

THE ADSORPTION AND DECOMPOSITION OF ETHYLENE ON Ni(100)

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The adsorption behavior of ethylene on Ni(100) at a variety of temperatures has been studied using temperature programmed desorption, and X-ray and UV photoemission. The adsorption of ethylene at 98 K results in molecular adsorption with a saturation C/Ni ratio of 0.76. Heating this surface to any temperature between 213 and 683 K reduces the C/Ni ratio to 0.5. Exposure to ethylene at 300 K leads to decomposition producing surface carbide, adsorbed hydrogen atoms and an adsorbed C_xH_{2x} species. A comparison with other work on Ni(111) indicates that ethylene adsorption processes are structure sensitive.

1. Introduction

The identification of the type of bonding, the amount of rehybridization and the surface species formed upon adsorption of ethylene on nickel is important in determining the extent of π -d bonding in hydrocarbon adsorption and catalytic reactions on group-VIII transition metals and has important mechanistic implications for catalytic methanation and Fischer-Tropsch synthesis. The adsorption and decomposition of ethylene on nickel surfaces has been studied extensively using many techniques including surface potential [1], magnetic methods [2,3], field emission [4], IR [5,6], LEED [7,8], TPD [7,8], AES [9,10], UPS [11,12] and HREELS [13]. Interpretation of the existing data is somewhat ambiguous and a clearer picture is certainly desirable.

The present study has two experimental goals.

(1) to determine the overall stoichiometry of the surface species and (2) to characterize the electronic structure of the adsorbed species. The first goal is realized by using XPS to monitor surface carbon coverages and mass spectrometry to monitor molecular hydrogen evolution during ethylene exposure and subsequent temperature programmed desorption, TPD. The second goal is realized by careful XPS and UPS measurements.

2. Experimental

The Ni(100) crystal and the instrumentation are discussed elsewhere [14]. After an initial clean-up, the sample was routinely recleaned following each experiment by heating in 1×10^{-5} Torr of O_2 for 100 s at 1200 K, followed by reduction in $\approx 1 \times 10^{-5}$ Torr of H_2 for 5 min at 1200 K. Auger spectra, taken while the sample cooled from 1200 to 100 K after cleaning, showed no detectable impurities. After several minutes at 100 K and just prior to C_2H_4 exposure, the sample was flashed quickly to 650 K to remove any hydrogen and carbon monoxide adsorbed

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from the background. No more than 200 s elapsed in cooling from 650 to 100 K and beginning the C_2H_4 exposure, during which time the background pressure was 4×10^{-10} Torr.

Ethylene (CP, minimum purity 99.5%, Union Carbide Corp., Linde Div.) was taken from a lecture bottle and passed through a $CO_2(s)$ /acetone trap before dosing. It was introduced into the sample chamber through a stainless steel multichannel array doser nozzle. The sample was positioned directly in front of the doser so the flux to the sample was high and the background pressure could be maintained in the low-to-mid 10^{-8} Torr range thereby reducing H_2 , and other background gas, coadsorption effects.

Standard TPD experiments were done by resistively heating the Ni(100) crystal. In warm-up experiments, the sample, presaturated by exposure to 40 L of C_2H_4 at 100 K, was heated slowly (≈ 60 s) to a desired temperature and then recooled to 100 K for spectroscopic analysis. During heating and cooling the total background pressure never exceeded 6×10^{-10} Torr and calculations indicate that readsorption of ethylene from the background during XPS measurements (30 min/XPS spectrum) was at most a 5% effect.

When the sample was exposed to ethylene at various other temperatures, saturation was reached with a 40 L exposure. When the exposure temperature was 273 K, the sample was cooled to 100 K for analysis. When the exposure temperature was above 310 K, the analysis temperature was 310 K. In both cases, the background pressure was less than 5×10^{-10} Torr.

For UPS, the cylindrical mirror analyzer (CMA) pass energy was 25 eV ($\Delta E = 0.4$ eV) and the spectra were stored digitally using 0.078 eV/channel in a multichannel analyzer (MCA). With respect to the sample normal, the photons were incident at an angle of 77° . The CMA was operated in an angle-integrated mode, the collection angles spanning the range $12-72^\circ$ and averaging 50° . The He I and He II spectra for the warm-up experiments were taken sequentially with the source operated to maximize the intensity of the line used, 182 kHz and 40 kHz at the Ni d-band maximum, respectively.

The XPS spectra were obtained using an Al K α source operated near 600 W (10 kV, 60 mA). With respect to the sample normal, photons were incident

at 67° . The detection geometry was the same as used for UPS. The CMA pass energy was 50 eV ($\Delta E = 0.8$ eV). The total instrument resolution was ≈ 1.2 eV due to the broad (0.9 eV) X-ray source linewidth. The spectra were taken using 0.078 eV/channel at the MCA, stored in a minicomputer and subsequently smoothed using a polynomial least-squares routine [15]. The binding energies (BEs) are referenced to $E_F = 0.0$ eV and the calibration was frequently checked by measuring the position of the Ni(2p $_{3/2}$) peak and defining its BE to be 852.2 eV.

3. Results and discussion

3.1. Temperature programmed desorption (TPD)

Fig. 1 shows several experiments for ethylene adsorption on Ni(100) at various temperatures. This work, and that shown in fig. 2, are part of a more

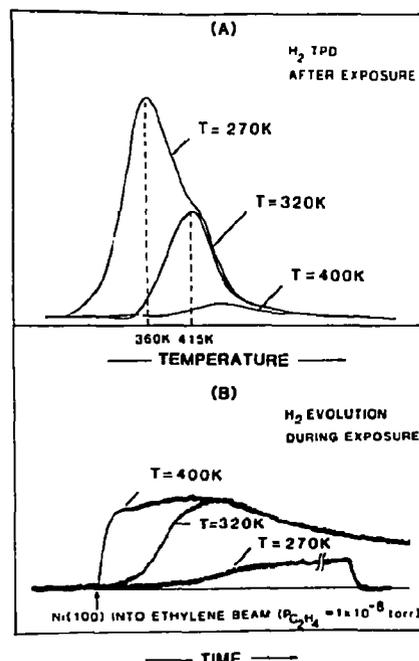


Fig. 1. (A) H_2 TPD spectra following saturation ethylene exposure to Ni(100) at various temperatures as indicated. (B) H_2 evolution during exposure of Ni(100) to ethylene at various temperatures as indicated.

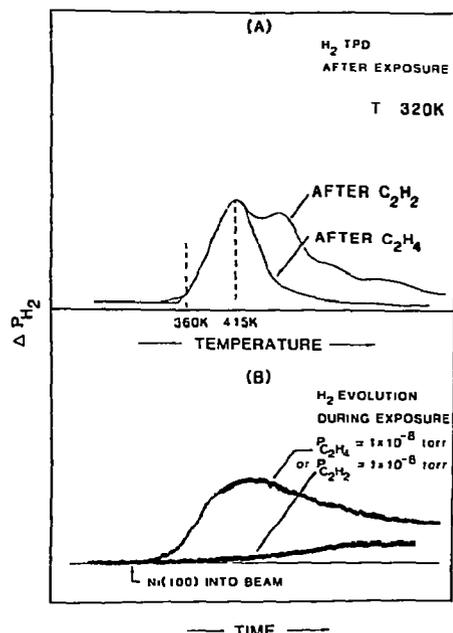


Fig. 2 Comparison of H_2 TPD following exposure (A) and the H_2 evolution during exposure (B), for ethylene and acetylene doses onto Ni(100) at 320 K.

extensive separate study that will be published elsewhere [16]. Fig. 1B shows that for C_2H_4 exposure at 270 K, no detectable H_2 is desorbed initially. Thus the overall initial surface stoichiometry is $H/C = 2$. With continued exposure, some hydrogen is evolved indicating ethylene decomposition. After saturation at 270 K, TPD shows, in fig. 1A, two desorption peaks, 360 and 415 K. The peak at 360 K is due to H(a) on Ni(100) [17,18] and that at 415 K is due to the decomposition of a surface species containing both hydrogen and carbon [16].

Fig. 1B also shows that no H_2 is initially evolved for ethylene exposure at 320 K. However, after an induction period, a significantly larger amount of hydrogen desorbs than when the temperature is 270 K. Subsequent thermal desorption, fig. 1A shows only one desorption peak at 415 K. Ancillary experiments showed that the 415 K desorption peak is populated initially for both 270 and 320 K exposures. The lack of hydrogen evolution with its concomitant filling, determines the stoichiometry of the 415 K desorption state to be C_xH_{2x} . Thus, exposure of

ethylene to Ni(100) at 320 K results in decomposition of the ethylene to form a surface carbide and a C_xH_{2x} species. The total amount of H_2 associated with the 415 K TPD peak is 21% of the saturation amount of hydrogen adsorbed on clean Ni(100) at 270 K ($\theta_H = 0.7$ monolayer (ML), based on the surface density of Ni atoms [19]). Thus, the coverage of surface C_xH_{2x} is less than 0.1 ML.

When the exposure temperature is 400 K, fig. 1 shows that H_2 evolves immediately indicating that the C_xH_{2x} species, giving rise to the 415 K H_2 desorption, is unstable at low coverages and 400 K and decomposes to give H(a) which recombines and desorbs.

When acetylene is exposed to Ni(100) at 320 K, fig. 2B shows that no hydrogen evolution occurs initially. TPD, after saturation exposure, fig. 2A, shows multiple H_2 desorption peaks, one of which (415 K) is like that observed for ethylene, the others indicating the formation and decomposition of a CH_x species which is not a significant contributor in the case of ethylene.

3.2. X-ray photoelectron spectroscopy (XPS)

XPS was used to measure the carbon coverage, θ_C , and to detect chemical changes in the adlayer with sample temperature. Since the XPS core level intensity is directly proportional to the atomic concentration in the surface layer and since no significant change occurs in deep, atomic-like core-level photoemission cross sections for different chemical environments comparison of the total C(1s) intensity from a CO-saturated Ni(100) surface at 98 K with that for adlayers from C_2H_4 adsorption gives an absolute determination of the carbon coverage in the latter. The saturation coverage of CO, $\theta_{CO,sat}$, is 0.69 ML on Ni(100) at 98 K [20]. Intrinsic and extrinsic loss processes which remove intensity from the main peak and give satellite structures were accounted for approximately in these experiments by taking a 20 eV wide spectrum in the C(1s) region and integrating the intensity above a linear background function throughout this range.

Fig. 3 and table 1 summarize the XPS results for several warm-up experiments following a saturation C_2H_4 exposure at 98 K. Compared to the saturation CO signal, the total C(1s) intensity measured for sa-

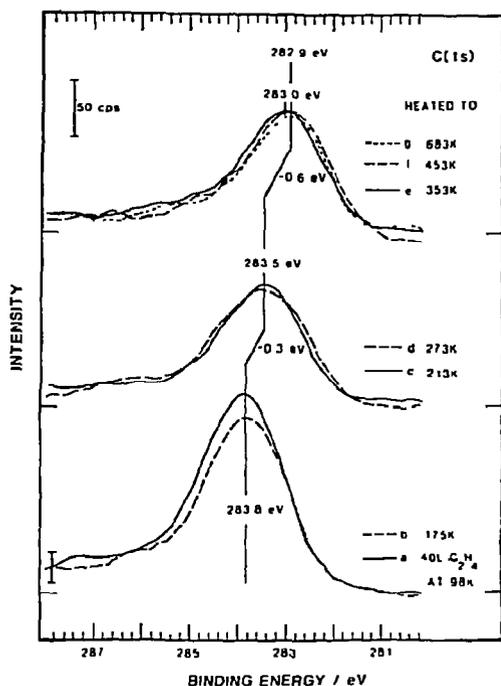


Fig. 3. C(1s) XPS spectra after saturation exposure of C_2H_4 to Ni(100) at 98 K and after incremental heating

turation C_2H_4 at 98 K is 1.10 ± 0.10 giving an absolute carbon coverage of 0.76 ML. Since the adsorption is molecular at this temperature, the saturation

ethylene coverage is 0.38 ML. For Ni(100) then, we have $C_2H_4(\text{sat})/H_2(\text{sat}) = 0.38/0.7 = 0.54$ which is in excellent agreement with published data for ethylene on tungsten [21].

Warming the saturated surface reduces the carbon coverage, presumably due to desorption of ethylene, and θ_C drops to 0.5 ML within experimental error for any temperature between 213 and 683 K. When the clean Ni(100) surface is exposed to C_2H_4 at temperatures 273–683 K, θ_C is always ≈ 0.58 which is larger than reached at these temperatures for the warm-up experiments (0.5), but less than the maximum carbon coverage (0.76) reached for C_2H_4 (a) at 98 K.

We note that ethylene adsorption on Ni(100) gives a $c(2 \times 2)$ LEED pattern at 80 K [12] and at room temperature [10]. Prolonged exposure at room temperature produces a $p(2 \times 2)$ pattern [10]. If the same species were present in these two cases, a $c(2 \times 2)$ pattern having a larger surface concentration should follow the $p(2 \times 2)$. Our results show that the carbon coverage is near 0.5 ML at saturation. This indicates that the $p(2 \times 2)$ structure (coverage = 0.25 ML) is associated either with a species containing two carbons [22], or a significant amount of disordered species when the $p(2 \times 2)$ pattern appears.

The peak positions and full width at half maximum (fwhm) values for the spectra of fig. 3 are also summarized in table 1. Saturation ethylene coverage at 98 K gives a C(1s) peak at 283.8 eV BE. Shifts

Table 1
XPS C(1s) binding energies, peak widths, peak areas and carbon coverages for C_2H_4 on Ni(100)

Condition	C(1s) BE (eV) ^{a)}	fwhm (eV)	Total C(1s) area ^{b)}	θ_C ^{c)}
(a) 40 L C_2H_4 at 98 K	283.8 ± 0.1	2.1 ± 0.1	1.00 ± 0.05	0.76
(b) heated to: 175 K	283.8	2.1	0.88	0.67
(c) 213 K	283.5	2.1	0.61	0.46
(d) 273 K	283.5	2.4	0.63	0.48
(e) 353 K	283.0	2.1	0.63	0.48
(f) 453 K	282.9	2.1	0.61	0.46
(g) 683 K	282.9	2.0	0.58	0.44
(h) 40 L C_2H_4 at 273 K	283.4	2.3	0.76	0.58
(i) 353 K	282.9	2.0	0.68	0.55
(j) 453 K	283.0	2.0	0.80	0.61
(k) 683 K	283.0	2.1	0.80	0.61

a) Referenced to $E_F = 0.0$ eV and Ni $2p_{3/2} = 852.2$ eV BE

b) Normalized to unity for condition (a).

c) Referenced to $\theta_{CO} = 0.69$ ML for saturation CO adsorption and 98 K [22]

are observed in two regions for both the warm-up and saturation exposure experiments. (1) between 175 and 213 K and (2) between 273 and 353 K. The peaks at 283.8 and 282.9 eV BE are identified with molecularly adsorbed C_2H_4 and a surface carbide, respectively. The fwhm of all the peaks is nearly constant at 2.1 eV, except for spectra taken at 273 K, indicating that only one type of surface carbon dominates at the various sample temperatures. This result is only qualitative because the BE shifts which occur in hydrocarbon decomposition processes are small so that species present in small concentration cannot be resolved.

As noted above, the situation at 273 K is somewhat different. Here, the fwhm of the C(1s) peak is 0.3 eV larger than for the other cases. This is taken as an indication of at least two distinctly different environments for the surface carbon that is present.

Both XPS and UPS (see below) show that distinct changes in the electronic structure occur during warm-up to 213 K or higher. This is attributed to dehydrogenation and is consistent with the TPD results. The XPS peak at 283.5 eV is assigned to a C_xH_{2x} species on the basis of the TPD results. The observed chemical shifts are not explainable in any simple fashion since changes in the final state relaxation with surface condition complicates any interpretation based on charge transfer in the initial state. Thus, the 0.5 eV shift that occurs between 273 and 353 K could indicate different chemical species or simply a change in screening of the core hole due to hydrogen desorption. The latter explanation is consistent with the TPD results which suggest that, at both temperatures, surface carbide and C_xH_{2x} coexist.

3.3. Ultraviolet photoemission spectroscopy (UPS)

Photoemission spectra obtained with He I and He II radiation following saturation exposure to ethylene at 98 K and subsequent warm-ups are shown in figs 4 and 5 respectively. The plots are difference spectra — adsorbate-covered Ni minus clean Ni, without any scaling of intensities. After the 98 K exposure, peaks are located and assigned as follows: π_{CC} , 4.7; π'_{CH_2} , 6.7; σ_{CH_2} and σ_{CC} , 8.4; π_{CH_2} , 9.6; and σ_{CH_2} , 13.1, all in the form [orbital designation, BE(eV)]. In addition, redistributed emission in the Ni d-band region causes sharply decreased intensity

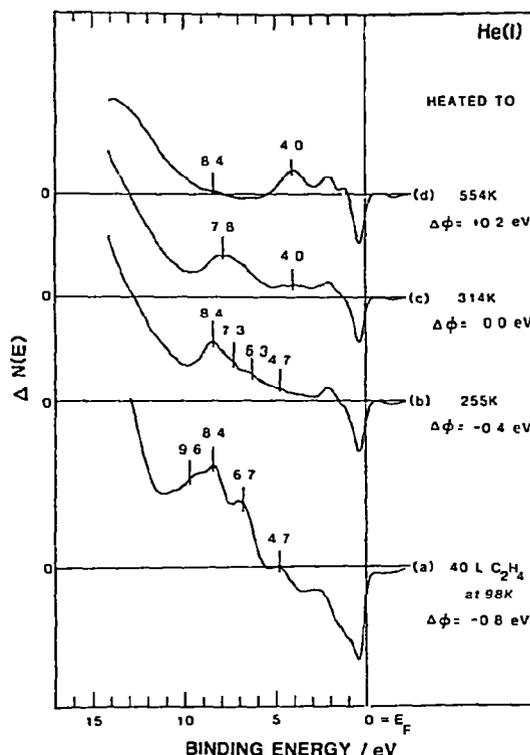


Fig. 4. Photoemission difference spectra $\Delta N(E)$ obtained with He I radiation after saturation exposure at 98 K to C_2H_4 , spectrum (a), and subsequent warm-up to various temperatures, spectra (b)–(d)

around 0.4 eV and a feature at 2.7 eV. The above assignments are consistent with molecular adsorption and were made using the notation of Jorgensen and Salem [23] and by comparison with the gas-phase spectrum [24] assuming that chemisorption does not alter the order of the ionization potentials. The levels observed after chemisorption undergo only small relative shifts from the gas phase with the exception of the highest-lying π level which undergoes a differential shift of 0.4 eV to higher BE upon adsorption. Thus, the bonding is primarily due to a π orbital interaction [25].

Warming the saturated surface to 260 K, figs. 4b and 5b, results in structure between 4.7 and 8.4 eV with the most prominent peak located at 8.4 eV in both He I and He II. In the latter spectrum a peak at 11.2 eV is also observed. Enhanced emission in the

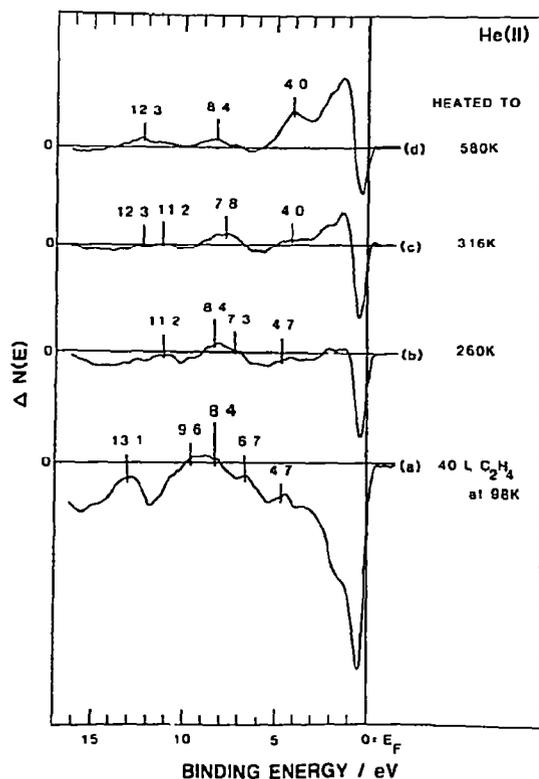


Fig. 5. Photoemission difference spectra obtained with He II radiation after saturation exposure to C_2H_4 and subsequent warm-up as in fig. 4

region around 2 eV is partially due to H(a) and the loss of total intensity reflects the desorption of C_2H_4 during warm-up. Further changes occur during warming to 315 K, figs. 4c and 5c, to give a broad peak in the 11–12 eV region of the He II spectrum and peaks at 7.8 and 4.0 eV in both spectra. Emission in the d-band region of Ni also changed. Heating to 560 K, figs. 4d and 5d, results in peaks located at 12.3, 8.4 and 4.0 eV with increased emission in the d-band region. This spectrum is characteristic of surface carbide.

It is difficult to interpret these spectra in detail, especially since the TPD results indicate the presence of both C_xH_{2x} and surface carbide when the surface is given a saturation exposure at temperatures less than 415 K. However, the results are in qualitative agreement with those of Horn et al. [12] who used the He I in an angle-resolved mode to study C_2H_4

adsorption on Ni(100) at 80 K. In warming from 80 to 273 K, they observed a gradual decrease in total adsorbate intensity and a new peak at 11 eV. In addition they found peaks at 8.3 and 6.6 eV after warming to 273 K. After warming to 273 K the 11 eV peak was accompanied by a broad weak feature lying between 6 and 8.5 eV. Horn et al. [12] also found, like us, that ethylene and acetylene adsorption leads to different species on Ni(100). This contrasts with work on Ni(111) [25,26] which indicates that, at room temperature, the same surface species are formed from both adsorbates. These variations with surface structure are consistent with the TPD results discussed above.

4. Summary

The results of this study may be summarized as follows.

(1) Exposure of C_2H_4 to Ni(100) at 98 K gives molecular adsorption and, at saturation, $\theta_{C_2H_4} = 0.38$ or $\theta_C = 0.76$ ML. Heating to any temperature between 213 and 683 K reduces θ_C to ≈ 0.5 ML due to ethylene desorption.

(2) At 300 K decomposition of ethylene produces a surface carbide, H(a) and a C_xH_{2x} species.

(3) Results which indicate that ethylene and acetylene adsorption give different surface species [12] are confirmed. Since Ni(111) results [25,26] indicate that ethylene and acetylene lead to the same surface species, we conclude that ethylene and acetylene chemisorption and/or reaction is structure sensitive. These results have potential implications for the interpretation of structure-sensitive hydrocarbon reactions.

Acknowledgement

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