# EVIDENCE FOR ETHYLIDYNE FORMATION ON Ni(111)

X.-Y. ZHU and J.M. WHITE

*Department of Chemistry, University of Texas, Austin, TX 78712, U.S.A.*

Received 20 May 1988; Accepted 11 July 1988

Evidence for ethylidyne formation and decomposition on Ni(111) was found in the thermal decomposition of ethylene and acetylene. The formation of ethylidyne depends critically on the initial acetylene or ethylene coverage: ethylidyne forms in detectable concentrations only when the initial acetylene coverage is above 70% of saturation or when the initial ethylene coverage is above 80% of saturation. This work is related to recent IR evidence for ethylidyne on supported Ni at atmospheric pressure.

## 1. Introduction

The formation of ethylidyne has been studied on many close-packed transition metal single crystal surfaces, including Pt(111) [1–3], Pd(111) [4], Rh(111) [5–7], Ir(111) [8], Ru(0001) [9–11] and $5 \times 20$ reconstructed Pt(100) [12]. In the presence of high CCH or CO coverages, ethylidyne also forms on Rh(100) [13]. Ethylidyne formation on silica and alumina-supported metal catalysts, including $Pt/SiO_2$, $Pd/SiO_2$ [14], $Pt/Al_2O_3$, $Ru/Al_2O_3$, $Rh/Al_2O_3$, and $Pd/Al_2O_3$ [15] has also been reported. While there have been no reports of ethylidyne formation on Ni(111) and other Ni single crystal surfaces, Lapinski and Ekerdt recently reported IR evidence of ethylidyne formation on alumina-supported nickel [16,17], which motivated this SSIMS study.

It has been widely observed that, at around room temperature, ethylene adsorbed on Ni(111) decomposes to di-$\sigma$ bonded acetylene, which further decomposes to CCH, CH, $CH_2$ and surface carbon [18–23]. No other hydrocarbon fragments have been reported to form on Ni(111) from acetylene or ethylene. However, a careful investigation of the reported EELS work shows that there was no evidence for or against the formation of ethylidyne around room temperature from high coverages of acetylene or ethylene dosed at low temperatures [19,20,22,24–26].

In this paper we report SSIMS evidence for ethylidyne formation from acetylene or ethylene saturated Ni(111). Since, at all coverages, adsorbed ethylene decomposes to acetylene on Ni(111), we present mainly results from acetylene. Other details of acetylene and ethylene decomposition on Ni(111) will be published elsewhere [27].

## 2. Experimental

All experiments were performed in a UHV chamber which has been described previously [28]. Base pressure was 3 to $4 \times 10^{-10}$ torr. The Ni(111) sample was a disk 1 cm in diameter and 1.5 mm thick. It was cooled to 90 K by liquid nitrogen and resistively heated to 1400 K. The temperature was measured by a chromel-alumel thermocouple spotwelded to the back of the crystal. The crystal was cleaned by sputtering (3keV $Ar^+$ with $> 2000$ nA current at 120 K for 8 min.) and annealing (1200 K, 8 min.) cycles. The cleanliness was monitored by AES.

$C_2D_2$ (99% atom D, MSD), $C_2H_4$ (99.9%, Linde) and $C_2D_4$ (99% atom D, MSD) were passed through an acetone-dry ice bath and dosed through a 3 mm ID stainless steel tube which terminated 1 cm from the sample surface. The pressure at the center of the directed molecular flux was estimated (based on the accumulation of condensible molecules) to be about 100 times that of the background pressure rise.

Acetylene and ethylene coverages were calibrated using the $H_2$ ($D_2$) TPD area and C/Ni Auger ratio. These calibrations were based on the assumption that the saturation coverage of hydrogen on Ni(111) at 120 K is 1 ML (H/Ni surface atomic ratio of unity) [29]. The AES C/Ni ratios were calibrated by measuring $H_2$ TPD and C/Ni AES ratios for $C_2H_4$ doses that decomposed completely to give $H_2$(g) and C(a). Since the calibration of high coverages was very important in this study, the AES ratios were carefully measured, with about 1% of error.

All the TPSSIMS experiments were done with a temperature ramp rate of 1.3 K/s and TPD with a ramp of 6.3 K/s. The argon ion current used in SSIMS was 4 nA/cm$^2$ rastered across the surface. On our experimental time scale, sputtering did not change the surface concentration.

## 3. Results and discussion

### (1) EVIDENCE OF ETHYLIDYNE FORMATION ON Ni(111)

SSIMS has been successfully applied to the study of ethylidyne formation and decomposition on Pt(111) [30,31], Ru(0001) [32] and K/Pt(111) [33]. In positive SSIMS for all three cases, ethylidyne gives an intense $CH_3^+$ signal, which is proportional to ethylidyne coverage. No other hydrocarbon fragments or parent ethylene contribute significantly to this signal. This secondary ion emission process can be understood intuitively if, during the argon ion bombardment, the C-C bond breaks and gives a $CH_3^+$ ion with high probability. We suppose that this signal (particularly its variations) monitors ethylidyne on Ni(111).

The main positive secondary ions of a $C_2D_2$-covered Ni(111) surface were $Ni^+$, $Ni_2D^+$, $CD_3^+$, $NiC_2D_2^+$, and $D^+$. Other acetylene related ions, with lower intensities, include $C^+$, $CD^+$, $C_2D^+$, $C_2D_2^+$, and $Ni_2^+$. Typical impurity ions ($K^+$, $Ca^+$, $Na^+$, $Al^+$, $NiH_2O^+$, and $Ni(H_2O)_2^+$) were also observed for species with

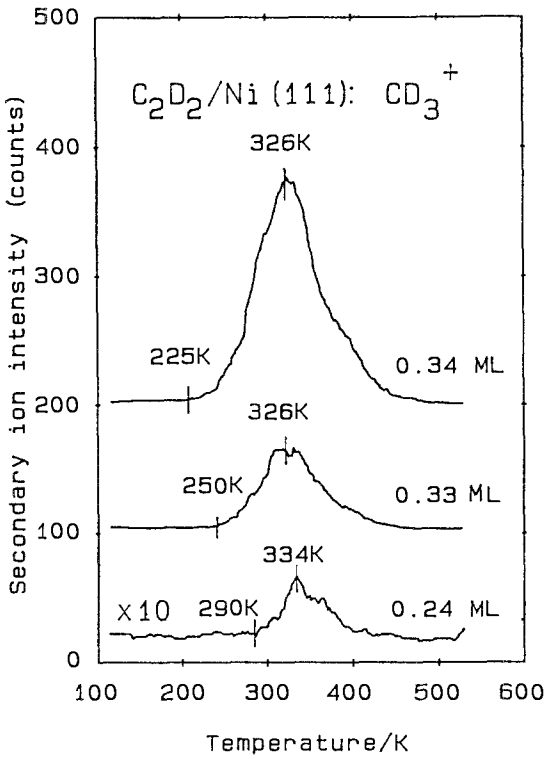


Fig. 1. Temperature programmed SSIMS spectra of $CD_3^+$. Acetylene was dosed through a directed doser for 100 s with background pressure rises of $1.2\times10^{-10}$, $2\times10^{-10}$ and $4\times10^{-9}$ torr respectively. The Ni(111) surface was at 120 K. Using a factor of 100 for the ratio of pressure at the center of the beam to the background pressure rise, the three doses are 1.2 L, 2 L and 40 L respectively. The molecular acetylene coverages are indicated on each curve in terms of the number of acetylene molecules per surface Ni atom.

surface concentrations below the Auger detection limit. The water-containing ions were present only at low temperatures and were from traces of background water adsorption (not seen in TPD).

Figure 1 shows three TPSSIMS spectra of $CD_3^+$ after 1.2 L (0.24 ML), 2 L (0.33 ML), and 40 L (0.34 ML) of $C_2D_2$ was dosed on Ni(111) at 120 K. The $CD_3^+$ peak intensity showed a dramatic coverage dependence. The peak intensity of $CD_3^+$ at 0.33 ML was less than 50% of that at 0.34 ML. Below 0.24 ML, no $CD_3^+$ could be detected. As discussed above, we attribute this signal to ethylidyne.

It has been well established by UPS [34], TPD [18], EELS [20,22], AES and LEED [21] that ethylene adsorbed on Ni(111) decomposes to acetylene at room temperature. SSIMS indicates, for all initial coverages, that this conversion process is actually completed below 240 K [27]. Thus if ethylidyne forms from acetylene, its formation is also expected on the ethylene-satured surface. We cannot rule out the possibility that a small fraction of the ethylidyne forms by

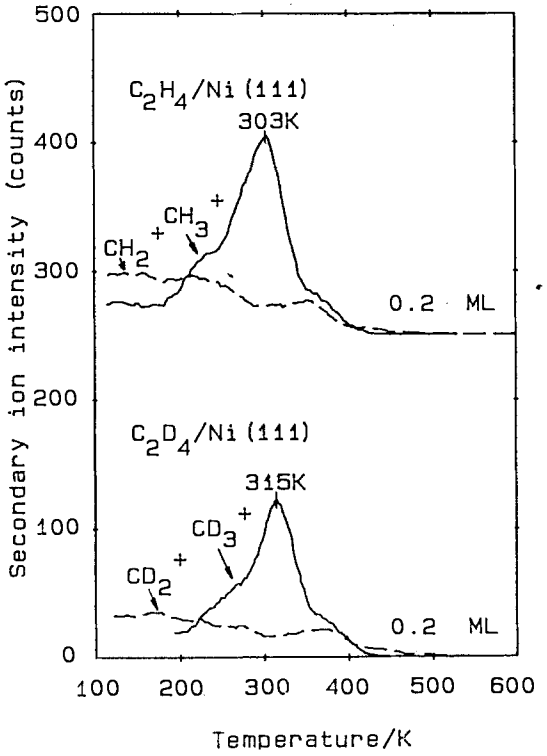


Fig. 2. Temperature programmed SSIMS spectra of $CD_3^+$ and $CD_2^+$ ($CH_3^+$ and $CH_2^+$) derived from ethylene. Both ethylenes were directly dosed at 120 K for 100 s with background pressure rises of $4\times10^{-9}$ torr.

direct rearrangement of ethylene [27]. Figure 2 shows two TPSSIMS spectra of $C_2D_4$ and $C_2H_4$ saturated Ni(111). $CD_3^+$ ($CH_3^+$) and $CD_2^+$ ($CH_2^+$) were followed in the temperature ramp after a saturation dose (40 L) of ethylene (0.20 ML decomposed) at 120 K. $CD_3^+$ ($CH_3^+$) was the most intense hydrocarbon fragment ion between 200 and 400 K. Other carbon- and hydrogen-containing secondary ions, whose intensities were higher than that of $CD_2^+$, were not found. Again, we ascribe the $CD_3^+$ ($CH_3^+$) as a fragment of ethylidyne. Importantly, no $CD_3^+$ ($CH_3^+$) was observed for coverages less than or equal to 0.16 ML.

This interpretation of ethylidyne formation is consistent with a recent report by Lapinski and Ekerdt of IR evidence for ethylidyne formation on alumina-supported Ni [16,17], where ethylene or acetylene was dosed onto hydrogen-covered or hydrogen-free Ni-$Al_2O_3$ at a pressure of 50 torr at 228 K and 248 K. Measurements as a function of temperature showed that ethylidyne was formed between 170 K and 300 K from $C_2H_4$ ($C_2D_4$) or $C_2H_2$ ($C_2D_2$) on hydrogen-covered or hydrogen-free Ni/alumina [17]. Under their experimental conditions ($10^{10}$ langmuirs), the surface was saturated and, because of its stability, the Ni(111) face should dominate the surface of the Ni particles. Ethylidyne bonds

most strongly to 3-fold hollow sites on metal surfaces. This has been shown both experimentally [1–15] and theoretically [35]. There is evidence for some ethylidyne formation on Rh(100) [13]. Recent studies on $Pd/Al_2O_3$ [36] and Rh(331) [37] showed that ethylidyne forms readily only on the (111) facets of Pd catalysts and Rh stepped surfaces. Thus, on $Ni/Al_2O_3$, ethylidyne was formed, most probably, on the (111) facets of the Ni particles.

(2) PATHWAY OF ETHYLIDYNE FORMATION AND DECOMPOSITION ON Ni(111)

As shown in fig. 1, the intensity of the ethylidyne signal shows a strong coverage dependence. This coverage dependence is also shown in the onset temperature of the signal, where $CD_3^+$ sets in at 290 K for 0.24 ML and 225 K for 0.34 ML. Since a 2 L dose (0.33 ML) gave almost saturation coverage, the 40 L dose (0.34 ML) must have simply filled in what few vacancies remained. We conclude that ethylidyne forms and accumulates on Ni(111) only at high acetylene coverages and that the driving force is the strong adsorbate-adsorbate repulsion at high coverages. This can be understood intuitively: A crowded surface will tend to form "standing-up" (in this case, ethylidyne), which occupy less surface area. Support for this is provided by a study on Rh(100) where ethylidyne was observed when the ethylene decomposition product, acetylide, or predosed CO was present in high concentrations [13]. Other evidence was reported by Marinova and Kostov [8] where different pathways of acetylene decomposition on Ir(111) were found and ethylidyne was formed at high coverages.

Comparison of the high temperature sides of the three spectra in fig. 1 reveals a small coverage-dependence in the decomposition of ethylidyne; the $CD_3^+$ signal extends to higher temperatures at higher coverages. The decay of the $CD_3^+$ signal corresponds to the desorption of molecular $D_2$ and decay of the surface deuterium signal (fig. 3). Other studies have shown that surface hydrogen on Ni gives an intense $Ni_2H^+$ signal in SSIMS [28]. Figure 3 shows two TPSSIMS spectra of $Ni_2D^+$ (normalized to $Ni^+$) at 0.24 and 0.33 ML and a $D_2$ TPD spectrum at 0.33 ML.

Since ethylidyne is probably formed from the rehydrogenation of surface acetylene, surface deuterium is consumed in the process. We would expect the surface deuterium concentration during ethylidyne formation to be lower at 0.33 ML than at 0.24 ML because much more ethylidyne is produced in the former. This is consistent with a lower $Ni_2D^+$ peak intensity at 0.33 ML than at 0.24 ML. The onset of the surface deuterium signal in fig. 3 represents the starting temperature of acetylene decomposition. As shown in fig. 3, acetylene starts to decompose earlier at 0.33 ML than at 0.24 ML. Thus, the initial C-H bond cleavage of acetylene is promoted by molecular acetylene.

The surface acetylene signal ($NiC_2D_2^+$), which was observed below 400 K, and a small molecular acetylene desorption below 170 K are not shown here. The maximum amount of decomposed acetylene from a 120 K acetylene saturated Ni(111) was 0.34 ML. This is consistent with literature results [21,23,24]. Details of acetylene decomposition will be published later [27].

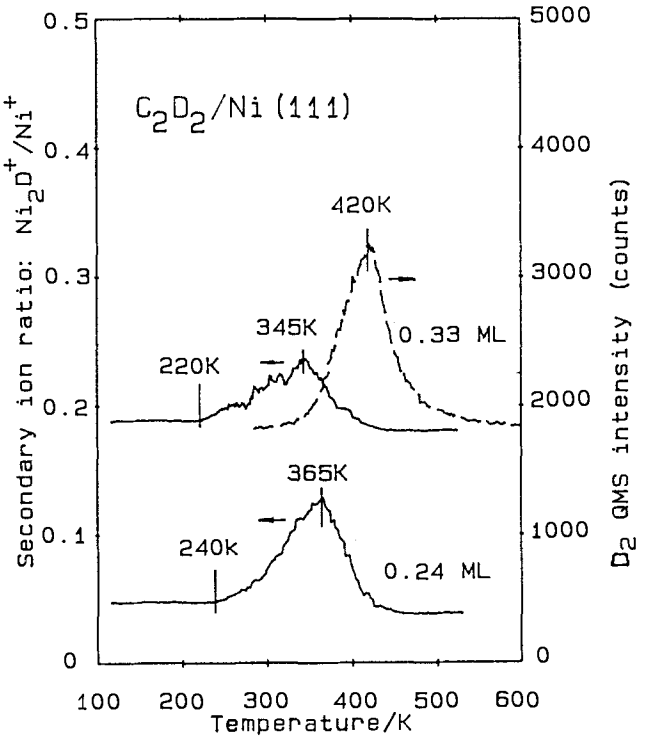


Fig. 3. Temperature programmed SSIMS spectra of $Ni_2D^+/Ni^+$ (solid curves) and temperature programmed desorption of $D_2$ (broken curve) from adsorbed acetylene (0.24 and 0.33 ML). The $Ni_2D^+$ signal is normalized to $Ni^+$ signal, which, to the first approximation removes ion yield variations due to work function changes. Same experimental conditions as fig. 1.

We suggest the following ethylidyne formation and decomposition pathway from acetylene-covered Ni(111) (0.33 ML), similar to that reported on Ru(0001) [10] and Pt(111) [38]:

$$\eta^2 - C_2D_2(a) \xrightarrow{220\text{–}330\ K} \eta^2 - CCD(a) + D(a)$$

$$D(a) + \eta^2 - C_2D_2(a) \xrightarrow{250\text{–}330\ K} \eta^3 - CCD_3(a)(\text{ethylidyne})$$

$$\eta^3 - CCD_3 \xrightarrow{>330\ K} D_2(g) + CCD, CD \text{ or } CD_2 \xrightarrow{600\ K} D_2(g) + C(a).$$

The formation of ethylidyne on Ni(111) from saturation ethylene proceeds via a similar pathway after ethylene decomposes to adsorbed acetylene below 240 K. This ethylidyne formation mechanism from ethylene is different from that reported on Pt(111) and Ru(0001), where there is no evidence for acetylene formation.Rather, the proposed mechanism for forming ethylidyne involves rearrangement of vinyl ($CHCH_2$) or rehydrogenation of vinylidene ($CCH_2$) on Pt(111) (summarized in [33]) and rearrangement of ethylene on Ru(0001) [9,11,32].

As shown in the lower part of fig. 2, $CD_3^+$ from ethylene peaks at 315 K, which

is lower than that from acetylene. This suggests that ethylidyne formation is enhanced by surface deuterium (hydrogen). An isotope effect was also found in the formation and decomposition of ethylidyne, where $CH_3^+$ peaks at 303 K and $CD_3^+$ at 315 K. This suggests that, for decomposition, C-H bond breaking is involved in the rate-determining steps leading to acetylene and surface hydrogen, and finally, to ethylidyne.

The ethylidyne coverage relative to other surface hydrocarbon species could not be determined in our experiments. However, high total coverages are crucial in the formation of ethylidyne. The relative ethylidyne concentration in the HREELS studies reported so far might be low, and this would explain why ethylidyne has not been identified on Ni(111) [19,20,22,24–26]. Further investigation of the coverage dependence of the HREELS spectrum of very high acetylene and ethylene coverages on Ni(111) is necessary to verify the existence of ethylidyne on this surface.

## 4. Summary

In summary, we have presented evidence for the presence of ethylidyne on Ni(111). The $CH_3^+$ ($CD_3^+$) SSIMS signal, which on Pt(111) [31] and Ru(001) [32] monitor ethylidyne, was measured. Ethylidyne was formed during the temperature ramp after saturation amounts of acetylene or ethylene were dosed on Ni(111) at 120 K. As the initial acetylene or ethylene coverage was lowered, the $CH_3^+$ signal dropped sharply and no signal appeared when the surface acetylene was lower than 70% of saturation or the surface ethylene was lower than 80% of saturation. The decomposition of ethylidyne has a small coverage dependence. Surface hydrogen enhances the formation of ethylidyne. Kinetic isotope effects were present in the formation and decomposition of ethylidyne.

## Acknowledgment

We would like to thank M.P. Lapinski, J.G. Ekerdt and M.A. Henderson for helpful discussions. This work is supported in part by the National Science Foundation, Grant CHE8505413.

## References

[1] L.L. Kesmodel, L.H. Dubois and G.A. Somorjai, Chem. Phys. Lett. 56 (1978) 267.
[2] H. Steiniger, H. Ibach and S. Lehwald, Surface Sci. 117 (1982) 685.
[3] P. Skinner, M.W. Howard, I.A. Oxton, S.F.A. Kettle, D.B. Powell and N. Sheppard, J. Chem. Soc., Faraday Trans. II, 77 (1981) 1203.

[4] L.L. Kesmodel and J.A. Gates, Surface Sci. 111 (1981) L747.
[5] L.H. Dubois, D.G. Gastner and G.A. Somorjai, J. Chem. Phys. 72 (1980) 5234.
[6] R.J. Koestner, M.A. Van Hove and G.A. Somorjai, Surface Sci. 121 (1982) 321.
[7] B.E. Koel, B.E. Bent and G.A. Somorjai, Surface Sci. 146 (1984) 211.
[8] Ts.S. Marinova and K.L. Kostov, Surface Sci. 181 (1987) 573.
[9] M.A. Barteau, J.Q. Broughton and D. Menzel, Appl. Surface Sci. 19 (1984) 92.
[10] J.E. Parmeter, M.M. Hills and W.H. Weinberg, J. Am. Chem. Soc. 108 (1986) 3563.
[11] M.M. Hills, J.E. Parmeter, C.B. Mullins and W.H. Weinberg, J. Am. Chem. Soc. 108 (1986) 3554.
[12] G.H. Hatzikos and R.I. Masel, Surface Sci. 185 (1987) 479.
[13] B.E. Bent, Ph.D. Thesis, Uni. of Calif., Berkeley, 1986.
[14] B.J. Brandy, M.A. Chesters, D.I. James, G.S. McDougall, M.E. Pemble and N.J. Sheppard, Philos. Trans. R. Soc. London A 318 (1986) 141.
[15] T.P. Beebe Jr. and J.T. Yates Jr., J. Phys. Chem. 91 (1987) 254.
[16] M.P. Lapinski and J.G. Ekerdt, J. Phys. Chem. 92 (1988) 1708.
[17] M.P. Lapinski and J.G. Ekerdt, to be published.
[18] J.E. Demuth, Surface Sci. 76 (1978) L603.
[19] J.E. Demuth and H. Ibach, Surface Sci. 78 (1978) L238.
[20] S. Lehwald and H. Ibach, Surface Sci. 89 (1979) 425.
[21] M.G. Cattania, M. Simonetta and M. Tescari, Surface Sci. 82 (1979) L615.
[22] J.C. Bertolini and J. Rousseau, Surface Sci. 83 (1979) 531.
[23] G. Casalone, M.G. Cattania, F. Merati and M. Simonetta, Surface Sci. 120 (1982) 171.
[24] L. Hammer, T. Hertlein and K. Muller, Surface Sci. 178 (1986) 693.
[25] J.E. Demuth and H. Ibach, Surface Sci. 85 (1979) 365.
[26] H. Ibach and S. Lehwald, J. Vac. Sci. Technol. 18 (2) (1981) 625.
[27] X.-Y. Zhu and J.M. White, in preparation.
[28] X.-Y. Zhu and J.M. White, J. Phys. Chem. (in press) and the references therein.
[29] K. Christmann, R.J. Behm, G. Ertl, M.A. Van Hove and W.H. Weinberg, J. Chem. Phys. 70 (1979) 4168.
[30] J.R. Creighton and J.M. White, Surface Sci. 129 (1983) 327.
[31] J.R. Creighton, K.M. Ogle and J.M. White, Surface Sci. 138 (1984) L137.
[32] C.M. Greenlief, P.L. Radloff, X.-L. Zhou and J.M. White, Surface Sci. 191 (1987) 93.
[33] X.-L. Zhou, X.-Y. Zhu and J.M. White, Surface Sci. 193 (1988) 387 and the references therein.
[34] J.E. Demuth and D.E. Eastman, Phys. Rev. Lett. 32 (1974) 1132.
[35] J. Silvestre and R. Hoffmann, Langmuir 1 (6) (1985) 621.
[36] T.P. Beebe, Jr. and J.T. Yates, Jr., Surface Sci. 173 (1986) L606.
[37] R. Levis, N. Winograd and L. DeLouise, J. Am. Chem. Soc. 109 (1987) 6873.
[38] N.R. Avery, Langmuir 4(2) (1988) 445.