

DFT Study of Formaldehyde and Methanol Synthesis from CO and H₂ on Ni(111)[†]

Ioannis N. Remediakis,* Frank Abild-Pedersen, and Jens K. Nørskov

Center for Atomic-scale Materials Physics, Department of Physics, Building 307,
Technical University of Denmark, 2800 Lyngby, Denmark

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We present a density-functional-theory study of formaldehyde and methanol synthesis from CO and H₂ on a Ni catalyst. We investigate the intermediate products of the reaction and calculate the reaction enthalpy and energy barrier for each elementary reaction, taking into account several different adsorption geometries and the presence of isomers of the intermediate products. Hydrogenation of CO is favored over desorption or dissociation of CO on flat Ni(111), to form the formyl radical (HCO) or its isomer, COH. Subsequent hydrogenation leads to formaldehyde (CH₂O), methoxy (CH₃O), and, finally, methanol (CH₃OH). The overall reaction barrier for formaldehyde and methanol formation is 2.0 eV.

1. Introduction

Syntheses of fuels, such as methanol, from steam reforming products, are processes of the utmost importance. Methanol is widely used in various chemical synthesis and for hydrogen storage and transportation. It can be liquefied under reasonable conditions and is therefore much easier to transport to points where it can be utilized than natural gas. Understanding the synthesis of methanol is crucial both for the fuel industry, as well as for the basic sciences. CO hydrogenation, in particular, is considered one of the most important reactions in heterogeneous catalysis, as it is the first, and perhaps the most important step in Fischer–Tropsch synthesis.¹ In addition to the practical issues of methanol synthesis, the reaction of CO with transition metal surfaces is of fundamental interest to catalytic chemistry, and it has been the subject of extensive theoretical modeling.^{2–4}

Methanol is typically synthesized with the aid of a Cu/ZnO/Al₂O₃ catalyst from syngas, which is a mixture of CO, CO₂, and H₂.^{5–7} Through detailed experiments, it has been shown that CO does not participate in the methanol synthesis on Cu. Also the presence of CO has no influence on the rate of methanol formation from CO₂ and H₂, implying that direct hydrogenation of CO is impossible using Cu catalysts.⁸ On the other hand, CO can be hydrogenated on Pd catalysts.^{9,10} Pd-based catalysts have been reported to be more effective than Cu-based ones for methanol synthesis.¹¹ Cu catalysts, however, are preferred instead of the ones based on Pd because of their lower cost. Recently, much research has been focused on the decomposition of methanol, because of its importance in the fuel cell industry.^{12–14}

In this work we propose an alternative method in the production of formaldehyde and methanol from CO and H₂, using a Ni catalyst. Ni has been known as a very active methanation catalyst, able to dissociate CO and subsequently form methane.^{15–18} On the basis of DFT calculations, it has been found that step sites are much more active than terrace sites for dissociating CO. In ref 3, it has been found that the energy barrier for CO dissociation on a step site is 1 eV lower than the energy barrier for CO dissociation on a terrace site.

The calculated barrier for CO dissociation at a step edge was about 2 eV in ref 3. This barrier is expected to be lower at higher CO coverage and can be easily overcome at the high temperature and pressure that are used in industrial reactors. The higher reactivity of step sites compared to terrace sites is seen in general on most transition metal surfaces.^{19,20} This indicates that the presence of steps on the surface will alter the proposed mechanism drastically. However, recent experiments and more detailed calculations of the present authors reveal that (a) CO dissociates *only* on step-edge sites of Ni and (b) step edge sites can be completely blocked, e.g., by depositing Ag on Ni(111). Ag atoms will be adsorbed mostly at step edges, making CO adsorption and dissociation at steps extremely unfavorable. Step-blocking elements have a strong preference toward bonding on step edges, as compared to terraces; as shown experimentally, such blocking of steps is efficient even at high temperatures. These results will be presented in a separate article.²¹ This finding will open up new possibilities for the production of alcohols using Ni-based catalysts. As we will show below, CO hydrogenation is favored on Ni(111) over desorption and dissociation of CO. It is therefore possible, in principle, to continue this hydrogenation until formaldehyde and, finally, methanol is reached.

In this paper, we propose a mechanism for methanol synthesis from CO and H₂ on a flat terrace of the Ni(111) surface, based on quantum mechanical simulations. The paper is organized as follows: in section 2, we review the method and the numerical parameters used in the calculations; in section 3, we discuss the adsorption energies of CO, H and all possible products in their reaction on Ni(111); in section 4, we describe the intermediate products of the methanol synthesis, their stability on the Ni(111) surface, and the energy barriers associated with their formation; finally, in section 5, we present our prediction for the overall reaction barrier and discuss possible implementations.

2. Method

The calculations were carried out using self-consistent density functional theory (DFT). The DACAPO package^{22,23} was employed.

The ionic cores and their interaction with valence electrons are described by ultra-soft pseudopotentials.²⁴ Exchange and

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* Corresponding author. E-mail: remed@fysik.dtu.dk.

TABLE 1: Energies of Adsorbed CO, H and Possible Products of Their Reaction on Ni(111)^a

molecules	energy (eV)
CO(g) + $\frac{1}{2}$ H ₂ (g)	0.00
CO(g) + H*	-0.39
CO* + $\frac{1}{2}$ H ₂ (g)	-1.56
CO* + H*	-1.95
C* + OH*	-0.17
C* + O* + H*	-0.40
HCO*	-0.77
CH* + O*	-0.97
COH*	-1.05

^a Key: * denotes adsorbed species; (g) denotes gas-phase species. Energies are relative to gas-phase CO and $\frac{1}{2}$ H₂.

correlation effects are taken into account via the generalized gradient approximation (GGA) and the revised Perdew–Burke–Ernzerhof (RPBE) functional.²⁵ The wave function was expanded in a plane-wave basis with a kinetic energy cutoff of 25 Ry. The valence electron density is obtained by self-consistent iterative diagonalization of the Hamiltonian,²⁶ with Pulay mixing of the output and input densities. Occupation of the one-electron states was calculated using a temperature of $k_B T = 0.2$ eV; all energies have been extrapolated to $T = 0$. The ionic degrees of freedom were relaxed using a conjugate-gradient minimization, until the maximum force component was smaller than 0.05 eV/Å. We considered spin-polarized electrons, to account for the magnetic moment of Ni.

We used the periodic slab approximation. Our unit cell contained three layers of Ni parallel to the (111) plane, separated by about 11 Å of vacuum. We used a (2×2) supercell. The topmost Ni atoms and all adsorbates were allowed to relax fully. The Brillouin zone of the system was modeled by nine special \mathbf{k} -points of the Chadi–Cohen type.²⁷

For the isolated atoms, radicals and molecules (CO, H, H₂, HCO, CH₂O, CH₃O, and CH₃OH), we used a large simple cubic supercell with a lattice constant of 8 Å, and Γ -point only to model the Brillouin zone. The other computational parameters were identical to those used for the slab calculations.

The location of transition states and the calculation of energy barriers was performed using the nudged elastic band method.²⁸ We used seven or nine configurations along the path. The path was relaxed, until the change in energy barrier was smaller than 0.003 eV.

3. Products of CO and H Reactions on Ni(111)

Table 1 summarizes the energies of adsorbed CO, H, and all possible products of their reaction on Ni(111), relative to gas-phase CO and H₂. Adsorbed COH is the most stable species that can be produced from one CO and one H atom on Ni(111). It is by far more stable than the products of CO dissociation, C + O + H or C + OH. The energies of C + O + H and C + OH are equal or higher than the energy of desorbed CO, meaning that CO would prefer to desorb rather than dissociate on a flat terrace of Ni(111), as, in addition, the energy barrier for the dissociation of CO on Ni(111) is approximately 3 eV³, about 1.5 eV higher than the energy barrier for the formation of COH or HCO. Therefore, it is impossible for CO to dissociate directly on flat terraces of Ni(111) even at relatively high temperatures.

A similar energy barrier has to be overcome in order for CH and O to be formed, as this process necessarily involves breaking of the strong C–O bond. Formation of CH and O on the flat Ni(111) is a complex process. In the minimum energy path, formyl (H–C–O) is first formed. This step is endothermic by

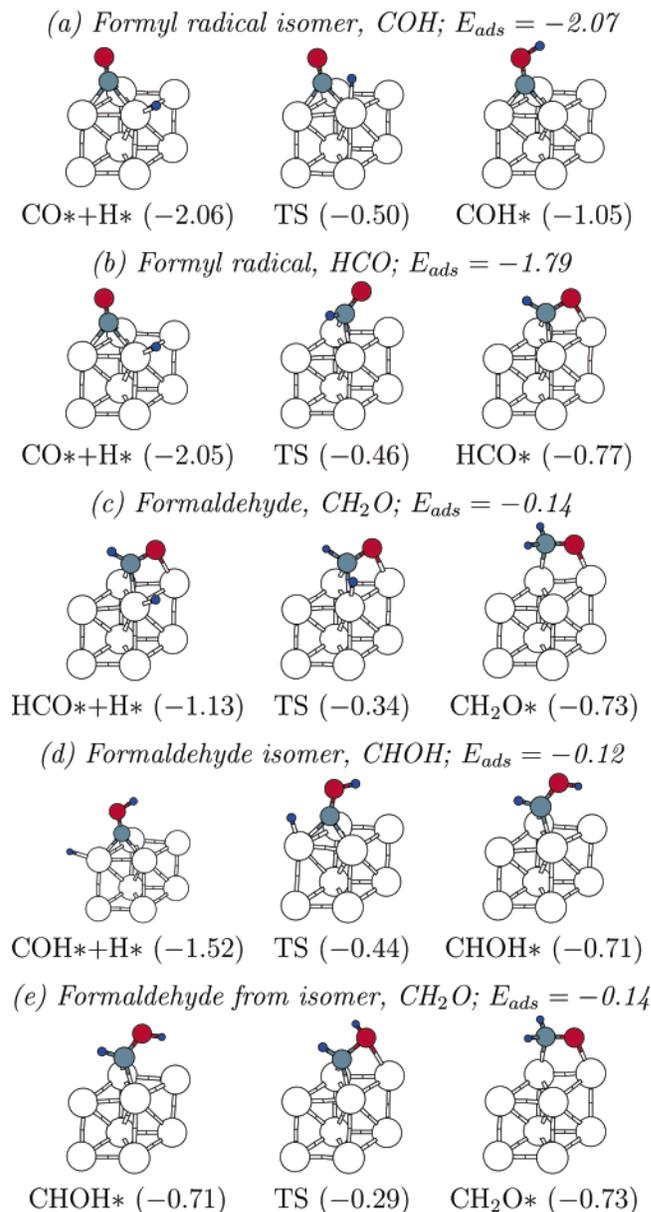


Figure 1. Reactions leading to formation of formaldehyde from CO and H₂ on Ni(111). Adsorption energies, E_{ads} , are relative to the gas-phase final product of each reaction. Energies (in eV per molecule) of the initial, transition and final states are relative to gas-phase CO + $\frac{1}{2}$ H₂ for reactions a and b and gas-phase CO + H₂ for reactions c–e. White, gray, red, and blue spheres represent Ni, C, O, and H atoms, respectively. Side views of only two topmost layers of Ni(111) are shown.

1.28 eV and has an energy barrier of 1.49 eV, as presented in the next section (see also Figure 1b). Following, HCO dissociates into CH and O, with an energy barrier of 1.35 eV. The total barrier for the reaction CO + H → CH + O is then 2.53 eV, rendering the methanation process unfavorable for the flat Ni(111). This byproduct can therefore be excluded under reaction conditions, but as the energetics show, it could appear in the thermodynamic equilibrium.

The only processes that could be competing with CO hydrogenation are CO and H desorption. As shown in detail below, the energies of the transition states for the COH and HCO formations are -0.50 and -0.44 eV. These values are lower than the energy of desorbed CO (-0.39 eV). Therefore, formation of COH and HCO is slightly favored over CO desorption. Desorption of H has a lower activation energy, but

the equilibrium coverage of H can be changed drastically by modifying the vapor pressure of H₂. Indeed, hydrogenated CO species have been observed on Ni(111) under elevated H₂ pressures.²⁹

This situation can, however, be changed once we take the presence of steps into account. C is extremely stable on a step edge of Ni(111). Preliminary calculations we have performed for Ni(211), a surface consisting of Ni(111) terraces and monatomic steps, show that C is stabilized by about 1 eV on a step edge, compared to the flat terrace, in accordance with the results of ref 3. The adsorption energies of CO, H, COH and HCO differ much less, typically by 0.2 eV, between step and terrace sites. Therefore, CO is expected to dissociate only on step-edge atoms of Ni(111).

However, as shown by recent experiments, step sites of Ni(111) can be blocked completely by depositing S or noble metals, for example Ag. S and Ag sit primarily on step edges, and CO cannot dissociate on the Ni(111) surface after S or Ag deposition.²¹ It is for a system where the step sites are blocked by other adsorbates, that the present study is of relevance. We therefore propose that once step edge sites of Ni(111) are blocked, CO can hydrogenate and subsequently form formaldehyde and/or methanol.

4. Intermediate Products

Methanol synthesis is considered to consist of the following elementary steps: adsorption of carbon monoxide (CO) on the catalyst surface, adsorption of hydrogen (H), formation of the formyl radical (COH or HCO), formation of formaldehyde (CH₂O), formation of the methoxy radical (CH₃O), and formation of methanol (CH₃OH). We now comment on each step separately.

Carbon Monoxide. CO binds to Ni(111) vertically, through C and O directly above it. CO was found to have a tendency to leave the surface, when we tried to bind the O atom, instead of C, to Ni. The minimum energy adsorption is obtained when C is above the hcp site of the Ni(111) surface; the adsorption energy is then -1.56 eV. The C-O bond length is 1.20 Å, longer than the corresponding length for the free molecule, which is found to be 1.16 Å (the experimental value³⁰ is 1.13 Å). The distances between C and the three neighboring Ni atoms are 1.96 Å. The adsorption energies for CO on other sites are -1.29 eV when C sits on top of a Ni atom, -1.47 eV when it sits on a bridge site between two Ni atoms, and -1.54 eV for C on the fcc site of Ni(111). In all cases, no significant change in the Ni-Ni bond lengths is observed. The experimental values for the heat of adsorption of CO on Ni(111) range between 1.35 and 1.55 eV and is very much coverage-dependent (see ref 31 and references therein).

Hydrogen. H binds on the fcc hollow site of Ni(111), with an adsorption energy of -2.67 eV (relative to atomic H) or -0.39 eV (relative to H₂). The three H-Ni bonds are 1.72 Å. The adsorption energies for H atop of a Ni atom and on an hcp hollow site of Ni(111) are -2.12 and -2.66 eV, relative to atomic H, respectively. The adsorption energies we find are almost identical to those calculated by Yang and Whitten using a configuration interaction method.³² The experimental value for the dissociative adsorption energy is 2.73 eV,³³ in excellent agreement with our result. H does not bind on a bridge site, between two Ni atoms; it slips spontaneously to the neighboring 3-fold fcc hollow site.

Formyl. We started by calculating the geometry of a free formyl radical. The minimum energy geometry was H-C-O, with the HCO angle equal to 125° and the lengths of the C-O

and O-H bonds equal to 1.13 and 1.20 Å, respectively. These values agree very well with the experimental values³⁰ of 127° and 1.11 and 1.17 Å, respectively. The radical was found to have a magnetic moment of 1 μ_B, as a result of the odd number of electrons it contains. The isomer, C-O-H, was found to have a higher energy of 1.76 eV, compared to H-C-O. In contrast, adsorbed COH has a lower energy than HCO by 0.28 eV. This is a new finding of this work, as previous studies assumed that HCO is the minimum energy state for an adsorbed formyl radical on Ni(111).^{12,34} The adsorption energy for COH is -2.07 eV relative to the free formyl radical, whereas the adsorption energy for HCO is -1.79 eV.

The adsorption geometry for COH is very similar to that of CO; C sits on the 3-fold hcp site, O is directly above it, and H is bonded to O. The average C-Ni bond length is 1.87 Å, slightly shorter than the C-Ni bonds in the case of CO. The C-O distance is 1.35 Å, the O-H distance is 0.99 Å, and the C-O-H angle is 110°. HCO binds to the bridge site, where C forms tetrahedral bonds to H, O, and two Ni surface atoms. The O atom is also bonded to a Ni atom. The C-O distance is 1.29 Å, the O-H distance is 1.11 Å, and the C-O-H angle is 116°. The average C-Ni distance is 1.97 Å.

COH is formed by combining adsorbed CO and H, as shown in Figure 1a. COH formation is endothermic by 0.99 eV. However, there is an initial attraction between CO and H. When CO and hydrogen occupy neighboring sites in our (2 × 2) supercell, the energy is 0.1 eV lower than the sum of the energies of an adsorbed CO molecule and an adsorbed H atom. This number need to be subtracted from the apparent energy barrier calculated using the values shown in Figure 1a. Therefore, the energy barrier for the formation of COH from adsorbed CO and H is 1.45 eV. In the transition state, H is sitting almost on top of a Ni atom, with a slightly elongated Ni-H bond. Formation of HCO by combining adsorbed CO and H is shown in Figure 1b. In the transition state, the C tetrahedron is heavily distorted, and O is still far away from Ni. The barrier for this reaction is 1.49 eV.

Formaldehyde. Formaldehyde binds quite weakly on Ni(111); its adsorption energy is only 0.14 eV. In the lowest energy geometry, formaldehyde binds along a bridge Ni(111) site, with C and O bonded to one Ni surface atom each. The C-Ni and O-Ni distances are 2.04 and 1.91 Å, respectively. The C-H and C-O bond lengths are 1.11 and 1.34 Å, respectively. For the free molecule, we calculate bond lengths of 1.12 (1.12) Å for the C-H bond and 1.22 (1.21) Å for the C-O bond, in excellent agreement with the experimental values shown in parentheses obtained from ref 30. The C-H distances do not change when the molecule is adsorbed, but the C-O bond is significantly elongated, due to the presence of the C-Ni and O-Ni bonds. The C-Ni bonds for adsorbed formaldehyde are longer than those formed for adsorbed CO, COH or HCO, a fact that is directly mirrored in the much lower adsorption energy. We also consider other geometries, with C or O on 3-fold hollow Ni(111) sites; the energy differences were typically on the order of 0.1 eV.

Formaldehyde can be formed directly by hydrogenation of adsorbed HCO; the reaction is shown in Figure 1c. In the transition state, H is almost atop a Ni(111) atom. The reaction is endothermic by 0.43 eV, and the energy barrier is 0.81 eV.

Alternatively, formation of formaldehyde can happen through hydrogenation of the more stable COH isomer, forming CHOH, as shown in Figure 1d. As was the case with formyl, the formaldehyde isomer is greatly stabilized due to the adsorption. For the gas-phase molecules, the energy of CH₂O is 2.23 eV

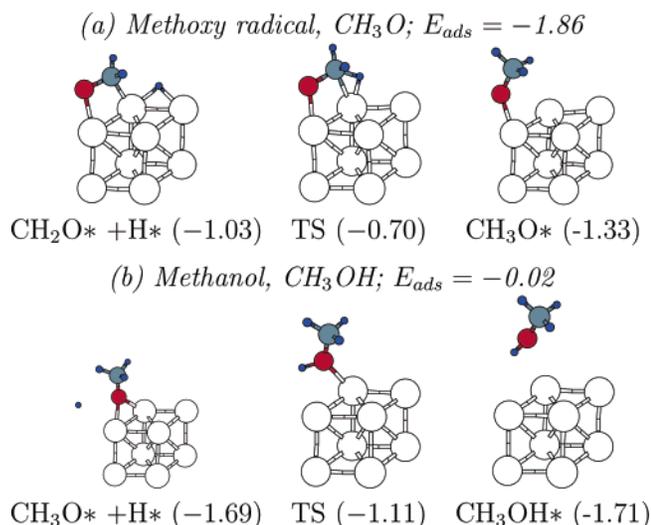


Figure 2. Reactions leading to formation of methanol from formaldehyde on Ni(111). Energies (in eV per molecule) of the initial, transition and final states are relative to gas-phase CO + $\frac{1}{2}$ H₂ (a) and gas-phase CO + 2H₂ (b). Notation is the same as in Figure 1.

lower than the energy of CHO_H; the difference in the adsorbed species, however, is only 0.02 eV. Formation of CHO_H is slightly favored over formation of CH₂O, as the transition state is 0.1 eV lower in energy.

The transport of H from O to H, leading to the reaction from CHO_H to CH₂O, is shown in Figure 1e. The gain in energy is only 0.02 eV, and the barrier associated with this reaction is 0.43 eV.

Methoxy. The methoxy radical (CH₃O) binds through oxygen on top of a Ni atom, with binding energy of 1.86 eV compared to the free radical. The C–O bond length for the adsorbed species is 1.43 Å, identical to the experimental value.³⁵ Its formation from adsorbed formaldehyde and hydrogen is exothermic by 0.21 eV, with a reaction barrier of 0.42 eV. The minimum energy initial, transition, and final states for methoxy formation are shown in Figure 2a.

We also performed calculations for the hydroxymethyl radical, CH₂OH. We observe the same effect of isomer stabilization by adsorption, as observed in formyl and formaldehyde. For the gas-phase free radicals, CH₂OH has lower energy than CH₃O by 0.23 eV; in contrast, adsorbed CH₃O has a lower energy than CH₂OH by 0.43 eV, rendering the formation CH₂OH much less favorable.

Methanol. Methanol is the lowest molecular weight alcohol. It has no unsaturated bonds, so it is not expected to bind strongly to a metal surface. Indeed, the strongest binding energy we calculated for methanol on Ni(111) was only 0.02 eV.

In all considered adsorption geometries, the metal–adsorbate distance was on the order of 3 Å, excluding the possibility for any covalent bond. Apparently, methanol is stabilized on transition metal surfaces by means of dipole–induced dipole interactions. Unfortunately, DFT has an intrinsic inadequacy in treating this type of bonding.

For gas-phase methanol, we calculate bond lengths to be 1.10 (1.09) Å for the C–H bonds, 1.43 (1.43) Å for the C–O bond, and 0.98 (0.95) Å for the O–H bond; the H–C–H angle was 109° (109°) and the C–O–H angle was 108° (109°). The values in parentheses are experimental values;³⁰ an excellent agreement between calculation and experiment is observed. On Ni(111), methanol is located on top of a Ni surface atom, with a O–Ni distance of 2.66 Å. The O–C bond is slightly tilted relative to the surface normal, so that the O–H bond is almost parallel to

TABLE 2: Energetics of the Elementary Reactions Discussed in the Text, as Calculated in the Present Work^a

reaction	ΔH	E_a
CO(g) + * \rightarrow CO*	-1.56	
$\frac{1}{2}$ H ₂ (g) + * \rightarrow H*	-0.39	
CO* + H* \rightarrow COH*	+0.91	1.45
COH* + H* \rightarrow CHO _H *	+0.72	1.00
CHO _H * \rightarrow CH ₂ O*	-0.02	0.43
CO* + H* \rightarrow HCO*	+1.19	1.49
HCO* + H* \rightarrow CH ₂ O*	+0.43	0.81
CH ₂ O* + H* \rightarrow CH ₃ O*	-0.21	0.42
CH ₃ O* + H* \rightarrow CH ₃ OH*	-0.02	0.61
CH ₃ OH* \rightarrow CH ₃ OH(g) + *	+0.01	–
overall reaction: CO + 2H ₂ \rightarrow CH ₃ OH	-1.71	

^a ΔH is the energy difference between products and reactants of each reaction; E_a is the energy barrier associated with the reaction. Both energies are given in eV per molecule.

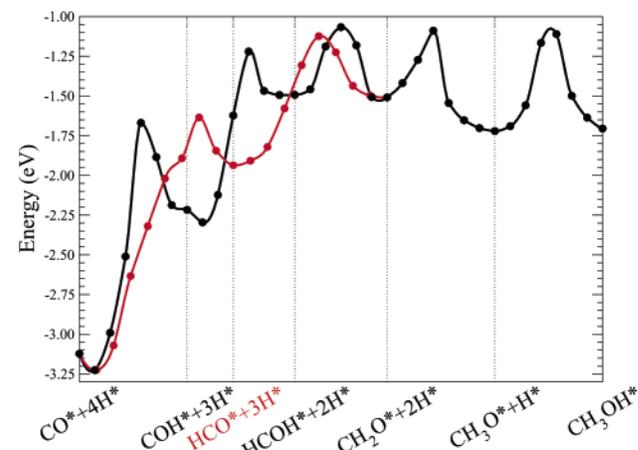


Figure 3. Energy along the reaction path for methanol synthesis on Ni(111). All energies are relative to the energy of CO(gas) + 2H₂(gas) + Ni(111). * denotes adsorbed species.

the surface. There is no significant difference in bond lengths or angles between gas-phase and adsorbed molecules.

The formation of methanol from adsorbed methoxy and H is shown in Figure 2b. Interestingly, when another H is present on the surface, methoxy prefers to move to the 3-fold hcp site with the C–O bond being perpendicular to the surface, as shown in the left panel of Figure 2b. In the transition state, the molecule is beginning to leave the surface. The final state of the reaction, with CH₃OH adsorbed on the surface, is exothermic by only 0.02 eV with a reaction barrier of 0.61 eV.

The enthalpy changes and energy barriers for the elementary reactions discussed above are summarized in Table 2. The reaction enthalpies (energy barriers) shown in this table are calculated by subtracting the sum of the energies of the adsorbed species from the final (transition) state energies. Although we placed the reactants as far away from each other as possible, there is some interaction energy ranging roughly from -0.1 to +0.1 eV. Therefore, the energy barriers and reaction enthalpies in Table 2 can be slightly different from the values one can derive from Figures 1 and 2.

5. Discussion

The independent reactions discussed in the previous section are put together in Figure 3. The energies are calculated relative to clean Ni(111) plus gas-phase CO and two H₂ molecules. All energies of the intermediate configurations are also shown. The two paths discussed before are represented by different colors

in Figure 3: the path involving the more stable COH is shown in black, while the path involving HCO, which has a slightly lower barrier, is shown in red.

The reader interested in comparing the energies presented in Figure 3 to those referred to in section 3 should add the energies of the appropriate number of adsorbed H atoms (-0.39 eV per half H_2 molecule). For example, the energy of adsorbed CO, which is the very first point in Figure 3, is $-1.56 - 4 \times 0.39$ eV = 3.12 eV. The energy of desorbed CO is $0.00 - 4 \times 0.39$ eV = -1.56 eV, etc. The same rule was applied when transforming the energies presented in Figures 1 and 2 into the energies presented graphically in Figure 3.

The overall barrier for formaldehyde formation, starting from CO and H adsorbed on Ni(111) is 2.00 eV, when the first step in the synthesis is HCO, and 2.06 eV when the first step in the synthesis is COH. The final state of the reaction, adsorbed CH_2O , is 1.60 eV higher in energy than adsorbed CO and H, but it is 0.73 eV lower in energy than gas-phase CO and H_2 . Similarly, the transition state of the formaldehyde synthesis has an energy 0.29 eV below the energy of the reactants. A very important message from the reaction energies presented in Figure 3 is that the highest transition state of the proposed methanol synthesis process has an energy more than 1.0 eV lower than the energy of the gas-phase reactants.

Formation of formaldehyde has a final-state energy very similar to the desorption energy of CO; the energy of adsorbed formaldehyde, as shown in Figure 1c, is -0.73 eV relative to gas-phase CO and H_2 . The energy of dissociative adsorption of H_2 is $2 \times (-0.39) = -0.78$ eV. Treating those numbers as equal, it is expected that about half the adsorbed CO molecules will form formaldehyde.

As mentioned before, formaldehyde was found to have an adsorption energy of only 0.14 eV. It is therefore possible that formaldehyde desorbs from the surface, instead of reacting with one more hydrogen to form the methoxy radical. At equilibrium, however, the methoxy radical will dominate, because its energy is 0.21 eV lower than the energy of adsorbed formaldehyde plus an adsorbed H atom. In order for the reaction to proceed, equilibrium between formaldehyde and methanol has to be established. This equilibrium will be in favor of methanol, as it has an energy that is 0.21 eV lower than adsorbed formaldehyde and 0.35 eV lower than gas-phase formaldehyde.

The highest transition state energy for the formaldehyde to methanol reaction is slightly lower than the highest transition state energy for the CO to formaldehyde reaction. Therefore, formation of methanol from CO and H will have to overcome roughly the same energy barrier of 2.0 eV. The final state, methanol, is 1.41 eV higher in energy than adsorbed CO and H. However, the highest transition state energy is more than 1 eV lower than the energy of gas-phase CO and $2H_2$.

Although the overall energy barrier of 2.0 eV may look high, it is possible to overcome this barrier under reasonable reaction conditions. To estimate the reaction rate, we use the Arrhenius formula, $r = \nu e^{-E_a/k_B T}$. By assuming a standard value for the preexponential factor, $\nu \approx 10^{13}$, and setting $E_a = 2.0$ eV, we obtain a reaction rate that becomes equal to 1 s $^{-1}$ at $T = 775$ K; this temperature is not unrealistic for industrial reactors. Moreover, the preexponential factor could be as high as 10^{17} ;³⁶ in this case, the temperature where $r \approx 1$ s $^{-1}$ is only 600 K. In addition, higher initial CO coverage could perhaps increase the reaction rate. At a higher CO coverage, several CO molecules are forced to share the same Ni atoms and therefore make weaker bonds to the catalyst surface. On the other hand, the more weakly bound products of the reaction, formaldehyde and

methanol, are subject to attractive dipole–dipole interactions between them. Therefore, higher initial CO coverage could increase the initial state energy and lower the energy of the transition state, thus lowering the apparent activation energy of the overall reaction. The proposed methanol synthesis reaction should be able to take place at a temperature well below the one estimated above.

In addition to elevated temperature, high pressure is also required. The difference between the binding energies of CO and H on Ni(111) indicates that a very high pressure of H_2 is required in order to get the ideal ration of 1:4 between the coverages of adsorbed CO and H, so that the proposed reaction will proceed efficiently. The exact value of the ratio between CO and H partial pressures required for the proposed reaction is not easy to calculate, as this would require a full modeling of the reaction rates, and it should also include coverage effects. Given the fact that DFT in general overestimates energy barriers, and that our results have been obtained at very low coverage, the actual rates in an experiment could be much higher than those estimated from our potential energy surface, shown in Figure 3.

In conclusion, we have shown that CO hydrogenation is the most likely reaction to happen when CO and H are coadsorbed on Ni(111), as it is well favored over dissociation of CO, and somewhat more likely to happen than CO desorption. Thus, the formed HCO or COH radical can then subsequently be hydrogenated to form formaldehyde. Formaldehyde can, with almost equal probabilities, desorb, dehydrogenate or attract two more H atoms and form methanol. The total energy barrier for formaldehyde and methanol synthesis is 2.0 eV. This energy barrier suggests that the reaction could easily take place at temperatures around 700 K. It should therefore be possible to use cheap Ni catalysts for methanol production from CO and H_2 , provided that the step sites of Ni(111) are blocked.

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