

The role of adsorption heats and bond energies in the assignment of surface reaction products: ethyne and ethene on Ni{110}

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Abstract

In order to understand the complex dissociation processes that occur on adsorption of hydrocarbons on surfaces, it is necessary to understand the energetics involved. From investigations of the adsorption of various hydrocarbon species on surfaces, it has been possible to calculate M–C bond energies. These could then be used to calculate the expected adsorption heats for various possible adsorbed species on surfaces for the assignment of adsorbate states from measured heats in conjunction with spectroscopic data. Heats of adsorption and sticking probabilities for C₂H₂ and C₂H₄ on Ni{110} at 300 K have been measured. The initial sticking probability and heat of adsorption for C₂H₂ are 0.8 and 190 kJ mol⁻¹, respectively, while those for C₂H₄ are 0.78 and 120 kJ mol⁻¹. In both cases, CCH species are formed on the surface initially, and for the adsorption of C₂H₂, CH₂ and CH are formed on the surface at higher exposures. Assuming the presence of these species on the surface, a value of the Ni–C bond strength of 191 kJ mol⁻¹ is found. This is in excellent agreement with the average value of 204 kJ mol⁻¹ calculated for hydrocarbon adsorption on the Ni{100} surface previously. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Bond energies; Hydrocarbon

1. Introduction

The study of the interaction of hydrocarbon molecules with transition metal surfaces has been the subject of many catalytic and surface science studies in recent years [1]. In general, many species are formed on the surface at room temperature and the exact identification of these

species can often be problematic. In order to understand the complex dissociation processes that may occur, it is necessary to understand the energetics of the appropriate adsorption processes and a knowledge of the relevant molecule-surface bond energies is essential. This investigation is a continuation of an effort to provide a database of M–C bond energies for hydrocarbon surface reactions. This database, as it becomes more complete, will be increasingly helpful in the prediction of reaction products and will help us to understand why certain reactions proceed on one surface but not on

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another. In addition, it can be used to calculate the expected heat of formation for various species that could be formed upon adsorption of molecules such as ethyne and ethene on a surface. This, together with spectroscopic data, helps with the assignment of measured heat of adsorption values to the formation of various species.

Hydrocarbon adsorption is usually irreversible and therefore, adsorption heats cannot be obtained by isosteric methods. Single crystal adsorption calorimetry [2,3] is thus the only direct technique available for the measurement of heats of adsorption for hydrocarbons on single crystal surfaces. Here, we present measurements of the sticking probability and heat of reaction for ethyne and ethene adsorption on the Ni{110} surface at 300 K. Hydrocarbon adsorption systems previously investigated using the calorimeter include the adsorption of ethene on Pt{110} [4], Pt{111} [6], Pt{100} [5], Ni{100} [7], Pd{100} [7] and Rh{100} [8]. The adsorption of ethyne has been investigated on Ni{100} and Pd{100} [7] and Rh{100} [8]. Results obtained by calorimetry on single crystal surfaces have recently been reviewed [9].

1.1. $C_2H_2/Ni\{110\}$

Various studies of the adsorption of ethyne on Ni{110} have been undertaken in the past [10–15]. The majority of these studies were performed at low temperatures where adsorption of the ethyne molecule is entirely molecular. Stroscio et al. [10] observed that the thermal decomposition of ethyne was more complex than that of ethene and this is supported by the studies of Demuth [13]. Demuth performed ultraviolet photoelectron spectroscopy (UPS) measurements of ethyne on Ni{110} and Ni{100} at 300 K. On Ni{110}, CCH and adsorbed H species were observed at low coverages (< 1.5 L exposure) and with increasing coverage, CH_2 species were also seen on the surface [13]. No evidence for atomic carbon could be found and

hence, it was postulated that CH_2 was formed on the surface via the reaction:



where $HCCH_{2* a}$ is an unstable intermediate. This reaction scheme was supported by the observation that the high coverage species were not formed from the initial CCH_a species, and the amount of H_2 desorbing during temperature programmed desorption (TPD) decreased with increasing exposure of the surface to C_2H_2 . All of the other studies of C_2H_2 adsorption on Ni{110} were performed at low temperature and therefore, no information about species present at 300 K is available.

1.2. $C_2H_4/Ni\{110\}$

Various studies of the adsorption of ethene on Ni{110} have been performed using electron energy loss spectroscopy (EELS), low energy electron diffraction (LEED), TPD, angle resolved ultraviolet photoelectron spectroscopy (ARUPS) and near edge X-ray absorption fine structure (NEXAFS) [10–12,16–18]. Again, most of these measurements were made at low temperature, and show that ethene adsorbs molecularly at low temperatures with no decomposition [10,12,16,17]. However, EELS measurements show that at room temperature ethene decomposes to form a CCH species and adsorbed H [10]. Further heating causes the formation of CH species and finally, above 500 K, a carbide layer is formed on the surface. TPD shows that molecular ethene desorbs from the surface at 270 K [10].

1.3. C_2H_2 and C_2H_4 on Ni{100}

There is one calorimetric study of the adsorption of ethyne and ethene on the Ni{100} surface at 300 K [7]. In this case, for both adsorbates, first CH, and then CCH, species were seen on the surface with increasing coverage. At very high coverage, molecular species were seen on the surface. The initial adsorption heats for

ethene and ethyne were 203 and 264 kJ mol⁻¹, respectively. These were used to obtain a mean value of ~204 kJ mol⁻¹ for the Ni–C bond energy.

2. Experimental

The calorimeter and recent improvements to the instrument design have been described in

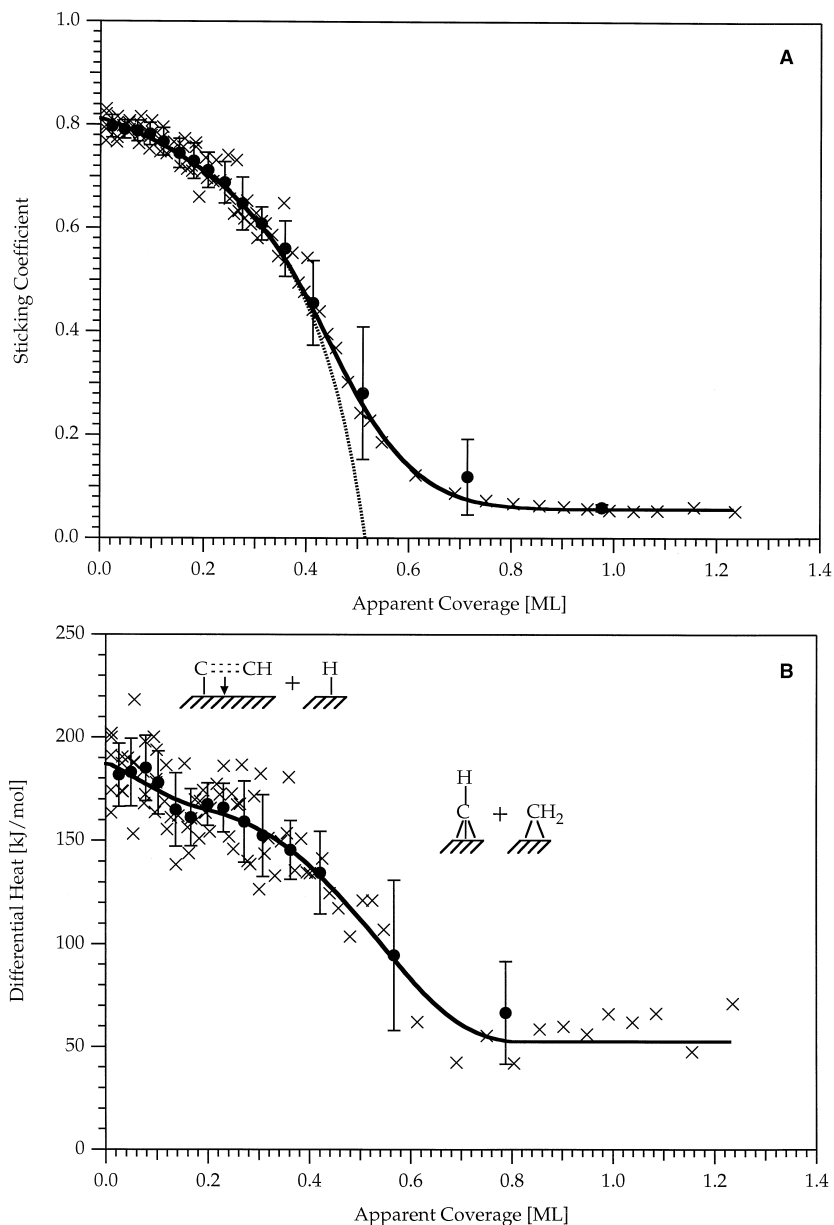


Fig. 1. Sticking probability (A) and heat of adsorption (B) for the reactive adsorption of ethyne on Ni{110} at 300 K. The dotted line in the sticking probability curve is a Kisliuk fit to the data, with $s_0 = 0.81$ and $K = 0.23$. Possible species that are formed on the surface at various coverages are marked on the adsorption heat curve. The CCH species formed on the surface is assumed to bond to the surface via both σ and π interactions. The π interaction is represented on the figure by an arrow which indicates transfer of electron density from the π bond in the CCH species to the surface. The full circles in the heat of adsorption figure indicate an average of 10 data points (data points are indicated by \times). The error bars show the corresponding statistical errors in the averaging process.

detail previously [2,3], and only a brief overview of the technique is given here. Molecules from a pulsed, supersonic molecular beam source are directed at a 200 nm thick single crystal surface which is freely supported in vacuum. The heat

released by the molecules during adsorption results in a temperature rise in the crystal, monitored remotely by a mercury–cadmium–telluride detector. After each run, the detector is calibrated by measuring the heat rise of the

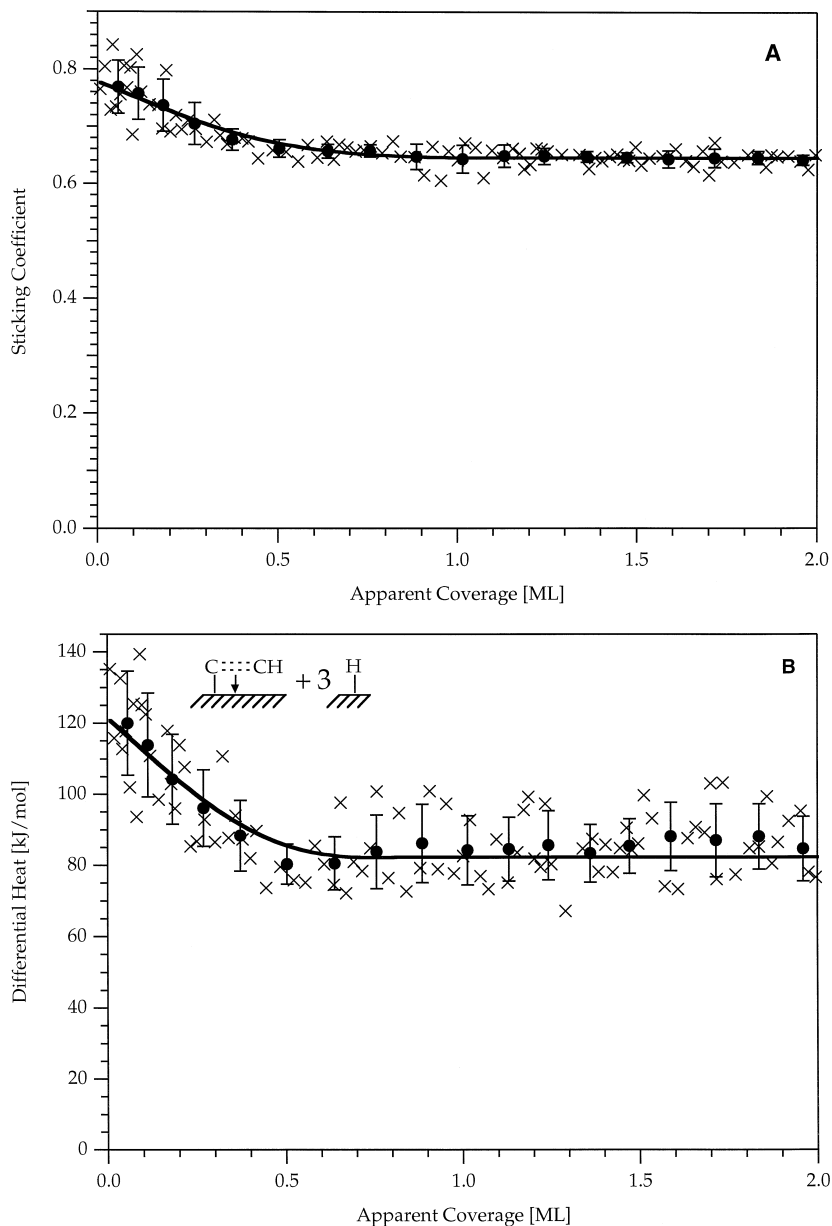


Fig. 2. Sticking probability (A) and heat of adsorption (B) for the reactive adsorption of ethene on Ni{110} at 300 K. Possible species that are formed on the surface at various coverages are marked on the figure. As before, the CCH species formed on the surface is assumed to bond to the surface via both σ and π interactions. The full circles in the heat of adsorption figure indicate an average of 10 data points (data points are indicated by \times). The error bars show the corresponding statistical errors in the averaging process.

sample due to a laser beam of known power impinging on the sample with the same spatial and temporal profile as the molecular beam. The beam intensity is calibrated by a spinning rotor gauge in an accumulation tube which can be moved into the beam path. The sticking probability for each gas pulse is measured using the King and Wells reflection detection method [19]. All measurements were performed in an ultra-high vacuum chamber with a base pressure of $\leq 8 \times 10^{-11}$ mbar. The Ni{110} crystal was cleaned by gentle argon ion sputtering and annealing to ~ 600 K until no contamination could be detected using Auger and sharp LEED spots could be observed.

Each set of data shown in this paper is the result of an average of six individual experimental runs. The scatter between the runs is reflected in the scatter of the data points and in the error bars and reflects the reproducibility of the experiment. The lines shown through the data points are a best fit using an averaging spline through the appropriate points and serve as a guide to the eye. We follow the usual convention and define the differential heat, q , as the negative of the measured enthalpy change.

3. Results

The sticking probability and heat of reaction as a function of coverage for ethyne on Ni{110} at 300 K are shown in Fig. 1. The initial sticking probability is 0.8 ± 0.02 and it drops continuously until a steady state sticking probability of 0.06 is achieved above ~ 0.7 ML coverage. The initial heat of reaction of ethyne on Ni{110} at 300 K is 190 ± 15 kJ mol $^{-1}$. This decreases virtually linearly until a coverage of approximately 0.4 ML is reached, at which point the differential heat is ~ 140 kJ mol $^{-1}$. At this point, there is a marked change in slope and the heat then linearly decreases until a steady state value of 50 kJ mol $^{-1}$ is reached above 0.7 ML coverage.

The steady state sticking probability, and heat, arise due to the desorption of molecules that occurs between pulses of the molecular beam. This leads to an apparent non-zero sticking and heat with increasing coverage. Saturation coverage is taken to be the point where the steady-state sticking and heat first occur, here at 0.7 ML coverage. The saturation coverage found is slightly higher than that of Weinelt et al. [15] who estimated it to be between 0.52 and 0.56 ML.

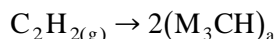
The sticking probability and differential heat as a function of coverage for the adsorption of ethene on Ni{110} at 300 K are shown in Fig. 2. Here, the initial sticking probability is 0.78 ± 0.04 . The sticking decreases surprisingly slowly with increasing coverage until a rather high steady state sticking probability of 0.65 is observed above 0.5 ML coverage. The differential heat for this system has a very similar shape to that of the sticking, with an initial heat value of 120 ± 15 kJ mol $^{-1}$. There is a steady decrease in the heat of adsorption down to a steady state heat value of 80 kJ mol $^{-1}$ above 0.5 ML coverage.

4. Discussion

4.1. $C_2H_2/Ni\{110\}$

Previous measurements of the adsorption of ethyne and ethene adsorption on the Ni{100} surface [7] show that CH and CCH species are formed, and calculations based on the formation of these species gave an average Ni–C bond strength of 204 kJ mol $^{-1}$. Using this value for the Ni–C bond strength, it is possible to calculate the expected heat of adsorption for the species that may form on Ni{110} on adsorption of ethyne at 300 K. Previous measurements on various Pt surfaces [5,9] show that very similar Pt–C bond energies are found on the various surface planes of Pt, whatever the species formed, which supports the notion of using the average value of the Ni–C bond energy derived from Ni{100} to calculate the expected adsorp-

tion energies for various species on Ni{110}. Table 1 shows the expected heats of adsorption for various species that could form on Ni{110} upon adsorption of ethyne. An example of how these values are calculated is shown for the formation of CH on the surface upon adsorption of ethyne. The reaction that occurs is:



The Ni–C bond strength can be calculated in two different ways from the calorimetric data. These two methods are reviewed in a recent paper by Brown et al. [9] and Gross et al. [20]. Here, the magnitude of the Ni–C bond strength is derived from the analysis of the reaction enthalpy for each possible species formed. This is known as the average bond energy (abe) method, and the heat of reaction observed is the difference in energy between the energy liberated by bond formation, and the energy required to break bonds. Values for $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, $\text{C}-\text{C}$ and $\text{C}-\text{H}$ are taken to be 962, 720, 376 and 412 kJ mol^{-1} , respectively [21]. The Ni–H bond strength is 266 kJ mol^{-1} which is calculated from the dissociation energy of H_2 (436 kJ mol^{-1}) and the metal– H_2 bond strength determined by TPD to be 96 kJ mol^{-1} [22]. In this reaction, six Ni–C bonds are formed and one $\text{C}\equiv\text{C}$ bond is broken. Hence, the heat of reaction, ΔH_{rxn} , is given by:

$$\begin{aligned} \Delta H_{\text{rxn}} &= D(\text{C}\equiv\text{C}) - 6D(\text{Ni}-\text{C}) \\ &= -262 \text{ kJ mol}^{-1} \end{aligned}$$

Calculations for the formation of other species on the surface were performed in a similar manner. From Table 1, the species with the energy closest to the measured zero coverage

heat of 190 kJ mol^{-1} for C_2H_2 on Ni{110} are di- σ ethyne and $\text{CCH} + \text{H}$. Adsorbed CH species and CH_2 species are not formed. The formation of adsorbed $\text{CCH} + \text{H}$ species is strongly supported by the UPS study of Demuth [13] which demonstrated the presence of CCH_{a} on the Ni{110} surface at low exposures (< 1.5 L). There is also agreement with the experiments for ethyne adsorption on Ni{100}, where CCH was observed on the surface at higher coverages [7]. The heat at the onset of CCH formation was estimated to be 160 kJ mol^{-1} on the Ni{100} surface. More detailed spectroscopic investigations would clearly be helpful in confirming the exact nature of the species on the Ni{110} surface, since calculations imply that several different species could form.

There is some discussion concerning the nature of adsorbed CCH on Ni [7]. It has been suggested that the structure of CCH on Ni{100} is comparable to that in the organometallic complex $\text{Os}_3(\text{CO})_9(\mu-\text{H})(\text{M}_3-\eta^2-\text{CCH})$ where the C–C π electrons interact strongly with the d electrons of two metal atoms [23]. This requires an estimate of the π interaction which depends on whether the adsorbate species contains a triple or a double bond between the C atoms. The formation of such a species on Ni{110} would account for the difference between the observed initial heat of adsorption (190 kJ mol^{-1}) and the value calculated (224 kJ mol^{-1}) based on the assumption that three σ bonds (and not one, as with the π bonded complex) were formed (see Table 1).

With exposures of ethyne above 1.5 L on the Ni{110} surface, Demuth [11] observed the presence of CH_2 on the surface formed via the

Table 1
Expected heats of adsorption for various possible species that could be formed on Ni{110} upon adsorption of ethyne

Species	2 CH_{a}	$\text{CCH}_{\text{a}} + \text{H}_{\text{a}}$ (three σ bonds)	$\text{CH}_2 + \text{C}_{\text{a}}$	quad- σ ethyne	di- σ ethyne	Measured heat at zero coverage
Adsorption heat (kJ mol^{-1})	262	224	262	230	166	190

The Ni–C bond strength is assumed to be 204 kJ mol^{-1} , the average value determined from investigations of hydrocarbon adsorption on Ni{100} [7].

reaction shown earlier. The calorimetric data shown in Fig. 1 show a marked slope change at a coverage of 0.4 ML, and it is postulated that this is due to the formation of the CH_2 species seen on the surface by Demuth. The heat of reaction at 0.4 ML is 140 kJ mol^{-1} . Assuming then that CH_2 and CH species are formed on the Ni{110} surface above 0.4 ML coverage, the reaction heat of 140 kJ mol^{-1} can now be used to estimate the Ni–C bond energy for the formation of CH_2 and CH species. Using the reaction scheme shown earlier and the values for Ni–H, $\text{C}\equiv\text{C}$ and so on given earlier, this reaction yields a Ni–C bond strength of 191 kJ mol^{-1} , in excellent agreement with the value of 204 kJ mol^{-1} derived for the Ni–C bond strength for hydrocarbon adsorption on Ni{100}. It is somewhat less than that which would result if the formation of CH and CH_2 occurred on the surface at low coverage, due to repulsive interactions between the newly formed CH and CH_2 species and the CCH species already present on the surface.

Having calculated a value for the Ni–C bond energy for hydrocarbon adsorption on Ni{110}, it is now possible to go back and calculate the expected π interaction energy for the CCH species formed initially upon adsorption of ethene on the Ni{110} surface. Assuming that one σ bond and two π bonds are formed, an estimate of the π interaction energy of the adsorbed CCH species can be made. A Ni–C bond energy of 191 kJ mol^{-1} (the value calculated for the formation of CH and CH_2 on the Ni{110} surface) gives a π interaction energy of $70\text{--}190 \text{ kJ mol}^{-1}$. This shows good agreement

with the value derived for CCH formation from ethyne on Ni{100} ($75\text{--}196 \text{ kJ mol}^{-1}$) [7].

Above 0.7 ML coverage, steady state sticking and heat are observed, with the steady state heat of adsorption of about 50 kJ mol^{-1} . This is identified with the adsorption of a π bonded ethyne species on the surface. This species has a short lifetime on the surface at 300 K and desorbs before the next gas pulse is dosed onto the surface. This species was also seen at high coverage on Ni{100} with an adsorption heat of between 40 and 50 kJ mol^{-1} [7].

The sticking probability for the adsorption of ethyne on the Ni{110} surface in the initial phase shows precursor mediated behaviour which has been fitted by the Kisliuk expression [24] as shown in Fig. 1. Fig. 1 shows that there is a deviation from the Kisliuk fit at coverages above approximately 0.4 ML, where CH and CH_2 species begin to be formed on the surface; with the generation of new species, such a deviation is to be expected. The Kisliuk fit gives a saturation coverage of 0.52 ML, but above this coverage the heat of adsorption curve has not reached steady state, demonstrating that true saturation is achieved at a higher coverage. The actual saturation coverage is around 0.7 ML of ethyne, counting its fragments as one species. Above this coverage a steady state sticking probability of 0.06 is observed.

4.2. $\text{C}_2\text{H}_4/\text{Ni}\{110\}$

The adsorption of ethene on the Ni{110} surface is more straightforward than that of ethyne. Table 2 shows the expected heats for various

Table 2

Expected heats of adsorption for various possible species that could be formed on Ni{110} upon adsorption of ethene

Species	$2 \text{ CH}_a + 2\text{H}_a$	$\text{CCH}_a + \text{H}_a$ (three σ bonds)	HCCH_2 (three σ bonds)	di- σ ethene	Measured heat at zero coverage
Adsorption heat (kJ mol^{-1})	212	174	122	64	120

The Ni–C bond strength is assumed to be 204 kJ mol^{-1} , the average value determined from investigations of hydrocarbon adsorption on Ni{100} [7].

species that can be formed on the Ni{110} surface when C₂H₄ is adsorbed. As in Table 1, the value for the Ni–C bond energy was taken to be 204 kJ mol⁻¹. The table suggests that HCCH₂ species are formed on the Ni{110} surface when ethene is adsorbed, but there is no evidence for the presence of this species from previous studies. EELS measurements by Strocio et al. [10] show that ethene decomposes at 300 K to give adsorbed CCH and H on the surface. No other decomposition products were seen on the surface with increasing coverage, although CH species were observed above 400 K. It is, therefore, concluded that CCH is formed on the Ni{110} surface when ethene is adsorbed at 300 K. The shape of the heat of adsorption implies that this is the only species adsorbed on the surface. The initial heat of 120 ± 15 kJ mol⁻¹ compares well with the measured heat of reaction of 133 kJ mol⁻¹ for ethene on Ni{100} at the onset of CCH formation, where it was concluded that π bonding is an important contribution [7]. This suggests that the CCH species formed on Ni{110} also has a large π interaction with the surface. Assuming that one σ bond and two π bonds are formed, an estimate of the π interaction energy of the adsorbed CCH species can be made. A Ni–C bond energy of 191 kJ mol⁻¹ (as derived earlier for the formation of CH and CH₂ species on the Ni{110} surface) gives a π interaction energy of between 62 and 183 kJ mol⁻¹ depending on whether the adsorbed CCH species contains C=C or C≡C. This is in excellent agreement with the π interaction energy values derived for Ni{100} [7] (62–183 kJ mol⁻¹ for ethene adsorption). Crystallographic investigations are required to determine the exact nature of the bonding of CCH to the Ni{110} surface and this would then allow a more exact calculation of the interaction energy of the Ni surface with the hydrocarbon species.

Saturation of the Ni{110} surface apparently occurs above 0.5 ML coverage and beyond this coverage, a steady state heat of 80 kJ mol⁻¹ and a surprisingly high sticking probability of

0.65 are measured. The very high steady state sticking probability at a relatively high coverage can be explained by the presence of a highly mobile (and therefore very efficient) extrinsic precursor state. This precursor state leads, during a 50 ms 1% monolayer gas pulse, to the adsorption of ethene as a π bonded species (giving the observed steady state adsorption heat) which, at coverages above 0.5 ML, then desorbs before the next pulse of gas is dosed onto the surface. Thus, the steady state sticking probability is very high. The initial adsorption may also be precursor mediated, but here an intrinsic precursor state is involved. This leads to the formation of CCH on the surface. Since the sticking probability falls with increasing coverage from 0.78 at zero coverage to 0.7 at 0.4 ML, we conclude that trapping into the intrinsic precursor state at empty sites is more efficient than trapping into the extrinsic precursor state at filled sites.

5. Conclusions

For both the adsorption of ethene and ethyne on the Ni{110} surface at 300 K, the presence of CCH species at low exposures on the surface is postulated. For the adsorption of both hydrocarbon species, it is concluded that CCH is partly σ and partly π bonded to the surface, as is the case for CCH species formed on Ni{100} [7]. At higher exposures of ethyne to the surface, CH₂ and CH species are formed. In both cases, a more complete analysis of the interaction energies could be made if further spectroscopic evidence for the species present on the surface was available. A calculation of the Ni–C bond energy assuming the presence of CH₂ and CH species on the Ni{110} surface gives a value of 191 kJ mol⁻¹. This is slightly smaller than the value derived previously for adsorption of hydrocarbons on the Ni{100} surface [7]. We would expect the M–C bond energy to be larger on Ni{110} than on Ni{100} due to the lower coor-

dination of the metal atoms in the {110} surface. However, this does not take into account any surface relaxation energy. This will be much larger for the {110} surface than for the {100} surface due to the highly corrugated nature of the {110} surface and therefore, counterbalances the effect of surface coordination leading to a lower M–C bond energy for adsorption on the {110} surface.

For the adsorption of both ethyne and ethene on Ni{110}, we have been able to eliminate some surface products from contention by calculating the expected adsorption heats for various possible reaction products (see Tables 1 and 2). However, because initial adsorption in both cases resulted in the formation of a σ – π bonded species, it was not possible to calculate exactly the adsorption heat for the CCH species. This highlights the need to use spectroscopic data in addition to calculating the expected adsorption heats to allow the assignment of adsorption heats to surface species.

For the adsorption of ethene on the Ni{110} surface a very large steady state sticking probability of 0.65 was observed, at an ethene coverage of 0.5 ML. This implies the presence of a highly mobile extrinsic precursor state at high coverages. Trapping at empty sites (probability 0.78) is more effective than at filled sites (probability < 0.7).

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References

- [1] G.A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley, New York, 1994.
- [2] C.E. Borroni-Bird, D.A. King, *Rev. Sci. Instr.* 62 (1991) 2177.
- [3] A. Stuck, C.E. Wartnaby, Y.Y. Yeo, J.T. Stuckless, N. Al-Sarraf, D.A. King, *Surf. Sci.* 349 (1996) 229.
- [4] A. Stuck, C.E. Wartnaby, Y.Y. Yeo, D.A. King, *Phys. Rev. Lett.* 74 (1995) 578.
- [5] Y.Y. Yeo, A. Stuck, C.E. Wartnaby, R. Kose, D.A. King, *J. Mol. Catal. A* 131 (1998) 31.
- [6] Y.Y. Yeo, A. Stuck, C.E. Wartnaby, D.A. King, *Chem. Phys. Lett.* 259 (1996) 28.
- [7] L. Vattuone, Y.Y. Yeo, R. Kose, D.A. King, in preparation.
- [8] R. Kose, W.A. Brown, D.A. King, in preparation.
- [9] W.A. Brown, R. Kose, D.A. King, *Chem. Rev.* 98 (1998) 856.
- [10] J.A. Stroschio, S.R. Bare, W. Ho, *Surf. Sci.* 148 (1984) 499.
- [11] J.E. Demuth, *Surf. Sci.* 84 (1979) 315.
- [12] C.E. Anson, B.J. Bandy, M.A. Chesters, B. Keiller, I.A. Oxtan, N. Sheppard, *J. Elec. Spec. Rel. Phen.* 29 (1983) 315.
- [13] J.E. Demuth, *Surf. Sci.* 93 (1980) 127.
- [14] B.J. Bandy, M.A. Chesters, M.E. Pemble, G.S. McDougall, N. Sheppard, *Surf. Sci.* 139 (1984) 87.
- [15] M. Weinelt, W. Huber, P. Zebisch, H.-P. Steinrück, P. Ulbricht, U. Birkenheuer, J.C. Boettger, N. Rösch, *J. Chem. Phys.* 102 (1995) 9709.
- [16] M. Weinelt, W. Huber, P. Zebisch, H.-P. Steinrück, M. Pabst, N. Rösch, *Surf. Sci.* 271 (1992) 539.
- [17] M. Weinelt, W. Huber, P. Zebisch, H.-P. Steinrück, B. Reichert, U. Birkenheuer, N. Rösch, *Phys. Rev. B* 46 (1992) 675.
- [18] U. Gutdeutsch, U. Birkenheuer, E. Bertel, J. Cramer, J.C. Boettger, N. Rösch, *Surf. Sci.* 345 (1996) 331.
- [19] D.A. King, M.G. Wells, *Surf. Sci.* 29 (1972) 454.
- [20] H. Gross, B.E. Koel, C.T. Campbell, D.A. King, in preparation.
- [21] D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, 73rd edn., CRC Press, Boca Raton, 1992.
- [22] E.M. Stuve, R.J. Madix, *J. Phys. Chem.* 89 (1985) 105.
- [23] F. Zaera, R.B. Hall, *J. Phys. Chem.* 91 (1987) 4318.
- [24] P. Kisliuk, *J. Phys. Chem. Solids* 3 (1957) 95.