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Electronic structure calculations and dynamics of CC coupling on nickel and cobalt

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The carbon–carbon coupling of C (carbide) and CH (methylidyne), C and CH$_2$ (methylene), and C and CH$_3$ (methyl) on nickel has been studied with density functional theory using 7- and 13-atom cluster models. Formation of CCH$_3$ (ethyldiene) turned out to be the most exothermic reaction on both clusters. Experimentally, CCH$_3$ has been identified unambiguously with a structure perpendicular to the metal surface. Thus for the C/CH$_3$ coupling forming CCH$_3$, we have determined the structure and potential energy surface in the coadsorbed state, transition state, and CC-formed state. The transition state is explicitly determined on the 7-atom cluster and the 13-atom cluster of both nickel and cobalt. We find transition state barriers of 57 kJ/mol for the Ni$_7$ cluster, 55 kJ/mol for the Co$_7$ cluster, 84 kJ/mol for the Ni$_{13}$ cluster, and 47 kJ/mol for the Co$_{13}$ cluster. The overall reaction energies are $-215$, $-184$, $-66$, and $-89$ kJ/mol, respectively. Analysis of the TS shows a dominant contribution of the CC bond to the reaction coordinate. Cluster size effects play a role in all studied CC coupling reactions. © 1995 American Institute of Physics.

I. INTRODUCTION

A very interesting and important topic in heterogeneous catalysis is the conversion of CH$_4$ to higher hydrocarbons. A well known method for CH$_4$ activation is its steam reforming producing CO and H$_2$ followed by the so-called Fischer–Tropsch synthesis to various hydrocarbons.$^1$ Whether CH$_4$ or higher hydrocarbons are produced depends strongly on the transition metal surface and on reaction conditions, but on Fe, Co, and Ru a wide range of hydrocarbons is formed, whereas over Ni and Pd CH$_4$ is the principal product, while Cu shows no reaction at all.$^2$ Kaminsky et al.$^3$ have detected CH$_3$, CH$_2$, and CH as intermediates on Ni(111). An alternative, direct route is dissociation of CH$_4$ to CH$_2$ species over a silica supported transition metal catalyst at temperatures around 600–900 K, followed by carbon–carbon coupling and hydrogenation at temperatures around 370 K.$^2$ Again, the role of the metal is important: Ru and Co give a wide range of products as does Ni but in much lower yields, Pt yields only C$_1$ and C$_2$ products, while Cu and Pd show no carbon–carbon coupling at all. Goodman and coworkers have identified C, CH, CCH$_2$ (vinylidene), and CCH$_3$ on Ru(0001) and Ru(1120) for this reaction using HREELS and TPD.$^7$ Belguet et al.$^6$ reported conversion of CH$_4$ on a Pt-catalyst producing higher hydrocarbons up to C$_6$ species.

Another important reaction in catalysis is C$_2$H$_4$ (ethylene) adsorption and its subsequent decomposition, which is well studied on Pt(111). Various mechanisms for C$_2$H$_4$ decomposition have been suggested, but almost all agree on CCH$_2$ as the main product. Suggested intermediate structures are CHCH$_2$ (vinyl) and CCH$_2$, C$_2$H$_3$ (ethyldiene),$^8$ or only CHCH$_3$ or CHCH$_2$.$^{10}$ Somorjai et al.$^8$ suggested a further decomposition of CCH$_3$ to CCH$_2$ and CCH (ethynyl). However, CCH$_3$ remains the only species from C$_2$H$_4$ decomposition on Pt(111), which has been identified unambiguously by various methods.$^{11}$ According to Fairbrother et al.$^{12}$ studying the reactions of adsorbed CH$_3$ on Pt(111), CH$_3$ reacts with H to form CH$_2$ or dehydrogenates to CH$_2$ and eventually C as shown by Zaera et al.$^{13}$ These species can then form a CC bond. Again, CCH$_3$ has been identified. According to them, C$_2$H$_2$, C$_2$H$_3$, CHCH$_3$, and CHCH$_2$ can all be ruled out, leaving C$_2$H$_2$ and CCH as the most likely other candidates. For the mechanism of CCH$_3$ formation Fairbrother et al.$^{12}$ suggest coupling of C and CH$_3$.

Zheng et al.$^{14}$ studied the carbon–carbon coupling reactions of CH$_2$/CH$_3$, CH$_2$/CH$_2$ and CH$_2$/CH$_2$ on Cr(110), Ti(0001), and Co(0001) using tight binding extended H"{u}ckel calculations and found a barrier for coupling CH$_2$/CH$_3$ and CH$_2$/CH$_2$ and an overall endothermicity. In contrast, the coupling between CH$_2$/CH$_2$ proceeded without a barrier and turned out to be exothermic. De Koster et al.$^{15}$ using atom superposition electron delocalization molecular orbital (ASED-MO) theory found on Rh(111) high barriers for coupling CH$_2$/CH$_2$, which they attributed to strong steric repulsion between the hydrogen atoms. Koerts et al.$^{16}$ also using ASED-MO theory searched for a low coupling barrier between C/C, C/CH, C/CH$_2$, and C/CH$_3$ on Rh(111). Except for C/CH$_2$, where a barrier of 95 kJ/mol was calculated, they found rather high barriers, but slightly exothermic overall reactions. The barrier height again correlated with the number of CH bonds, i.e., the highest barrier was found for C/CH$_3$ coupling followed by C/CH and C/C coupling. Kang et al.$^7$ studied theoretically ethylene and acetylene chemisorption on Pt(111) using again ASED-MO theory. They determined transition states and could thus compute activation barriers for their suggested intermediates. For CCH$_3$ they predicted a structure perpendicular to the surface, which is also found experimentally.$^{17}$ for CCH$_2$ a bent structure, and the energetics of perpendicular and bent CCH turned out to be almost the same with a slight preference for the perpendicular structure. However, they computed a small barrier for CCH decomposition to form C and CH. Furthermore, for the rearrangement of CCH$_2$ to CCH$_3$ they computed a barrier of

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203 kJ/mol and an endothermicity of 77 kJ/mol, which suggests no formation of CH$_3$ at all, contrary to experiment. Instead, they suggested formation of CCH, which according to them is exothermic by 13 kJ/mol. Carter and Koel$^{16}$ estimated surface reaction energies on Pt(111) and used these data to eliminate possible reaction pathways. According to them C$_2$H$_4$ adsorbs, isomerizes to CH$_2$CH, dehydrogenates to CCH$_3$, which isomerizes to CH$_2$CH, which dehydrogenates further to CHCH, CCH, and finally CC. One of their conclusions is the absence of C and CCH$_2$. They predict that CH$_3$ is the most stable C$_1$ species and ethylidene (CHCH$_3$) the most stable C$_2$ species. Shustorovich$^{15}$ et al. used a bond order conservation (BOC) model to study among others the decomposition of C$_2$H$_4$ on Pt(111). According to them, this species is dehydrogenated to CHCH$_2$, followed by dehydrogenation to CCH$_2$, which is then predicted to isomerize to adsorbed CHCH (acetylene), which then desorbs. In their model CCH$_3$ is not likely to form starting from C$_2$H$_4$.

In addition to the abundant data on C$_2$H$_2$ and C$_2$H$_4$ chemisorption on Pt(111), we have also found some C$_2$H$_2$/C$_2$H$_4$ chemisorption experiments on Ni and Co surfaces. According to Lehwald$^{20}$ et al. and Demuth$^{21}$ C$_2$H$_4$ directly decomposes to chemisorbed C$_2$H$_2$ on Ni(111), while CCH is formed on Ni(110), according to Stroscio$^{22}$ et al. Zaera$^{23}$ studied C$_2$H$_4$ decomposition on Ni(100) and found evidence for CCH$_2$ formation. By raising the crystal temperature, they found evidence for subsequently CHCH, CCH, and C. Zhu et al.$^{25}$ showed the existence of CCH$_3$ on Ni(111) at high coverages of CHCH and CH$_2$CH$_2$. Albert$^{26}$ et al. chemisorbed CHCH and CH$_2$CH$_2$ on Co(0001), but found no further reaction of adsorbed CHCH. However, adsorbed CH$_2$CH$_2$ decomposed according to them by a simultaneous scission of all CH bonds followed by CC bond scission. Finally, Lapinski$^{26}$ et al. presented ir evidence for CCH$_3$ formation on a alumina supported nickel catalyst starting from CH$_2$CH$_2$, while Anderson et al.$^{27}$ reported the same for a silica supported cobalt catalyst.

We can conclude that in both direct CH$_4$ dissociation and C$_2$H$_4$ decomposition CCH$_3$ plays an important role. In addition, almost every possible C$_2$H$_x$ species is proposed as an intermediate by theoreticians as well as experimentalists. We think that it is interesting to investigate the reaction between a fully dehydrogenated C species and a CH$_3$ species, thereby avoiding the steric repulsion between hydrogen atoms, which results in a very high activation barrier as shown by others. Furthermore, the product CCH$_3$ has been detected by various methods and on various substrates, as discussed above. Therefore, we have calculated the potential energy surface at the coadsorbed state (CS), the transition state (TS), and the CC-formed state (CC/$S$) of C/CH$_3$ using an $ab$ initio density functional approach, and treated the kinetics of the system by employing transition state theory. Specifically, we have taken a one layer 7-atom cluster, and a 13-atom spherical cluster of Ni and Co to model the substrate, in addition to our work on CH bond activation on these metals.$^{28}$ Thus we have studied the following reactions:

\[
\begin{align*}
\text{CH}_3a + C_a & \rightarrow \text{CCH}_3a, \\
\end{align*}
\]

and

\[
\begin{align*}
\text{CCH}_3a & \rightarrow \text{CH}_3a + C_a.
\end{align*}
\]

In Sec. II we give computational details, in Sec. III we discuss the electronic structure calculations, in Sec. IV the kinetic treatment, and in Sec. V we draw some conclusions.

II. METHODS

We have performed quasirelativistic calculations based on density functional theory (DFT) using the Amsterdam Density Functional program package (ADF) developed by Baerends$^{29}$ et al. The exchange-correlation potential used is based on quantum Monte Carlo simulations of Ceperley and Alder$^{30}$ of a homogeneous electron gas which has been parameterized by Vosko, Wilk, and Nusair.$^{31}$ To correct for the overbinding inherent to the local density approximation (LDA),$^{32}$ we have used a gradient corrected exchange energy functional$^{33}$ in combination with the Stoll correction$^{34}$ for correlation. For carbon a frozen core potential is used for the $1s$ electrons; for nickel and cobalt the electrons up to $3p$ are frozen. Relativistic effects were taken into account by first order perturbation theory.$^{35}$ The basis sets are of double $\zeta$ quality, with the exception of the nickel and cobalt $d$ orbitals, which are triple $\zeta$’s. On all atoms polarization functions are

\[
\begin{align*}
\text{CH}_3a & \rightarrow \text{CH}_3a + C_a.
\end{align*}
\]
included. As models for the substrate, we have used a one layer 7-atom cluster and a spherical 13-atom cluster [Figs. 1(a) and 1(b)], which have been discussed extensively before.36 For nickel clusters the bond distance was fixed at the bulk value of 2.49 Å, for cobalt clusters at the bulk value of 2.50 Å. Adsorption energies are calculated using Ziegler’s transition state method37 and are given relative to the gas phase fragments with the same geometry. The CS was calculated by coadsorbing the two fragments at separated threefold sites at optimal adsorbate–substrate distances determined in previous studies.36 On the 13-atom cluster these sites are at the top and the bottom of the cluster. The additional degrees of freedom of the CH2 fragments were not allowed to relax, i.e., for all CH2 species we kept the CH distances at 1.08 Å, the HCH angles at 109.48°, the substrate–CH angles of CH3 at 109.48°, the substrate–CH angles of CH2 at 125.26° and the substrate–CH angles of CH at 180°.

The TS of CCH3 was explicitly calculated by a four dimensional grid in the MC1, MC2, and CC distances and the CH3 tilt angle with respect to the activated CC bond (θ) [Figs. 1(a) and 1(b)]. The grid point energies were fitted to a second-order polynomial in the MC1, MC2, and CC distances and θ. The CC’S was determined by optimizing the MC1 and CC distances, keeping the product CCH3 at optimal adsorbate–substrate distances determined by coadsorbing the two fragments at separated threefold sites at optimal adsorbate–substrate distances determined in previous studies.36 Of the 13-atom clusters, these were at the top and the bottom of the cluster. The additional degrees of freedom of the CH2 fragments were not allowed to relax, i.e., for all CH2 species we kept the CH distances at 1.08 Å, the HCH angles at 109.48°, the substrate–CH angles of CH3 at 109.48°, the substrate–CH angles of CH2 at 125.26° and the substrate–CH angles of CH at 180°.

### III. ELECTRONIC STRUCTURE CALCULATIONS

Optimal parameters and energies of the CS and the CC’S of C/CH and C/CH2 on Ni2 and Ni13, together with the CS, the TS and the CC’S of C/CH3 on Ni7, Ni13, Co2, and Co13 are shown in Table I. We conclude that formation of CCH (CC’S) is endothermic on both clusters by 61–62 kJ/mol. Formation of CCH2 (CC’S) and CCH3 (CC’S) is strongly exothermic on Ni7, but the exothermicity is reduced on Ni13. For the Ni13 clusters we also optimized the adsorption energy of CCHx (CC’S) as a function of the MC1 and CC distances for optimal CH distances of CHx in the gas phase. Although the effect on the CH distance was pronounced, optimal CH distances of 1.09, 1.11, and 1.13 Å for CH, CCH2, and CCH3, respectively, the effect on the adsorption energies was maximal 3 kJ/mol. For the most exothermic reaction, the formation of CCH3, we determined the TS on Ni7, Ni13, Co2, and Co13. We find transition state barriers of 57 kJ/mol on Ni7, 84 kJ/mol on Ni13, 55 kJ/mol on Co2, and 47 kJ/mol on Co13. The geometry of the TS differs significantly between the 7- and 13-atom clusters of the same metal, but are quite similar for the 7-atom clusters as well as for the 13-atom clusters. Analysis of the TS shows a dominant contribution of the CC distance to the imaginary frequency, which characterizes the reaction coordinate. Therefore, we expect a correlation between CC bond distance and barrier height. Indeed, the TS of Ni7/CCH3 with a CC bond of 2.39 Å gives a slightly higher barrier (57 kJ/mol) than the TS of Co2/CCH3 with a CC bond of 2.33 Å and a barrier height of 55 kJ/mol. The effect is more pronounced on the 13-atom clusters. The TS of Ni13/CCH3 has a CC bond distance of 2.15 Å and a barrier height of 84 kJ/mol, whereas the TS of Co13/CCH3 has a CC bond distance of 2.09 Å and a barrier height of only 47 kJ/mol. Although in both cases the difference in CC bond length is 0.06 Å, the effect on barrier height is very different. We attribute this to the more compact TS at the 13-atom clusters. Except for the MC1 distance, the MC2 and CC distances and the tilt angle are significantly smaller on the 13-atom clusters, which results in a larger effect on the transition state barrier height, when the CC bond length changes. The same conclusion can be drawn starting from the CC’S state. For Ni13/CCH3 the CC bond changes from 1.57 to 2.39 Å, an increase of 0.82 Å in going from the CC’S to the TS. The barrier height for this CC cleavage reaction is 272 kJ/mol. For Co13/CCH3 the CC bond changes from 1.58 to 2.33 Å, an increase of 0.75 Å with a corresponding barrier height of 239 kJ/mol. For Ni13/CCH3 and Co13/CCH3 the changes in CC bond length are respectively 0.59 and 0.54 Å with corresponding barrier heights of 150 and 136 kJ/mol.

Comparison of our CS results with the infinitely separated state (ISS) of adsorbed C/CH2 showed up the existence of cluster size effects. This can be seen from Table II, which shows the charge on C, C of CHx, H of CHx, the CHx fragment, and on the cluster for all studied systems, together with the difference in energy between the adsorbed C/CHx in the ISS and the CS. The large positive energy difference indicates that adsorption in the ISS is far more favorable than in the ISS. The magnitude and sign of this energy difference clearly prohibits interpretation in terms of a barrier to move along the surface. We discuss first the results for C/CH. The CC’S shows a positive charge on C (0.33e on Ni7, 0.55e on Ni13). Also, the total charge on the cluster is by more than two electrons positive on the CS at Ni7 (2.06e), and by almost two electrons on Ni13 (1.99e). The CH fragment is
C/CH, followed by C/CH₂, and C/CH₃ on Ni₇ as well as that the energy difference between ISS and CS is largest for parts of the potential energy surface can be compared. Again and we feel therefore that the relative energetics at these f strongly. This effect is present at the CS, the TS, and the CC coupling on Ni₇.

<table>
<thead>
<tr>
<th>System</th>
<th>q₁C</th>
<th>q₂C</th>
<th>Σ-q₁</th>
<th>q₁CH</th>
<th>Σ-q₂</th>
<th>EISS-ECS</th>
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<td>Ni₇/C/C (ISS)</td>
<td>-0.39</td>
<td>-0.39</td>
<td>0.13</td>
<td>-0.26</td>
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<td>0.03</td>
<td>0.36</td>
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<td>-0.53</td>
<td>0.28</td>
<td>-0.25</td>
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<tr>
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<td>-1.55</td>
<td>1.37</td>
<td>-0.18</td>
<td>0.77</td>
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<tr>
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<td>-0.54</td>
<td>0.45</td>
<td>-0.09</td>
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<td>Ni₇/C/CH₂ (CS)</td>
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<td>-1.72</td>
<td>1.53</td>
<td>-0.19</td>
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<td>-1.27</td>
<td>1.08</td>
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Strongly polarized at the CS and the CC/S as a result of excessive (negative) charge on C and positive charge on H of CH. The total charge on the CH fragment is as a result also strongly negative at the CS and to a lesser extend at the CC/S. All these observations hold for C/CH₂ too, but they are less pronounced. It is expected that C/CH attracts more charge than C/CH₂, resulting in a negatively charged CH fragment and a positively charged substrate, but the charge effects seem a bit large. The charge effects at the CC/S of C/CH and C/CH₂ could have their cause in the restriction of the CC/S to be perpendicular to the surface, whereas they have probably bent structures. However, the charge effects at the CS and the absence of them at the ISS, together with the large energy difference between ISS and CS suggests the occurrence of finite cluster size effects. For C/CH₂ the charge is always slightly positive on the metal substrate, slightly negative on the CH₂ fragment, and slightly more negative on C in all cases. This is in line with our expectation. The polarization within the CH₂ fragment is however again very strong. This effect is present at the CS, the TS, and the CC/S and we feel therefore that the relative energetics at these parts of the potential energy surface can be compared. Again the large charge effects are absent at the ISS. Table II shows that the energy difference between ISS and CS is largest for C/CH, followed by C/CH₂, and C/CH₃ on Ni₇ as well as Ni₁₃. The difference is always largest on the 13-atom clusters.

Studies on adsorption of H/CH₃ showed an energy difference between the ISS and the CS of −29 kJ/mol. Also, no large charge effects were observed. Therefore, in this case the energy difference can be interpreted as a barrier, which has to be overcome to move infinitely separated adsorbed H and CH₃ to adjacent threefold sites. Studies on different coadsorbed positions of C/CH₃ showed an energy difference of −22 kJ/mol between separated threefold sites and adjacent threefold sites. In this case the large charge effects were again observed for both positions, suggesting the comparability of the relative energetics. The energy difference of 22 kJ/mol thus indicates a barrier of this size to overcome to move coadsorbed C/CH₃ to adjacent positions. We conclude that when both C and CH₃ are adsorbed (CS, TS, or CC/S), this gives rise to large charge effects, due to the finite size of our cluster models. This effect is absent at the ISS and in the coadsorption of H/CH₃.

Carter and Koel estimated surface reaction energies for many CₓHₙ species. For the CC coupling of C/CH, C/CH₂, and C/CH₃ on Pt(111) forming CCH, CCH₂, and CCH₃, they estimated reaction energies of, respectively, −84, −92, and −218 kJ/mol. Thus according to them all these reactions are thermodynamically favorable on Pt(111). However, for the CCH and CCH₂ products they assumed bicoordinated structures and for CCH₃ a perpendicular structure, while we restricted the CCH, CCH₂, and CCH₃ products to perpendicular positions to the surface for reasons of symmetry. Demuth and Ibach did not find CC stretch frequencies on Ni(111) indicative of perpendicular CCH or CCH₂ species. Thus should these species be formed, their CC axis is not perpendicular to the surface.

The work of Shustorovich et al. is interesting, because they computed chemisorption data of CₓHₓ on both Ni(111) and Pt(111). Monocoordinated CₓHₓ species with a CC-axis perpendicular to the surface and bicoordinated CₓHₓ species with a skewed CC axis have comparable adsorption energies according to the BOC model. For the CC coupling of C/CH, C/CH₂, and C/CH₃ on Pt(111) forming CCH, CCH₂, and CCH₃, they estimated reaction energies of, respectively, 0, −75, and +33 kJ/mol. On Ni(111) these enthalpies are +105, +8, and +88 kJ/mol, respectively. For the CC bond formation of C/CH₃, Shustorovich gives activation barriers of 79 kJ/mol on Pt(111) and 121 kJ/mol on Ni(111), and for the bond cleavage 46 kJ/mol on Pt(111) and 33 kJ/mol on Ni(111). Thus according to Shustorovich, Pt(111) is the more reactive metal for CC bond formation, although all chemisorption energies are larger on Ni(111). In fact, CC coupling does not take place at all on Ni(111) according to Shustorovich. Also, his reaction enthalpies on Pt(111) are less exothermic or even endothermic compared to those of Carter and Koel. For the C/CH₃ reaction on Pt(111), Carter et al. and Shustorovich give very different results: according to the first it is exothermic by 218 kJ/mol, while Shustorovich gives an endothermicity of 33 kJ/mol. We can compare our results with those of Carter and Koel and those of Shustorovich. On first sight, our exothermicity of 215 kJ/mol for the C/CH₃ coupling on Ni₇ compares very well with the exothermicity of 218 kJ/mol for the same reaction on Pt(111) given by Carter and Koel. If we keep in mind the alleged lesser reac-
tivity of Ni(111), it seems better to compare with our 13atom cluster results. In that case our reaction energies of +61, −14, and −66 kJ/mol for C/CH, C/CH2, and C/CH3 coupling show the same trend as those of Carter and Koel of, respectively, −84, −92, and −218 kJ/mol on Pt(111). This is also in agreement with Shustorovich’ notion that Pt(111) is the more reactive metal. Shustorovich’ model probably underestimates the exothermicity of the studied surface reactions, as can be concluded from the comparison of his results on Pt(111) with those of Carter and Koel. We disagree with Shustorovich that the transition state barriers for CC bond formation are higher than those of CC bond cleavage.

Kang et al.7 have computed the structure of CCH3 on Pt(111). They found a structure perpendicular to the surface with an adsorbate–substrate distance of 1.20 Å, a CC bond distance of 1.70 Å, CH bond distances of 1.20 Å, and CCH bond angles of 108°. For CCH they also found a preference for a structure perpendicular to the surface, but at a onefold site, with an adsorbate–substrate distance of 1.55 Å, a CC bond distance of 1.36 Å, and a CH bond distance of 1.15 Å. Koestner et al.41 using a LEED analysis, found on Rh(111) a perpendicular CCH3 species at a threefold site with a CC bond distance of 1.45 Å, and a MC bond distance of 2.03 Å, which corresponds with an adsorbate–substrate distance of 1.31 Å. For Pt(111) they give values of 1.50 Å for the CC bond distance and 2.00 Å for the MC distance, which corresponds with an adsorbate–substrate distance of 1.19 Å. It is clear that the computed and experimentally determined CC bond distance on Pt(111) differ significantly. Our computed MC1 distances of CCH3 (CC’S) of 1.85 Å on Ni7 and 1.88 Å on Co7, corresponding with adsorbate–substrate distances of 1.16 and 1.21 Å, respectively, and our CC bond lengths of 1.57 Å on Ni7 and 1.58 Å on Co7 seem to be reasonable values.

IV. KINETIC CALCULATIONS

We have computed rate constants using transition state theory. An important advantage of this approach is that the complete potential energy surface is not required. Instead, only the local parts at the coadsorbed state, the transition state, and the CC-formed state need to be determined to compute kinetics. In particular, rotational and vibrational frequencies together with masses of the intermediates and barrier heights determine the rate constant. The formula for CC bond formation is given by

\[ k_{CC}^{\text{TST}} = \frac{k_B T}{h} \frac{Q_v^2}{Q_{\text{tot}}} e^{-E_{\text{crit}}/k_B T} \]

and for CC bond cleavage by

\[ k_{CC}^{\text{TST}} = \frac{k_B T}{h} \frac{Q_v^2}{Q_{\text{tot}}} e^{-E'/\text{crit}/k_B T}. \]

The translational partition function describes the two translations of CH3, which is a mobile species,36 on the substrate. The connection between \( k_{CC}^{\text{TST}} \) and \( k_{CC}^{\text{TST}} \) and between \( k_{CC}^{\text{TST}} \) and \( k_{CC}^{\text{TST}} \) is discussed in the Appendix. To evaluate \( k_{CC}^{\text{TST}} \) and \( k_{CC}^{\text{TST}} \), we need to calculate the translational, vibrational, and rotational partition functions for the CS, the TS and the CC’S.

To find out which degrees of freedom cancel, we characterized them at the different geometries bearing in mind that our cluster represents an (infinite) surface of infinite mass. Therefore, overall translations and rotations of the cluster are irrelevant and internal lattice vibrations (phonons) are neglected. With these premises we have determined the degrees of freedom at the TS. Three modes determine the absolute position of C: one MC stretch (MC1), and two vibrations of C parallel to the surface (one in the mirror plane and one perpendicular to it). Three modes determine the absolute position of CH3: one MC stretch (MC2), one CC stretch, and one vibration of CH3 parallel to the surface and perpendicular to the mirror plane. Three modes determine the orientation of CH3: the CH3 tilt in the mirror plane (\( \theta \)), the CH3 tilt perpendicular to the mirror plane, and one internal CH3 rotation around the internal C3 axis. Finally, there are six internal CH3 modes: three CH stretches and three internal bending modes adding up to a total of 15 degrees of freedom. For the CS we have again the six internal modes of CH3 and the three modes determining its orientation. Furthermore, we have the MC2 stretch and the two vibrational modes parallel to the surface, which are translations, because CH3 is a very mobile species. Together with the MC1 stretch and the two vibrations of C parallel to the surface (one in the mirror plane and one perpendicular to it), they add up to 15 degrees of freedom. For the CC’S we have again the six internal CH3 modes and the three modes determining its orientation. Furthermore, we have one MC1 stretch, the two vibrational modes of C parallel to the surface (one in the mirror plane and one perpendicular to it), one CC stretch, and the two vibrational modes of CH3 parallel to the surface (one in the mirror plane and one perpendicular to it). Together, these modes add up again to a total of 15 degrees of freedom. The six internal CH3 modes, the internal CH3 rotation and the CH3 tilt perpendicular to the mirror plane cancel at all geometries. Therefore, only the following modes need explicit computation. For the CS two translations of CH3 on the surface, the MC1 stretch, the MC2 stretch, the two vibrations of C parallel to the surface (one in the mirror plane and one perpendicular to it), and \( \theta \). For the TS the CC stretch, the MC1 stretch, MC2 stretch, the two vibrations of C parallel to the surface (one in the mirror plane and one perpendicular to it), one vibration of CH3 parallel to the surface and perpendicular to the mirror plane, and \( \theta \). For the CC’S the MC1 stretch, the CC stretch, the two vibrations of C parallel to the surface (one in the mirror plane and one perpendicular to it), the two vibrations of CH3 parallel to the surface (one in the mirror plane and one perpendicular to it), and \( \theta \). C was kept at a threefold site at all geometries, because it was shown to be very immobile.36 Therefore, the MC1 stretch and one vibration of C parallel to the surface and in the mirror plane are always varied such that their combination keeps C at the threefold site. Effectively, this reduces our degrees of freedom to be optimized from seven to six. The frequencies are displayed in Table III for the 7- and 13-atom clusters of
nickel and cobalt. The imaginary frequency at the TS is dominated by the CC stretch in all cases.

As discussed in Sec. I, CCH$_3$ has been identified experimentally by various methods. Goodman et al.,
Steiniger et al.,
Parmenter et al.,
Kesmodel et al.,
Koel et al.,
and Skinner et al.,
give vibrational frequencies of CCH$_3$ (CC'S) on Ru(1120), Ru(0001), Pt(111), Pd(111), Rh(111), and the organometallic cluster Co$_9$(CCH)$_3$CO$_9$. These groups measured the symmetrical and asymmetrical CH stretch, the symmetrical and asymmetrical scissors mode, and the rocking vibration of the CH$_3$ group, in addition to the CC stretch and the MC stretch. Our choice of modes results in the cancellation of various partition functions, which allows computation of rate constants. However, it makes comparison with this data less straightforward. Therefore, we will restrict the comparison to the CC stretch and the MC stretch. For the CC stretch frequency we found values of 1082, 1058, 950, and 910 cm$^{-1}$ on Ni$_7$, Co$_7$, Ni$_{13}$, and Co$_{13}$, respectively. Experimentally they range between 1080–1163 cm$^{-1}$. For the MC stretch frequency we found values of 380, 395, 354, and 340 cm$^{-1}$ on Ni$_7$, Co$_7$, Ni$_{13}$, and Co$_{13}$, respectively. Experimentally they range between 220–600 cm$^{-1}$. Although no data on Ni or Co surfaces could be found, it is clear from these data that our computed frequencies seem correct and are well suited for the computation of rate constants via vibrational partition functions.

These rate constants for CC bond formation and cleavage are calculated according to Eqs. (3) and (4), and are shown in Table IV at different temperatures. It is clear from Table IV that for all temperatures and for all clusters CC bond formation prevails over CC bond cleavage. We see that the rate constant for CC bond formation is a factor 6–13 larger on Ni$_7$ compared to Co$_7$ in the temperature range studied, although the barrier height on Ni$_7$ is slightly higher at the electronic potential energy surface. This is due to the effect of vibrational zero-point energies and temperature on the barrier height. This is more clearly seen from Table V, which gives the barrier heights at the electronic potential energy surface ($E$), including zero-point energy differences ($E_{\text{act}}$), and including temperature effects ($E_{\text{act}}$). $E_{\text{act}}$ is given by the slope of Arrhenius plots, which are shown in Figs.

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**TABLE III.** Vibrational frequencies, $v_i$ (cm$^{-1}$), of the CS, the TS, and the CC'S, of the 7- and 13-atom cluster models.

<table>
<thead>
<tr>
<th>System</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
<th>$v_5$</th>
<th>$v_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>1663</td>
<td>742</td>
<td>246</td>
<td>683</td>
<td>171</td>
<td>32</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>573</td>
<td>421</td>
<td>246</td>
<td>167</td>
<td>75</td>
<td>32</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>2166</td>
<td>1082</td>
<td>380</td>
<td>187</td>
<td>177</td>
<td>142</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>1635</td>
<td>551</td>
<td>530</td>
<td>465</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>531</td>
<td>421</td>
<td>336</td>
<td>233</td>
<td>75$^*$</td>
<td>28</td>
</tr>
<tr>
<td>Co$_7$/CCH$_3$</td>
<td>2040</td>
<td>950</td>
<td>354</td>
<td>187$^*$</td>
<td>177$^*$</td>
<td>121</td>
</tr>
<tr>
<td>Co$_{13}$/CCH$_3$</td>
<td>1001</td>
<td>895</td>
<td>438</td>
<td>365</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co$_7$/CCH$_3$</td>
<td>537</td>
<td>427</td>
<td>286</td>
<td>118</td>
<td>100$^i$</td>
<td>46</td>
</tr>
<tr>
<td>Co$_{13}$/CCH$_3$</td>
<td>2274</td>
<td>1058</td>
<td>395</td>
<td>161</td>
<td>153</td>
<td>110</td>
</tr>
<tr>
<td>Co$_7$/CCH$_3$</td>
<td>1068</td>
<td>634</td>
<td>556</td>
<td>529</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co$_{13}$/CCH$_3$</td>
<td>553</td>
<td>427$^b$</td>
<td>348</td>
<td>240i</td>
<td>118$^b$</td>
<td>28</td>
</tr>
<tr>
<td>Co$_{13}$/CCH$_3$</td>
<td>2114</td>
<td>910</td>
<td>340</td>
<td>161$^b$</td>
<td>153$^b$</td>
<td>121</td>
</tr>
</tbody>
</table>

$^*$Modes of the Ni$_7$ cluster.
$^b$Modes of the Co$_7$ cluster.

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**TABLE IV.** Rate constants for CC bond formation ($k_{CC}$) (m$^2$ s$^{-1}$) and CC bond cleavage ($k_{CC}$) (s$^{-1}$) for the 7- and 13-atom cluster models for different temperatures.

<table>
<thead>
<tr>
<th>System</th>
<th>$T$</th>
<th>$k_{CC}$</th>
<th>$k_{CC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>250</td>
<td>5.99$\times$10$^{-17}$</td>
<td>1.64$\times$10$^{-14}$</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>500</td>
<td>1.10$\times$10$^{-11}$</td>
<td>1.81$\times$10$^{-13}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>750</td>
<td>9.10$\times$10$^{-10}$</td>
<td>2.33$\times$10$^{-14}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>1000</td>
<td>9.62$\times$10$^{-9}$</td>
<td>9.07$\times$10$^{-16}$</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>250</td>
<td>4.91$\times$10$^{-9}$</td>
<td>1.36$\times$10$^{-12}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>500</td>
<td>8.62$\times$10$^{-13}$</td>
<td>4.37$\times$10$^{-10}$</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>750</td>
<td>6.80$\times$10$^{-12}$</td>
<td>3.64$\times$10$^{-14}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>1000</td>
<td>2.19$\times$10$^{-10}$</td>
<td>1.13$\times$10$^{-17}$</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>250</td>
<td>4.51$\times$10$^{-18}$</td>
<td>2.21$\times$10$^{-14}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>500</td>
<td>1.60$\times$10$^{-12}$</td>
<td>1.04$\times$10$^{-14}$</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>750</td>
<td>1.56$\times$10$^{-10}$</td>
<td>1.01$\times$10$^{-10}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>1000</td>
<td>1.73$\times$10$^{-9}$</td>
<td>1.08$\times$10$^{-12}$</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>250</td>
<td>3.62$\times$10$^{-16}$</td>
<td>4.55$\times$10$^{-13}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>500</td>
<td>1.93$\times$10$^{-11}$</td>
<td>5.23$\times$10$^{-10}$</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>750</td>
<td>9.94$\times$10$^{-10}$</td>
<td>1.42$\times$10$^{-10}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>1000</td>
<td>8.05$\times$10$^{-9}$</td>
<td>2.51$\times$10$^{-9}$</td>
</tr>
</tbody>
</table>

---

**TABLE V.** Electronic energy ($E$) (kJ/mol), critical energy ($E_{\text{act}}$) (kJ/mol), activation energy ($E_{\text{act}}$) (kJ/mol), and Arrhenius pre-exponential ($A_{\text{pre}}$) for CC bond formation (m$^2$ s$^{-1}$) and CC bond cleavage (s$^{-1}$) for the 7- and 13-atom cluster models.

<table>
<thead>
<tr>
<th>System</th>
<th>Reaction</th>
<th>$E$</th>
<th>$E_{\text{act}}$</th>
<th>$E_{\text{act}}$</th>
<th>$A_{\text{pre}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>CC bond formation</td>
<td>57</td>
<td>44</td>
<td>52</td>
<td>3.98$\times$10$^{-16}$</td>
</tr>
<tr>
<td>Ni$_7$/CCH$_3$</td>
<td>CC bond cleavage</td>
<td>271</td>
<td>255</td>
<td>260</td>
<td>2.96$\times$10$^{-14}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>CC bond formation</td>
<td>84</td>
<td>73</td>
<td>80</td>
<td>2.81$\times$10$^{-16}$</td>
</tr>
<tr>
<td>Ni$_{13}$/CCH$_3$</td>
<td>CC bond cleavage</td>
<td>150</td>
<td>135</td>
<td>140</td>
<td>1.99$\times$10$^{-14}$</td>
</tr>
<tr>
<td>Co$_7$/CCH$_3$</td>
<td>CC bond formation</td>
<td>55</td>
<td>48</td>
<td>55</td>
<td>1.00$\times$10$^{-10}$</td>
</tr>
<tr>
<td>Co$_7$/CCH$_3$</td>
<td>CC bond cleavage</td>
<td>240</td>
<td>223</td>
<td>228</td>
<td>7.25$\times$10$^{-13}$</td>
</tr>
<tr>
<td>Co$_{13}$/CCH$_3$</td>
<td>CC bond formation</td>
<td>47</td>
<td>40</td>
<td>47</td>
<td>1.81$\times$10$^{-16}$</td>
</tr>
<tr>
<td>Co$_{13}$/CCH$_3$</td>
<td>CC bond cleavage</td>
<td>136</td>
<td>122</td>
<td>126</td>
<td>8.37$\times$10$^{-13}$</td>
</tr>
</tbody>
</table>
the TS is essentially the same. In combination with the computed frequencies, we conclude that our TS is rather tight. The pre-exponentials for CC bond cleavage denote that there is a slight gain in entropy in going from the CC/S to the TS, which seems natural. Inspection of Table III shows that the frequencies of the CC/S are indeed higher than those of the TS.

V. CONCLUSIONS

We have studied the CC coupling of C/CH, C/CH$_2$, and C/CH$_3$ on Ni$_7$ and Ni$_{13}$ cluster models using density functional theory. Formation of CCH$_3$ turned out to be the most exothermic reaction on both clusters. Experimentally, CCH$_3$ frequencies of the CC bond are higher than those of the CC/S, which seems natural. Inspection of Table III shows that the frequencies of the CC/S are indeed higher than those of the TS.

ACKNOWLEDGMENTS

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APPENDIX: DERIVATION OF RATE CONSTANT EQUATIONS

We can write down the following for CC bond formation:

$$
\frac{d}{dt} N_{\text{CC} \text{H}_3} = k_{\text{CC}}^{\text{TST}} N_C N_{\text{CH}_3},
$$

(A1)

where, $N_{\text{CC} \text{H}_3}$ is the number of adsorbed CCH$_3$ molecules, $N_C$ is the number of adsorbed C molecules, and $N_{\text{CH}_3}$ is the number of adsorbed CH$_3$ molecules. $k_{\text{CC}}^{\text{TST}}$ is the transition state theory reaction rate constant given by

$$
k_{\text{CC}}^{\text{TST}} = \frac{k_B T}{h} \frac{Q_1 \cdots Q_{t_s}}{Q_{t_1} Q_{t_2} \cdots Q_{t_s}} e^{-E_{\text{cal}}/k_B T}.
$$

(A2)

The translational partition functions $Q_{t_1}$ and $Q_{t_2}$ can be combined and are of the form...
As written as or equivalently, $k_{\text{TST}}$ can be canceled. Note that the surface area $S$ in Eqs. (A3) and (A6) cancel.

For the CC bond cleavage we can write down the following:

$$\frac{d}{dt} \frac{N_{\text{CCH}_3}}{S} = -k_{\text{C}}^{\text{TST}} N_{\text{CCH}_3}.$$  
(A8)

Here, $N_{\text{CCH}_3}$ is again the number of adsorbed CCH$_3$ molecules, and $k_{\text{C}}^{\text{TST}}$ is the transition state theory rate constant for CC bond cleavage given by

$$k_{\text{C}}^{\text{TST}} = k_B T \frac{Q_{v_1}^V \cdots Q_{v_6}^V}{Q_{v_1}^{V_1} \cdots Q_{v_6}^{V_6}} e^{-\Delta_f^V k_B T}.  \quad (A9)$$

Changing to surface concentrations Eq. (A8) can be written as

$$\frac{d}{dt} \frac{N_{\text{CCH}_3}}{S} = -k_{\text{C}}^{\text{TST}} \frac{1}{S} N_{\text{CCH}_3}.  \quad (A10)$$

or equivalently,

$$\frac{d}{dt} [\text{CCH}_3] = -k_{\text{C}}^{\text{TST}} [\text{CCH}_3].  \quad (A11)$$

or

$$\frac{d}{dt} [\text{CCH}_3] = -k_{\text{C}}^{\text{TST}} [\text{CCH}_3].  \quad (A12)$$

Therefore, $k_{\text{C}}^{\text{TST}}$ and $k_{\text{C}}^{\text{TST}}$ are equivalent.


