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Citation for published version (APA):

Burghgraef, H., Jansen, A. P. J., & Santen, van, R. A. (1995). Electronic structure calculations and dynamics of CC coupling on nickel and cobalt. *Journal of Chemical Physics*, 103(15), 6562-6570.
<https://doi.org/10.1063/1.470383>

DOI:

[10.1063/1.470383](https://doi.org/10.1063/1.470383)

Document status and date:

Published: 01/01/1995

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Electronic structure calculations and dynamics of CC coupling on nickel and cobalt

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(Received 10 March 1995; accepted 13 July 1995)

The carbon-carbon coupling of C (carbide) and CH (methyldyne), C and CH₂ (methylene), and C and CH₃ (methyl) on nickel has been studied with density functional theory using 7- and 13-atom cluster models. Formation of CCH₃ (ethyldyne) turned out to be the most exothermic reaction on both clusters. Experimentally, CCH₃ has been identified unambiguously with a structure perpendicular to the metal surface. Thus for the C/CH₃ coupling forming CCH₃, 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 Ni₇ cluster, 55 kJ/mol for the Co₇ cluster, 84 kJ/mol for the Ni₁₃ cluster, and 47 kJ/mol for the Co₁₃ 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 CH₄ to higher hydrocarbons. A well known method for CH₄ activation is its steam reforming producing CO and H₂ followed by the so-called Fischer-Tropsch synthesis to various hydrocarbons.¹ Whether CH₄ 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 CH₄ is the principal product, while Cu shows no reaction at all.² Kaminsky *et al.*³ have detected CH₃, CH₂, and CH as intermediates on Ni(111). An alternative, direct route is dissociation of CH₄ to CH_x species over a silica supported transition metal catalyst at temperatures between 600–900 K, followed by carbon-carbon coupling and hydrogenation at temperatures around 370 K.⁴ 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 C₁ and C₂ products, while Cu and Pd show no carbon-carbon coupling at all. Goodman and coworkers have identified C, CH, CCH₂ (vinylidene), and CCH₃ on Ru(0001) and Ru(11 $\bar{2}$ 0) for this reaction using HREELS and TPD.⁵ Belgued *et al.*⁶ reported conversion of CH₄ on a Pt-catalyst producing higher hydrocarbons upto C₆ species.

Another important reaction in catalysis is C₂H₄ (ethylene) adsorption and its subsequent decomposition, which is well studied on Pt(111). Various mechanisms for C₂H₄ decomposition have been suggested, but almost all agree on CCH₃ as the main product. Suggested intermediate structures are CHCH₂ (vinyl) and CCH₂,⁷ CH₂CH₃ (ethyl) and CHCH₃ (ethyldiene),⁸ or only CHCH₃⁹ or CHCH₂.¹⁰ Somorjai *et al.*⁸ suggested a further decomposition of CCH₃ to CCH₂ and CCH (ethynyl). However, CCH₃ remains the only species from C₂H₄ decomposition on Pt(111), which has been identified unambiguously by various methods.¹¹ According to Fairbrother *et al.*,¹² studying the reactions of adsorbed CH₃

on Pt(111), CH₃ reacts with H to form CH₄ or dehydrogenates to CH₂ and eventually C as shown by Zaera *et al.*¹³ These species can then form a CC bond. Again, CCH₃ has been identified. According to them, C₂H₄, CH₂CH₃, CHCH₃, and CHCH₂ can all be ruled out, leaving CCH₂ and CCH as the most likely other candidates. For the mechanism of CCH₃ formation Fairbrother *et al.*¹² suggest coupling of C and CH₃.

Zheng *et al.*¹⁴ studied the carbon-carbon coupling reactions of CH₃/CH₃, CH₃/CH₂ and CH₂/CH₂ on Cr(110), Ti(0001), and Co(0001) using tight binding extended Hückel calculations and found a barrier for coupling CH₃/CH₃ and CH₃/CH₂ and an overall endothermicity. In contrast, the coupling between CH₂/CH₂ 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 CH₃/CH₂, 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/CH₂, and C/CH₃ on Rh(111). Except for C/CH₂, 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/CH₃ 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 CCH₃ they predicted a structure perpendicular to the surface, which is also found experimentally,¹⁷ for CCH₂ 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 CCH₂ to CCH₃ they computed a barrier of

203 kJ/mol and an endothermicity of 77 kJ/mol, which suggests no formation of CCH_3 at all, contrary to experiment. Instead, they suggested formation of CCH , which according to them is exothermic by 13 kJ/mol. Carter and Koel¹⁸ estimated surface reaction energies on Pt(111) and used these data to eliminate possible reaction pathways. According to them C_2H_4 adsorbs, isomerizes to CH_3CH , dehydrogenates to CCH_3 , which isomerizes to CH_2CH , 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_2 is the most stable C_1 species and ethylidene (CHCH_3) the most stable C_2 species. Shustorovich *et al.*¹⁹ used a bond order conservation (BOC) model to study among others the decomposition of C_2H_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_2H_4 .

In addition to the abundant data on C_2H_2 and C_2H_4 chemisorption on Pt(111), we have also found some $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ chemisorption experiments on Ni and Co surfaces. According to Lehwald *et al.*²⁰ and Demuth,²¹ C_2H_4 directly decomposes to chemisorbed C_2H_2 on Ni(111), while CCH is formed on Ni(110), according to Strosio *et al.*²² Zaera *et al.*²³ studied C_2H_4 decomposition on Ni(100) and found evidence for CHCH_2 formation. By raising the crystal temperature, they found evidence for subsequently CHCH , CCH , and C . Zhu *et al.*²⁴ showed the existence of CCH_3 on Ni(111) at high coverages of CHCH and CH_2CH_2 . Albert *et al.*²⁵ chemisorbed CHCH and CH_2CH_2 on Co(0001), but found no further reaction of adsorbed CHCH . However, adsorbed CH_2CH_2 decomposed according to them by a simultaneous scission of all CH bonds followed by CC bond scission. Finally, Lapinski *et al.*²⁶ presented ir evidence for CCH_3 formation on a alumina supported nickel catalyst starting from CH_2CH_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_2H_4 decomposition CCH_3 plays an important role. In addition, almost every possible C_2H_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^f) 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:

and

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 *et al.*²⁹ The exchange-correlation potential used is based on quantum Monte Carlo simulations of Ceperley and Alder³⁰ of a homogeneous electron gas which has been parametrized 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 functional³³ in combination with the Stoll correction³⁴ 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 ζ quality, with the exception of the nickel and cobalt d orbitals, which are triple ζ s. On all atoms polarization functions are

FIG. 1. Definition of optimized parameters on a one layer 7-atom cluster (a), and a spherical 13-atom cluster (b). Hydrogen atoms are denoted by diagonally cross-hatched small circles, carbon by a filled black medium circle, and metal atoms by large circles with diagonal lines. The dotted lines denote the C_{3v} axes of the CH_3 group with respect to the CC bond. The MC_1 bond (C), the MC_2 bond (CH_3), the CC bond, and the tilt angle θ were optimized. For both clusters the bond distance of the bulk was used.

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 three-fold 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 CH_x fragments were not allowed to relax, i.e., for all CH_x species we kept the CH distances at 1.08 Å, the HCH angles at 109.48°, the substrate–CH angles of CH_3 at 109.48°, the substrate–CH angles of CH_2 at 125.26° and the substrate–CH angles of CH at 180°.

The TS of CCH_3 was explicitly calculated by a four dimensional grid in the MC_1 , MC_2 , and CC distances and the CH_3 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 MC_1 , MC_2 , and CC distances and θ . The CC^fS was determined by optimizing the MC_1 and CC distances, keeping the product CCH_x at a three-fold site, and keeping substrate–CC angles all at 180° (perpendicular positions). Vibrational calculations were performed using the conventional GF method,³⁸ where G is the kinetic energy matrix and F the force constant matrix. Kinetic properties were calculated according to transition state theory.³⁹

III. ELECTRONIC STRUCTURE CALCULATIONS

Optimal parameters and energies of the CS and the CC^fS of C/CH and C/ CH_2 on Ni_7 and Ni_{13} , together with the CS, the TS and the CC^fS of C/ CH_3 on Ni_7 , Ni_{13} , Co_7 , and Co_{13} are shown in Table I. We conclude that formation of CCH (CC^fS) is endothermic on both clusters by 61–62 kJ/mol. Formation of CCH_2 (CC^fS) and CCH_3 (CC^fS) is strongly exothermic on Ni_7 , but the exothermicity is reduced on Ni_{13} . For the Ni_{13} clusters we also optimized the adsorption energy of CCH_x (CC^fS) as a function of the MC_1 and CC distances for optimal CH distances of CCH_x 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 CCH, CCH_2 , and CCH_3 , respectively), the effect on the adsorption energies was maximal 3 kJ/mol. For the most exothermic reaction, the formation of CCH_3 , we determined the TS on Ni_7 , Ni_{13} , Co_7 , and Co_{13} . We find transition state barriers of 57 kJ/mol on Ni_7 , 84 kJ/mol on Ni_{13} , 55 kJ/mol on Co_7 , and 47 kJ/mol on Co_{13} . 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 Ni_7/CCH_3 with a CC bond of 2.39 Å gives a slightly higher barrier (57 kJ/mol) than the TS of Co_7/CCH_3 with a CC bond of 2.33 Å and a barrier height of

TABLE I. Geometries (Å) and energies (kJ/mol) of the coadsorbed state (CS), the transition state (TS) and the CC-formed state (CC^fS) for the 7- and 13-atom cluster models.

System	R_{MC_1}	R_{MC_2}	R_{CC}	θ	E
$\text{Ni}_7/\text{C/CH}$ (CS)	1.84	1.84	2.88	0.0°	0
Ni_7/CCH (CC^fS)	1.98	3.03	1.31	0.0°	62
$\text{Ni}_7/\text{C/CH}_2$ (CS)	1.84	2.04	2.89	0.0°	0
Ni_7/CCH_2 (CC^fS)	1.90	3.02	1.41	0.0°	–152
$\text{Ni}_7/\text{C/CH}_3$ (CS)	1.84	2.43	2.99	0.0°	0
Ni_7/CCH_3 (TS)	1.81	2.32	2.39	43.3°	57
Ni_7/CCH_3 (CC^fS)	1.85	3.09	1.57	0.0°	–215
$\text{Ni}_{13}/\text{C/CH}$ (CS)	1.80	1.91	6.40	0.0°	0
$\text{Ni}_{13}/\text{CCH}$ (CC^fS)	2.03	3.09	1.31	0.0°	61
$\text{Ni}_{13}/\text{C/CH}_2$ (CS)	1.80	2.04	6.60	0.0°	0
$\text{Ni}_{13}/\text{CCH}_2$ (CC^fS)	1.95	3.07	1.41	0.0°	–14
$\text{Ni}_{13}/\text{C/CH}_3$ (CS)	1.80	2.39	7.05	0.0°	0
$\text{Ni}_{13}/\text{CCH}_3$ (TS)	1.82	2.16	2.15	25.9°	84
$\text{Ni}_{13}/\text{CCH}_3$ (CC^fS)	1.91	3.17	1.56	0.0°	–66
$\text{Co}_7/\text{C/CH}_3$ (CS)	1.77	2.45	3.04	0.0°	0
Co_7/CCH_3 (TS)	1.79	2.30	2.33	43.3°	55
Co_7/CCH_3 (CC^fS)	1.88	3.14	1.58	0.0°	–184
$\text{Co}_{13}/\text{C/CH}_3$ (CS)	1.81	2.41	7.10	0.0°	0
$\text{Co}_{13}/\text{CCH}_3$ (TS)	1.83	2.15	2.09	23.8°	47
$\text{Co}_{13}/\text{CCH}_3$ (CC^fS)	1.96	3.21	1.55	0.0°	–89

55 kJ/mol. The effect is more pronounced on the 13-atom clusters: The TS of $\text{Ni}_{13}/\text{CCH}_3$ has a CC bond distance of 2.15 Å and a barrier height of 84 kJ/mol, whereas the TS of $\text{Co}_{13}/\text{CCH}_3$ 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 MC_1 distance, the MC_2 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^fS state. For Ni_7/CCH_3 the CC bond changes from 1.57 to 2.39 Å, an increase of 0.82 Å in going from the CC^fS to the TS. The barrier height for this CC cleavage reaction is 272 kJ/mol. For Co_7/CCH_3 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 $\text{Ni}_{13}/\text{CCH}_3$ and $\text{Co}_{13}/\text{CCH}_3$ 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/ CH_x showed up the existence of cluster size effects. This can be seen from Table II, which shows the charge on C, C of CH_x , H of CH_x , the CH_x fragment, and on the cluster for all studied systems, together with the difference in energy between the adsorbed C/ CH_x in the ISS and the CS. The large positive energy difference indicates that adsorption in the CS 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^fS shows a positive charge on C (0.33e on Ni_7 , 0.55e on Ni_{13}). Also, the total charge on the cluster is by more than two electrons positive on the CS at Ni_7 (2.06e), and by almost two electrons on Ni_{13} (1.99e). The CH fragment is

TABLE II. Charge (in electrons) on C (q_{C1}), on C of CH_3 (q_{C2}), on H of CH_x (Σq_{H}), on CH_x (q_{CH_x}), and on M_x (Σq_{M_x}) based on a Mulliken population analysis for the infinitely separated state (ISS) of adsorbed C/CH_x , the coadsorbed state (CS), the transition state (TS) and the CC-formed state (CC^fS), together with the energy difference (kJ/mol) between the ISS and the CS for the 7- and 13-atom cluster models.

System	q_{C1}	q_{C2}	Σq_{H}	q_{CH_x}	Σq_{M_x}	$E_{\text{ISS}} - E_{\text{CS}}$
Ni ₇ /C/CH (ISS)	-0.39	-0.39	0.13	-0.26	0.65	474
Ni ₇ /C/CH (CS)	-0.57	-1.75	0.26	-1.49	2.06	
Ni ₇ /CCH (CC^fS)	0.33	-1.13	0.19	-0.94	0.61	
Ni ₇ /C/CH ₂ (ISS)	-0.39	-0.42	0.30	-0.12	0.51	399
Ni ₇ /C/CH ₂ (CS)	-0.56	-1.59	0.82	-0.77	1.33	
Ni ₇ /C/CH ₂ (CC^fS)	0.04	-1.19	0.60	-0.59	0.55	
Ni ₇ /C/CH ₃ (ISS)	-0.39	-0.30	0.33	0.03	0.36	303
Ni ₇ /C/CH ₃ (CS)	-0.59	-1.53	1.36	-0.17	0.76	
Ni ₇ /CCH ₃ (TS)	-0.60	-1.37	1.30	-0.07	0.67	
Ni ₇ /CCH ₃ (CC^fS)	-0.35	-1.17	1.02	-0.15	0.50	518
Ni ₁₃ /C/CH (ISS)	-0.52	-0.46	0.10	-0.36	0.88	
Ni ₁₃ /C/CH (CS)	-0.65	-1.65	0.31	-1.34	1.99	
Ni ₁₃ /CCH (CC^fS)	0.55	-1.20	0.13	-1.07	0.52	453
Ni ₁₃ /C/CH ₂ (ISS)	-0.52	-0.53	0.28	-0.25	0.77	
Ni ₁₃ /C/CH ₂ (CS)	-0.65	-1.72	0.92	-0.80	1.45	
Ni ₁₃ /CCH ₂ (CC^fS)	0.01	-1.20	0.64	-0.56	0.55	335
Ni ₁₃ /C/CH ₃ (ISS)	-0.52	-0.41	0.27	-0.14	0.66	
Ni ₁₃ /C/CH ₃ (CS)	-0.66	-1.70	1.47	-0.23	0.89	
Ni ₁₃ /CCH ₃ (TS)	-0.58	-1.49	1.42	-0.07	0.65	280
Ni ₁₃ /CCH ₃ (CC^fS)	-0.34	-1.23	1.08	-0.15	0.49	
Co ₇ /C/CH ₃ (ISS)	-0.46	-0.38	0.36	-0.02	0.48	
Co ₇ /C/CH ₃ (CS)	-0.59	-1.55	1.37	-0.18	0.77	300
Co ₇ /CCH ₃ (TS)	-0.55	-1.39	1.32	-0.07	0.62	
Co ₇ /CCH ₃ (CC^fS)	-0.22	-1.21	1.00	-0.21	0.43	
Co ₁₃ /C/CH ₃ (ISS)	-0.60	-0.54	0.45	-0.09	0.69	300
Co ₁₃ /C/CH ₃ (CS)	-0.58	-1.72	1.53	-0.19	0.77	
Co ₁₃ /CCH ₃ (TS)	-0.53	-1.60	1.57	-0.03	0.56	
Co ₁₃ /CCH ₃ (CC^fS)	-0.25	-1.27	1.08	-0.19	0.44	

strongly polarized at the CS and the CC^fS 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 extent at the CC^fS . All these observations hold for C/CH_2 too, but they are less pronounced. It is expected that C/CH attracts more charge than C/CH_2 , resulting in a negatively charged CH_x fragment and a positively charged substrate, but the charge effects seem a bit large. The charge effects at the CC^fS of C/CH and C/CH_2 could have their cause in the restriction of the CC^fS 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/CH_3 the charge is always slightly positive on the metal substrate, slightly negative on the CH_3 fragment, and slightly more negative on C in all cases. This is in line with our expectation. The polarization within the CH_3 fragment is however again very strong. This effect is present at the CS, the TS, and the CC^fS 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/CH_2 , and C/CH_3 on Ni₇ as well as Ni₁₃. The difference is always largest on the 13-atom clus-

ters. Studies on adsorption of H/CH_3 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 CH_3 to adjacent threefold sites. Studies on different coadsorbed positions of C/CH_3 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/CH_3 to adjacent positions. We conclude that when both C and CH_x are adsorbed (CS, TS, or CC^fS), 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/CH_3 .

Carter and Koel¹⁸ estimated surface reaction energies for many C_xH_x species. For the CC coupling of C/CH , C/CH_2 , and C/CH_3 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 Ibach⁴⁰ 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.*¹⁹ is interesting, because they computed chemisorption data of C_xH_x on both Ni(111) and Pt(111). Monocoordinated C_2H_x species with a CC-axis perpendicular to the surface and bicoordinated C_2H_x species with a skewed CC axis have comparable adsorption energies according to the BOC model. For the CC coupling of C/CH , C/CH_2 , and C/CH_3 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/CH_3 , 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 exotherm or even endotherm compared to those of Carter and Koel. For the C/CH_3 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/CH_3 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 13-atom 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^fS) 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

$$k_{\text{CC}}^{\text{f TST}} = \frac{k_{\text{B}}T}{h} \frac{Q_v^{\ddagger}}{Q_{\text{t}}Q_v} e^{-E_{\text{crit}}/k_{\text{B}}T} \quad (3)$$

and for CC bond cleavage by

$$k_{\text{CC}}^{\text{c TST}} = \frac{k_{\text{B}}T}{h} \frac{Q_v^{\ddagger}}{Q_v} e^{-E'_{\text{crit}}/k_{\text{B}}T}. \quad (4)$$

The translational partition function describes the two translations of CH₃, which is a mobile species,³⁶ on the substrate. The connection between $k_{\text{CC}}^{\text{f TST}}$ and k_{CC}^{f} and between $k_{\text{CC}}^{\text{c TST}}$ and k_{CC}^{c} is discussed in the Appendix. To evaluate

$k_{\text{CC}}^{\text{f TST}}$ and $k_{\text{CC}}^{\text{c TST}}$, we need to calculate the translational, vibrational, and rotational partition functions for the CS, the TS and the CC^fS.

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 premisses 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 (θ), the CH₃ tilt perpendicular to the mirror plane, and one internal CH₃ rotation around the internal C_{3v} 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^fS 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 θ . 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 θ . For the CC^fS 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 θ . 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

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

System	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Ni ₇ /C/CH ₃ (CS)	1663	742	683	387		
Ni ₇ /CCH ₃ (TS)	573	421	246	167 <i>i</i>	75	32
Ni ₇ /CCH ₃ (CC f S)	2166	1082	380	187	177	142
Ni ₁₃ /C/CH ₃ (CS)	1633	551	530	465		
Ni ₁₃ /CCH ₃ (TS)	531	421 ^a	336	233 <i>i</i>	75 ^a	28
Ni ₁₃ /CCH ₃ (CC f S)	2040	950	354	187 ^a	177 ^a	121
Co ₇ /C/CH ₃ (CS)	1001	895	438	365		
Co ₇ /CCH ₃ (TS)	537	427	286	118	100 <i>i</i>	46
Co ₇ /CCH ₃ (CC f S)	2274	1058	395	161	153	110
Co ₁₃ /C/CH ₃ (CS)	1068	634	556	529		
Co ₁₃ /CCH ₃ (TS)	553	427 ^b	348	240 <i>i</i>	118 ^b	28
Co ₁₃ /CCH ₃ (CC f S)	2114	910	340	161 ^b	153 ^b	121

^aModes of the Ni₇ cluster.^bModes of the Co₇ cluster.

nickel and cobalt. The imaginary frequency at the TS is dominated by the CC stretch in all cases.

As discussed in Sec. I, CCH₃ has been identified experimentally by various methods. Goodman *et al.*,⁵ Steiniger *et al.*,¹¹ Parmeter *et al.*,⁴² Kesmodel *et al.*,⁴³ Koel *et al.*,⁴⁴ and Skinner *et al.*⁴⁵ give vibrational frequencies of CCH₃ (CC f S) on Ru(1120), Ru(0001), Pt(111), Pd(111), Rh(111), and the organometallic cluster Co₃(CCH₃)CO₉. These groups measured the symmetrical and asymmetrical CH stretch, the symmetrical and asymmetrical scissors mode, and the rocking vibration of the CH₃ 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 Ni₇, Co₇, Ni₁₃, and Co₁₃, respectively. Experimentally they range between 1080–1163 cm^{-1} .^{15,11,33–36} For the MC stretch frequency we found values of 380, 395, 354, and 340 cm^{-1} on Ni₇, Co₇, Ni₁₃, and Co₁₃, respectively. Experimentally they range between 220–600 cm^{-1} .^{15,11,33–36} 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 Ni₇ compared to Co₇ in the temperature range studied, although the barrier height on Ni₇ 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_{crit}), and including temperature effects (E_{act}). E_{act} is given by the slope of Arrhenius plots, which are shown in Figs.

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

System	T	k_{CC}^f	k_{CC}^c
Ni ₇ /CCH ₃	250	$5.99 \cdot 10^{-17}$	$1.64 \cdot 10^{-40}$
Ni ₇ /CCH ₃	500	$1.10 \cdot 10^{-11}$	$1.81 \cdot 10^{-13}$
Ni ₇ /CCH ₃	750	$9.10 \cdot 10^{-10}$	$2.33 \cdot 10^{-04}$
Ni ₇ /CCH ₃	1000	$9.62 \cdot 10^{-09}$	$9.07 \cdot 10^{+00}$
Ni ₁₃ /CCH ₃	250	$4.91 \cdot 10^{-23}$	$1.36 \cdot 10^{-15}$
Ni ₁₃ /CCH ₃	500	$8.62 \cdot 10^{-15}$	$4.37 \cdot 10^{-01}$
Ni ₁₃ /CCH ₃	750	$6.80 \cdot 10^{-12}$	$3.64 \cdot 10^{+04}$
Ni ₁₃ /CCH ₃	1000	$2.19 \cdot 10^{-10}$	$1.13 \cdot 10^{+07}$
Co ₇ /CCH ₃	250	$4.51 \cdot 10^{-18}$	$2.21 \cdot 10^{-34}$
Co ₇ /CCH ₃	500	$1.60 \cdot 10^{-12}$	$1.04 \cdot 10^{-10}$
Co ₇ /CCH ₃	750	$1.56 \cdot 10^{-10}$	$1.01 \cdot 10^{-02}$
Co ₇ /CCH ₃	1000	$1.73 \cdot 10^{-09}$	$1.08 \cdot 10^{+02}$
Co ₁₃ /CCH ₃	250	$3.62 \cdot 10^{-16}$	$4.55 \cdot 10^{-13}$
Co ₁₃ /CCH ₃	500	$1.93 \cdot 10^{-11}$	$5.23 \cdot 10^{+00}$
Co ₁₃ /CCH ₃	750	$9.94 \cdot 10^{-10}$	$1.42 \cdot 10^{+05}$
Co ₁₃ /CCH ₃	1000	$8.05 \cdot 10^{-09}$	$2.51 \cdot 10^{+07}$

2(a)–2(b) for both Ni₇/Co₇ and Ni₁₃/Co₁₃. The intercepts of the Arrhenius plots give the pre-exponentials (A_{plot}), which are also given in Table V. We see that inclusion of zero-point energies lowers barrier heights for both CC bond formation as well as CC bond cleavage, reflecting the relatively low vibrational frequencies at the TS and the relatively high frequencies at the CS and the CC f S. The effect of temperature is the population of excited levels, which affects the TS more strongly than the CS and the CC f S, because of its lower frequencies. The temperature averaged barrier (E_{act}) will therefore be higher than the critical barrier E_{crit} , where only the zero-point energy differences are taken into account. For CC bond formation on Ni₁₃ and Co₁₃ the barrier height at the electronic potential energy surface (E), including zero-point energy differences (E_{crit}), and temperature averaged (E_{act}), is substantially lower on Co₁₃. Therefore, the rate constants on these clusters are far more larger on Co₁₃ than on Ni₁₃ at all temperatures. If there is no entropy of activation, the pre-exponential factor is approximately $10^{-6} \text{m}^2 \text{s}^{-1}$ for CC bond formation, which is a bimolecular surface reaction, and approximately 10^{+13}s^{-1} for CC bond cleavage, which is a unimolecular surface reaction.³⁰ The pre-exponentials for CC bond formation denote therefore that there is essentially no entropy of activation and that thus the entropy in the CS and

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

System	Reaction	E	E_{crit}	E_{act}	A_{plot}
Ni ₇ /CCH ₃	CC bond formation	57	44	52	$3.98 \cdot 10^{-06}$
Ni ₇ /CCH ₃	CC bond cleavage	271	255	260	$2.96 \cdot 10^{+14}$
Ni ₁₃ /CCH ₃	CC bond formation	84	73	80	$2.81 \cdot 10^{-06}$
Ni ₁₃ /CCH ₃	CC bond cleavage	150	135	140	$1.99 \cdot 10^{+14}$
Co ₇ /CCH ₃	CC bond formation	55	48	55	$1.00 \cdot 10^{-06}$
Co ₇ /CCH ₃	CC bond cleavage	240	223	228	$7.25 \cdot 10^{+13}$
Co ₁₃ /CCH ₃	CC bond formation	47	40	47	$1.81 \cdot 10^{-06}$
Co ₁₃ /CCH ₃	CC bond cleavage	136	122	126	$8.37 \cdot 10^{+13}$

FIG. 2. Arrhenius plots for the bimolecular CC formation (k_{CC}^f) and unimolecular CC bond cleavage (k_{CC}^c) on Ni_7/CCH_3 and Co_7/CCH_3 (a), and on Ni_{13}/CCH_3 and Co_{13}/CCH_3 (b). The following markers are used: Δ : k_{CC}^f nickel; ∇ : k_{CC}^f cobalt; $\diamond$: k_{CC}^c nickel; $\square$: k_{CC}^c cobalt. The intercepts reflect the pre-exponentials, the slopes reflect the activation energies.

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^fS to the TS, which seems natural. Inspection of Table III shows that the frequencies of the CC^fS 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 has been identified unambiguously with the CC axis perpendicular to the metal surface. Therefore, we have determined the structure and potential energy surface at the CS, the TS, and the CC^fS of C/CH_3 on Ni_7 , Co_7 , Ni_{13} , and Co_{13} . We find CC coupling 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. This indicates that the barrier for CC bond scission is on all studied clusters very high. Dehydrogenation reactions are therefore more likely to occur than CC bond scission reactions, once the CC^fS is formed. Analysis of the TS shows a dominant contribution of the CC bond to the reaction coordinate,

and the barrier height correlates with the change of the CC bond in going from the CS to the TS and from the CC^fS to the TS. The magnitude of this effect is different for the 7-clusters and the 13-clusters.

Finite cluster size effects were observed for all CC coupling reactions by comparing the charge distributions on C, CH_x , and on the substrate at all studied parts of the potential energy surface, in combination with the energy difference between the adsorbed C/CH_x in the ISS and the CS. For the CC^fS of C/CH and C/CH_2 a possible cause of the positive charge on C is the restriction of geometries perpendicular to the surface. For C/CH_3 the charge is always slightly positive on the substrate, slightly negative on CH_3 , and slightly more negative on C, which is in line with our expectation. However, the polarization within the CH_3 fragment is again very strong. This effect is present at the CS, the TS, and the CC^fS and we feel therefore that the relative energies at these parts of the potential energy surface are comparable. Coadsorption of H/CH_3 showed no finite cluster effects.

We have seen that the rate constant for CC bond formation is a factor 6–13 larger on Ni_7 compared to Co_7 , 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. For CC bond formation on Ni_{13} and Co_{13} the barrier height is always substantially lower on Co_{13} , whether zero-point energies and temperature effects are included or not. Therefore, the rate constants on these clusters are always far more larger on Co_{13} than on Ni_{13} . The TS was shown to be rather tight.

ACKNOWLEDGMENTS

All calculations were performed with the ADF program on the Cray Y-MP4/464 at SARA, Amsterdam. This work has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure and Scientific Research (NWO). The computer time on the Cray Y-MP4/464 was subsidized by the Foundation for the use of supercomputers, National Computing Facilities (NCF).

APPENDIX: DERIVATION OF RATE CONSTANT EQUATIONS

We can write down the following for CC bond formation:

$$\frac{d}{dt} N_{CCH_{3a}} = k_{CC}^{fTST} N_{C_a} N_{CH_{3a}}, \quad (A1)$$

where, $N_{CCH_{3a}}$ is the number of adsorbed CCH_3 molecules, N_{C_a} is the number of adsorbed C molecules, and $N_{CH_{3a}}$ is the number of adsorbed CH_3 molecules. k_{CC}^{fTST} is the transition state theory reaction rate constant given by

$$k_{CC}^{fTST} = \frac{k_B T}{h} \frac{Q_{v_1}^\dagger \cdots Q_{v_5}^\dagger}{Q_{t_1} Q_{t_2} Q_{v_1} \cdots Q_{v_4}} e^{-E_{crit}/k_B T}. \quad (A2)$$

The translational partition functions Q_{t_1} , and Q_{t_2} can be combined and are of the form

$$(2\pi m_{\text{CH}_3} k_B T / h^2) S. \quad (\text{A3})$$

All vibrational partition functions Q_v are of the form

$$\frac{1}{1 - e^{-(h\nu)/(k_B T)}}. \quad (\text{A4})$$

In Eqs. (A2)–(A4), k_B denotes Boltzmann's constant, T temperature, h Planck's constant, E_{crit} the barrier energy including zero-point energy differences, ν the frequency of the particular vibrational mode, S the surface area, and m_{CH_3} the mass of CH_3 . The translational modes of CH_3 enter because CH_3 is a mobile species. As a consequence of our tight TS, the activated CCH_3 is immobile and bound to one specific site. Changing to surface concentrations Eq. (A1) can be written as

$$\frac{1}{S} \frac{d}{dt} N_{\text{CCH}_3a} = k_{\text{CC}}^f \text{TST} S \frac{N_{\text{C}_a}}{S} \frac{N_{\text{CH}_3a}}{S}, \quad (\text{A5})$$

or equivalently,

$$\frac{d}{dt} [\text{CCH}_3]_a = k_{\text{CC}}^f \text{TST} S [\text{C}]_a [\text{CH}_3]_a, \quad (\text{A6})$$

or

$$\frac{d}{dt} [\text{CCH}_3]_a = k_{\text{CC}}^f [\text{C}]_a [\text{CH}_3]_a. \quad (\text{A7})$$

We therefore have $k_{\text{CC}}^f = k_{\text{CC}}^f \text{TST} S$. Note that the surface area S in Eqs. (A3) and (A6) cancel.

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

$$\frac{d}{dt} N_{\text{CCH}_3a} = -k_{\text{CC}}^c \text{TST} N_{\text{CCH}_3a}. \quad (\text{A8})$$

Here, N_{CCH_3a} is again the number of adsorbed CCH_3 molecules, and $k_{\text{CC}}^c \text{TST}$ is the transition state theory rate constant for CC bond cleavage given by

$$k_{\text{CC}}^c \text{TST} = \frac{k_B T}{h} \frac{Q_{v_1}^\dagger \cdots Q_{v_5}^\dagger}{Q_{v_1} \cdots Q_{v_6}} e^{-E'_{\text{crit}}/k_B T}. \quad (\text{A9})$$

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

$$\frac{1}{S} \frac{d}{dt} N_{\text{CCH}_3a} = -k_{\text{CC}}^c \text{TST} \frac{1}{S} N_{\text{CCH}_3a}, \quad (\text{A10})$$

or equivalently,

$$\frac{d}{dt} [\text{CCH}_3]_a = -k_{\text{CC}}^c \text{TST} [\text{CCH}_3]_a, \quad (\text{A11})$$

or

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

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

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