>
</tr>
<tr>
<td>H_2CO</td>
<td>−2.56</td>
<td>−2.72</td>
<td>6.3%</td>
</tr>
<tr>
<td>H_2COH</td>
<td>−1.68</td>
<td>−1.83</td>
<td>8.9%</td>
</tr>
<tr>
<td>H_2COH</td>
<td>−0.45</td>
<td>−0.48</td>
<td>6.7%</td>
</tr>
</tbody>
</table>

*E% is the fractional stabilization (E% = (E_{ads,sub} − E_{ads})/E_{ads}) caused by the H_{sub}.
**3.2.1. Pathway 1.** The relative energetics of the surface and subsurface cases for pathway 1 are shown in Figures 1 and 2. We first note that in both the surface and subsurface cases at each step the barrier to hydrogenation is always lower than the barrier to C–O bond breaking which indicates that pathway 1 favors methanol formation. We also see that formaldehyde H₃CO* is a possible intermediate along this pathway. The adsorption energy of formaldehyde on the Ni(110) surface (~1.25 eV), given in Table 1, is lower than the adsorption energies of all the intermediates listed there, and it is not significantly higher than the barrier to either C-hydrogenation to give H₃CO* (0.65 eV) or C–O bond breaking (0.91 eV). This suggests that formaldehyde could be a gaseous product of pathway 1.

The first possible step in pathway 1 could either be C-hydrogenation of CO* to give HCO* (Figure 3a) or C–O bond breaking of CO* (Figure 3e) to give C + O. Hydrogenation of CO* to HCO* through TS1.1 has a barrier of 1.08 eV without H_{sub} (Figure 1) and 0.93 eV with H_{sub} (Figure 2). In this step, CO* begins in a short-bridge site, while H* is in a pseudo-three-fold site. As H* approaches CO*, CO* shifts away from H* into a pseudo-three-fold site, with O tilted further away from H*. The reverse of this reaction step is thermodynamically favorable and has a very low barrier (0.14 and 0.28 eV with and without H_{sub} respectively). This indicates that HCO* would be short-lived. C–O bond breaking of CO* through TS1.1′ has a barrier of 1.72 eV both with and without H_{sub}, although the total energy of the step is 0.87 eV without H_{sub} but only 0.55 eV with H_{sub}, presumably due to H_{sub} stabilizing C* + O* to a greater extent than it stabilizes CO*.

Overall in this step, C-hydrogenation of CO* is favored over C–O bond breaking. The next possible steps in pathway 1 are C-hydrogenation of HCO* to H₂CO* through TS1.2 (Figure 3b) and C–O cleavage of HCO* to give CH* + O* through TS1.2′ (Figure 3f). C-hydrogenation of HCO* has a barrier of 0.53 eV without H_{sub} and 0.62 eV with H_{sub}. The other possibility, C–O cleavage to give CH* + O*, has a barrier of 0.94 eV without H_{sub} and 1.16 eV with H_{sub}. Again, both with and without H_{sub} further hydrogenation along pathway 1 is favored over C–O cleavage. After this, H₂CO* can undergo either C-hydrogenation to H₃CO* through TS1.3 (Figure 3c) or C–O cleavage through TS1.3′ to CH₂* + O* (Figure 3g). The C-hydrogenation of H₃CO* has a 0.65 eV barrier without H_{sub} and a 0.61 eV barrier with H_{sub}. The C–O bond breaking of H₂CO* through TS1.3′ has a barrier of 0.89 eV without H_{sub} and 0.90 eV with H_{sub}. Yet again, hydrogenation in this step is favored over C–O bond breaking. Finally, H₃CO* can undergo O-hydrogenation to H₃COH* through TS1.4 (Figure 3d) or C–O bond breaking through TS1.4′ to give CH₃* + O* (Figure 3h). O-hydrogenation of H₃CO* has a 1.04 eV barrier without H_{sub} and a 0.93 eV barrier with H_{sub}. The C–O bond breaking of H₂CO* has a barrier of 1.91 without H_{sub} and 1.56 eV with H_{sub}. As the relative energetics of these two possible reaction steps show, the H₃CO* intermediate is very likely to further react to produce methane rather than methanol. Overall, pathway 1 strongly favors methanol production over methane production, as well as the production of formaldehyde depending on the reaction conditions, as also reported for the reaction of CH₃OH on Zn/Pt(111) surfaces.⁴⁴

**3.2.2. Pathways 2–4.** The energy diagrams of pathways 2–4 are shown in Figures S4–S9, and details of the analysis are presented in section S3 of the Supporting Information. Overall, pathway 1 is at every turn the most favorable pathway. Ultimately, both with and without subsurface hydrogen, our results suggest that hydrogenation of CO* on a Ni(110) surface is most likely to yield methanol, as pathway 1 toward methanol is at each step the most favorable pathway. However, if they are accessed, then pathways 2–4 are each at least slightly more likely to yield methane than they are methanol. Of

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**Table 2. Activation (E_{act}) and Reaction (E_{react}) Energies for Each Reaction Step of Pathway 1 Both with and without Subsurface Hydrogen**

<table>
<thead>
<tr>
<th>reaction</th>
<th>E_{act} (eV)</th>
<th>E_{react} (eV)</th>
<th>E_{act,sub} (eV)</th>
<th>E_{react,sub} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO* → C* + O*</td>
<td>1.72</td>
<td>0.87</td>
<td>1.72</td>
<td>0.55</td>
</tr>
<tr>
<td>CO* + H* → HCO*</td>
<td>1.08</td>
<td>0.80</td>
<td>0.93</td>
<td>0.79</td>
</tr>
<tr>
<td>HCO* → CH* + O*</td>
<td>0.94</td>
<td>−0.23</td>
<td>1.16</td>
<td>−0.13</td>
</tr>
<tr>
<td>HCO* + H* → H₂CO*</td>
<td>0.53</td>
<td>0.13</td>
<td>0.62</td>
<td>0.09</td>
</tr>
<tr>
<td>H₂CO* → CH₂* + O*</td>
<td>0.89</td>
<td>0.25</td>
<td>0.90</td>
<td>0.31</td>
</tr>
<tr>
<td>H₂CO* + H* → H₃COH*</td>
<td>0.65</td>
<td>−0.13</td>
<td>0.61</td>
<td>−0.14</td>
</tr>
<tr>
<td>H₂CO* → CH₂* + O*</td>
<td>1.91</td>
<td>−0.16</td>
<td>1.56</td>
<td>−0.18</td>
</tr>
<tr>
<td>H₂CO* + H* → H₃COH*</td>
<td>1.04</td>
<td>0.49</td>
<td>0.93</td>
<td>0.48</td>
</tr>
</tbody>
</table>

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**Figure 1.** Energy diagram for pathway 1 when subsurface hydrogen is not present. Each dashed line represents an offshoot of pathway 1 in which the C–O bond breaks, leading, eventually, to the formation of methane and water. The colors are used to make the offshoots more visually distinguishable from one another. An asterisk (*) denotes an adsorbed species.
pathways 2–4, the most energetically favorable is pathway 3. It diverges from pathways 1 and 2 at HCO*, where HCOH* is produced rather than H2CO*.

3.3. BOMD Simulations of H Impinging on CO-Adsorbed Ni(110). In order to investigate CO hydrogenation from gaseous atomic hydrogen, including the role of Eley–Rideal and hot-atom reaction mechanisms, we ran BOMD simulations of H impinging on CO-adsorbed Ni(110). The kinetic energy (temperature) of the impinging H was set to 1200 °C to mimic the conditions of the TPD experiments described in the following subsection. Of the 100 trajectories that were studied, 42 led to reflection of the hydrogen atoms back to vacuum (denoted “Reflected H” in Figure 4), 41 involved thermalization of hydrogen on the surface (“Surface H” in Figure 4), 12 resulted in subsurface hydrogen followed by diffusion back to the surface (“Subsurface H” in Figure 4), and 4 resulted in thermalized bulk hydrogen (“Bulk H” in Figure 4).

Two trajectories followed a hot-atom mechanism, forming COH* but only for 0.25 ps and then dissociated back to CO* +

Figure 2. Energy diagram for pathway 1 when subsurface hydrogen is initially present as a full (6-atom) monolayer and emerges to the surface before becoming a reactant.

Figure 3. Initial, transition, and final states for each of the hydrogenation steps possible for CO and its intermediates along pathway 1 to H3COH, specifically, hydrogenation of (a) CO to HCO, (b) HCO to H2CO, (c) H2CO to H2CO, and (d) H2CO to H2CO. Initial, transition, and final states for C–O bond breaking reactions for each of the intermediates along pathway 1. Specifically: (e) CO to C + O, (f) HCO to CH + O, (g) H2CO to CH2 + O, and (h) H3CO to CH3 + O. Only reactions in the presence of Hsub are shown, as there are no substantive visual differences between the surface and subsurface cases.

Figure 4. The z-axis of impinging hydrogen atom along the BOMD trajectories.
H* (*COH* intermediate in Figure 4), as expected given that the barrier from CO* + H* to COH* is 1.40 eV, while the barrier of the reverse reaction is only 0.25 eV (see TS4.1 of Figure S8). A few trajectories were identified as possibly forming HCO*; however, they also do not form stabilized HCO*, as the barrier from CO* + H* to HCO* is 1.10 eV, but the barrier of the reverse reaction is only 0.28 eV (see TS1.1 of Figure 1). As seen in Figure 3a, HCO* is adsorbed on the Ni surface with both C and O bonded to surface Ni atoms, and with H tilted to the C−O bond. Thus, the z-axis of the hydrogen in HCO* is similar to that for surface H, so it is difficult to distinguish it from “surface H” in Figure 4. Hence, our simulation results show that Eley–Rideal and hot-atom mechanisms are unlikely to play an significant role in the initial steps of hydrogenation of CO* to methanol. This is in contrast to the situation for H + CO2* on Ni(110) where the Eley–Rideal and hot-atom mechanisms are dominant.36

3.4. TPD Measurements. To confirm our theoretical results regarding the role of surface hydrogen, subsurface hydrogen, and incident gas-phase atomic hydrogen in the reaction mechanisms associated with CO hydrogenation on Ni(110) surface, we have carried out three sets of TPD experiments. A 4.8 L exposure of CO on clean Ni(110) at 90 K results in surface saturation coverage of 1 ML, and accordingly, it was the CO exposure used in all following experiments.

We first probed the interaction between CO and surface D. Surface D was produced by the dissociative adsorption of D2, which does not produce subsurface D on Ni(110) when dosed at 90 K. After saturating the surface with adsorbed D, it was then exposed to CO. TPD results, blue curves in Figure 5a,b, indicate that surface D does not effectively hydrogenate CO to CD2O or CD3OD, in accordance with the literature.97 and our calculations in pathway 1 that the formation of H3COH is much less thermodynamically favorable when the reactants are surface H atoms. However, different behavior was seen between subsurface D and adsorbed D. After exposing D atoms on Ni(110) to produce subsurface D and then dosing CO, both CD2O and CD3OD desorbed from Ni(110), as indicated by the black curves in Figure 5a,b. The desorption of CD2O and CD3OD occurs at the temperature at which subsurface D desorbs, suggesting that subsurface D rather than surface D is the reactive species in the hydrogenation of CO.

To investigate the role of Eley–Rideal or hot-atom mechanisms in the hydrogenation of CO, the CO saturated surface was exposed to incident gas-phase atomic D. As shown in the red curves in Figure 5a,b, negligible amounts of CD2O and CD3OD desorbed. This, coupled with CO desorption in the TPD experiment, is consistent with the BOMD results that an Eley–Rideal or hot-atom mechanism does not contribute significantly in the hydrogenation of CO. In all three sets of the TPD measurements, no methane was detected, as the formation of methane from CO-hydrogenation on Ni(110) involves higher barriers than for methanol formation.

To summarize, the TPD experiments confirm our DFT predictions in two ways. First, the experiments demonstrate the production of methanol and formaldehyde from CO hydrogenation on Ni(110), instead of the formation of methane. Second, the different outcomes among the three sets of TPD experiments prove our hypothesis regarding the role of subsurface hydrogen in the mechanism of this reaction, based on our DFT calculations and BOMD simulations. Hence, the combination of theoretical and experimental studies allows us to reveal details of the reaction mechanisms for CO hydrogenation on a Ni(110) surface.

4. DISCUSSION

The total energy change for the formation of H2CO* from CO* and four H* atoms is 1.18 eV (Figure 1) when those H atoms begin adsorbed to the Ni(110) surface, and −0.54 eV (Figure 2) when those H atoms begin as Hsub atoms (here assuming that two additional Hsub atoms remain as passive participants). If H2CO* then desorbs from the surface into the gas-phase, these energy changes are 1.63 and −0.06 eV, respectively. Comparison of the pathways with and without Hsub clearly shows that, regardless of which pathway is followed, the formation of H2CO* is far more thermodynamically favorable when the reactant H atoms are Hsub. This is because each time a Hsub atom emerges to the surface before reacting the energy of the system is lowered by roughly 0.6 eV, which has been noted in previous studies.21–25 The most favorable pathway, with and without subsurface hydrogen, was found to be pathway 1, in which CO undergoes sequential hydrogenation of C to give H2CO* (passing through a formaldehyde intermediate), followed by hydrogenation of O to give methanol. The other pathways that were studied all appeared likely to give either a roughly even mix of methane and methanol or slightly more methane than methanol. Our calculations indicate that formaldehyde would be formed from desorption of the H2CO* intermediate though methanol formation from H2CO* is more energetically favorable than dissociation.

We find that our results are consistent with those of the recent experimental study by Roiaz et al.,15 if not with its conclusions. Employing infrared–visible sum frequency gen-
eration (IR–vis SFG) spectroscopy as well as X-ray photoelectron spectroscopy (XPS), Roiai et al. investigated the surface-adsorbed species during the CO hydrogenation reaction and reported the presence of a measurable amount of carbon, suggesting CO dissociation and therefore CO methanation. However, our results suggest that while CO dissociation is certainly a possibility methanol production should be more favorable and that the most notable intermediates of the methanol production pathway such as formaldehyde have far lower adsorption energies to Ni(110) than do C atoms. Thus, we suggest that methanol and formaldehyde in fact are significant products of this reaction but may not be measured by the techniques employed by the authors.

In comparison with previous results for other catalyst surfaces for CO hydrogenation, we find that bare Ni(110) occupies a middle ground between Cu and Co(111)/Ni(111) in terms of the favored production of methanol or methane. Both Cu(111) and Cu(211) have a weak binding ability and a very high C–O bond breaking energy; hence, they prefer methanolation (via pathway 1) to methanation. In contrast, Co(111) and Ni(111) show good catalytic performance to methane due to the low dissociation barriers from HCO* to CH* and H2CO* to CH2* as well as high barriers from H2CO* to H2COH*. For Ni(110), as shown in Table 2, hydrogenation is always more favorable than dissociation along pathway 1, which indicates a preference for methanol synthesis over methanation. Meanwhile, the ability of Ni(110) to bind these species is higher than that of Cu(111)/Cu(211). As shown in Table S4, the binding energies of CO*, HCO*, H2CO*, and H2CO* are all stronger than the corresponding C–O bond breaking energies. Hence, on Ni(110) the energies follow the order C–O hydrogenation < C–O dissociation < desorption (for each intermediate), while on Cu(111) the order is not monotonic among these steps. Furthermore, considering the methanation process through pathway 1, Co(111) and Ni(111) are energetically much less favorable for hydrogenation of CO* to H2COH* than Cu surfaces. Bare Ni(110) again locates the middle ground between Cu and Co(111)/Ni(111) surface, as presented in Figure 6, in which the energies are relative to the energy of CO* + 4H* adsorbed on each surface.

Subsurface hydrogen atoms generally increase the adsorption energies of surface adsorbates through significantly altering the average charge of the surface Ni atoms31 and subsequently modifying the electronic structure of the surface Ni atoms. Also, they affect the reaction barriers by raising surface Ni atoms by ~0.2 Å on average. Note that the upward displacement of the Ni atoms raises the energy of the Ni d bands which favors bonding with the surface species and reduces reaction barriers.54,45 Furthermore, the emergence of a subsurface hydrogen atom to the surface causes the electronic energy of the system to be lowered by roughly 0.6 eV, so the overall effective barriers for Ni(110) + Hsub are much lower than those for bare Ni(110). In particular, the barriers in each elementary step for Ni(110) + Hsub are even lower than those for bare Cu(111) and Cu(211), as shown in Figure 6. Note that the pathway on Cu(211) was calculated using the PBE functional combined with the TSsurf dispersion corrections38 and pathways for the other surfaces were obtained using just PBE. Energies calculated from these two functionals are generally different by a few tenths of an eV, so this should not affect the overall energetic trends in Figure 6. Methanol is produced in industry from syngas mainly through commercial Cu/ZnO/Al2O3 catalysts. Although the active sites of the catalysts are still under debate,9,39 Cu(211) and Cu(111) are generally considered as the surfaces that are energetically favorable for the reaction. Here, by combined with our TPD measurements and the reaction pathway calculations, we show that the Ni(110) with subsurface hydrogen is an alternative approach for the methanol production.

5. CONCLUSIONS

We explored the role of gas-phase atomic hydrogen, surface hydrogen, and subsurface hydrogen on the mechanisms of CO hydrogenation to methanol on a Ni(110) surface through a combined theoretical and experimental study. We first calculated all possible reaction pathways for the hydrogenation of CO on Ni(110) to yield methanol, with and without subsurface hydrogen. For the various intermediates along those pathways, we also investigated the relative energetics of C–O bond breaking, which would lead to methane rather than methanol production. The most favorable pathway is the production of methanol along a pathway involving the sequential hydrogenation of CO to an H2CO* intermediate, followed by a final hydrogenation to give methanol. We also found that while subsurface hydrogen uniformly increased adsorption energies of the adsorbates the degree to which they were increased was inconsistent leading to a mixed effect on reaction barriers and reaction energies. However, we did find several reaction steps for which the difference in barrier height between the surface and subsurface cases was nearly as high as 0.4 eV, which suggests that the impact of subsurface hydrogen could be large. In addition, our BOMD simulation results suggest that translationally hot H atoms impinging on the CO-adsorbed Ni(110) surface are unlikely to overcome the reaction barriers associated with the initial hydrogenation steps of CO through Eley–Rideal or hot-atom mechanisms.

Finally, our experimental measurements confirm the production of both methanol and formaldehyde from CO hydrogenation on a Ni(110) surface through the subsurface hydrogen. Overall, our theoretical and experimental results indicate that the formation of formaldehyde and methanol is most likely due to some of the H atoms going into subsurface upon exposure to the CO covered surface through heating the system, rather than via the direct reaction from impinging hydrogen through an Eley–Rideal or hot-atom mechanism. Our study provides useful insight into the mechanisms by

Figure 6. Energy diagrams for pathway 1 on several metal surfaces. The energies are relative to the energy of CO* + 4H* adsorbed on surfaces, except the Ni(110) + Hsub case, where the energies are relative to CO* + 6Hsub. The curves for Cu(111), Co(111), and Ni(111) are adapted from ref 9 and Cu(211) is from ref 38.
which formaldehyde and methanol can be produced from CO and hydrogen on a Ni(110) surface.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b09914.

Adsortion energies of CO, details of the simplifications in pathways, and descriptions of pathways 2–4 (PDF)

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