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Studies of Adsorption and Surface Reactivity of Metals by Secondary Ion Mass Spectrometry

II. Adsorption of Ethylene on Nickel

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The adsorption of ethylene on nickel was studied by secondary ion mass spectrometry (SIMS) at temperatures 77, 295 and 350 K. Two distinct types of adsorption were observed at 77 K but only one at the higher temperatures. At all temperatures the adsorbed ethylene was found to undergo a series of reactions in which other hydrocarbon species were formed. The results are discussed in terms of those found by other techniques.

INTRODUCTION

Nickel is a widely used catalyst for the hydrogenation of unsaturated hydrocarbons. It is therefore informative to study the interaction of ethylene with a nickel surface since this must be an important step in the hydrogenation reaction.

The results of ir experiments (*1–3*) suggest that ethylene is adsorbed on the surface in the form Ni–CH_2–CH_2–Ni. This is in contrast with the results obtained from photoemission experiments (*4*) where it is suggested that ethylene is bonded to the surface by means of its π bond. Thus some independent method of approach is necessary to ascertain which of these is actually formed.

It has been found by a variety of techniques, including FEM (5), high field magnetic methods (*6*) and ir (*1–2*), that the ethylene on the surface undergoes self-hydrogenation and dimerization even at low temperatures and at higher temperatures the C–C bond is broken. Self-hydrogenation has also been shown to occur by deuterium exchange experiments (*7*).

With the exception of the deuterium exchange experiments, all of the above techniques provide evidence for surface carbide formation at high temperatures. However, there is disagreement about the temperature at which the carbide is formed; the results fall in the range 350–640 K.

The application of SIMS to this system is intended to indicate the scope of this, relatively new, technique. It is hoped that SIMS can confirm, and to a certain extent clarify and extend, the results obtained by other techniques.

METHOD

A description of the SIMS apparatus and its principles of operation are described elsewhere (*8*, *9*). Briefly, it consists of two separately pumped, bakeable chambers, an analytical chamber and a preparation chamber, connected by a gate valve. The sample may be cleaned in the preparation chamber or exposed to gases at pressures up to 1 atm. The SIMS spectra are then obtained by moving the sample to the analysis chamber by means of a UHV bellows system. Gases may be admitted to the sample during analysis at pressures up to 10^{-6} Torr (1 Torr = 133.3 N m^{-2}). Base pressures of 2×10^{-10} Torr are attainable in both of the chambers.

The secondary ions were produced by bombarding the sample with argon ions accelerated to 3 keV. The current density was 10^{-9}–10^{-10} A cm^{-2}.

Argon, both for the primary ion source and for the ion beam etching, was purified by passing it through a sieve trap cooled by a mixture of acetone and solid carbon dioxide.

The 99.99% pure polycrystalline nickel was supplied by Goodfellow Metals and the Specpure ethylene was supplied by B.O.C.

RESULTS

The purity of the ethylene was checked by glc and found to consist of 3 vpm ethane and 0.3 vpm methane.

The system was baked overnight and the nickel sample was cleaned by argon ion etching at 100 μA cm^{-2} for 30 min. A spectrum was run to ensure the cleanliness of the surface; this spectrum is shown in Fig. 1. The peaks in this spectrum at mass numbers 23 and 39 are due to Na^+ and K^+ impurities to which this technique is extremely sensitive. The peaks at 27, 52 and 56 are due to Al^+, Cr^+ and Fe^+; these are due to secondary ions emanating from the stainless steel probe and the aluminum sample clip.

The temperature was then lowered to 77 K and a further spectrum was run to ensure that no impurities had condensed on the sample at the low temperature.

Ethylene was then admitted to the sample in 5 Langmuir doses (1 Langmuir = 10^{-6} Torr s) and a spectrum was run after each dose.

The first dose caused an increase in the intensity of each of the peaks assigned to Ni^+ (mass numbers 58 and 60) and Ni_2^+ (116, 118 and 120). Fairly intense peaks also occurred at mass numbers 86 and 88 which were assigned to $NiC_2H_4^+$. In addition, small peaks were observed at mass numbers 84 and 90 assigned to $^{58}NiC_2H_2^+$ and $^{60}NiC_2H_6^+$ (the other isotope of each of these coincides with one of the peaks due to $NiC_2H_4^+$). After correcting for the isotopic abundance of ^{58}Ni and ^{60}Ni the intensities of the $NiC_2H_2^+$ and $NiC_2H_6^+$ were approximately equal.

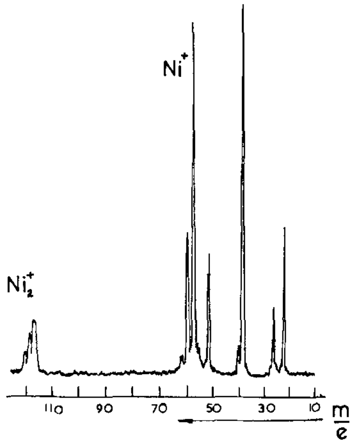

Fig. 1. SIMS spectrum of nickel foil after argon ion etching.

The remaining, less intense, peaks which appeared in the spectrum were assigned to $Ni_2C_2H_4^+$ (mass numbers 144, 146 and 148) $C_2H_x^+$ where x = 1–5 (mass numbers 25, 26, 27, 28 and 29), and CH_y^+ where y = 1–3 (mass numbers 13, 14, and 15); see Fig. 2.

The admission of further doses of ethylene caused new peaks to appear. The intensities of all of the above peaks, except those due to $NiC_2H_2^+$ and $NiC_2H_6^+$, reached a maximum constant value after the admission of about 40 Langmuirs of ethylene. The intensities of the peaks due to $Ni_2C_2H_2^+$ and $Ni_2C_2H_6^+$ remained approximately equal and reached a constant value of about one-tenth of the intensity of the $NiC_2H_4^+$ peaks after the admission of about 50 liters of ethylene. Fig. 3 shows the spectrum obtained after a saturation dose of ethylene had been admitted at 77 K.

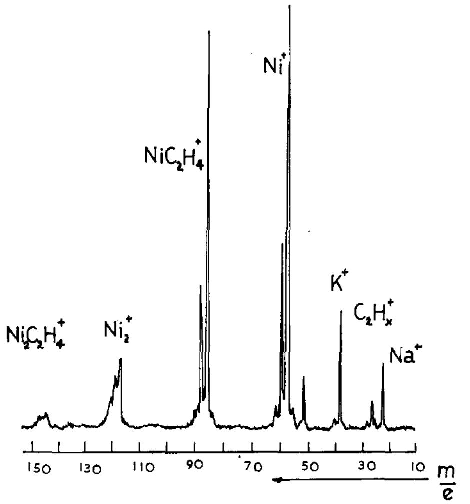

FIG. 2. SIMS spectrum of nickel foil after the admission of 5 Langmuirs of ethylene at 77 K.

On warming the saturated surface to room temperature (over a period of about 30 min) it was found that the peak intensity of Ni^+ increased by about 30% while the $NiC_2H_4^+$ peak intensity decreased to about 10% of its value at 77 K. There was a 30% decrease in the heights of each of the Ni_2^+ and $Ni_2C_2H_4^+$. The peaks due to $C_2H_x^+$ and CH_y^+ disappeared from the spectrum along with those due to $NiC_2H_2^+$ and $NiC_2H_6^+$. No new species appeared in the spectrum. Pumping overnight caused all of the ethylene to be desorbed.

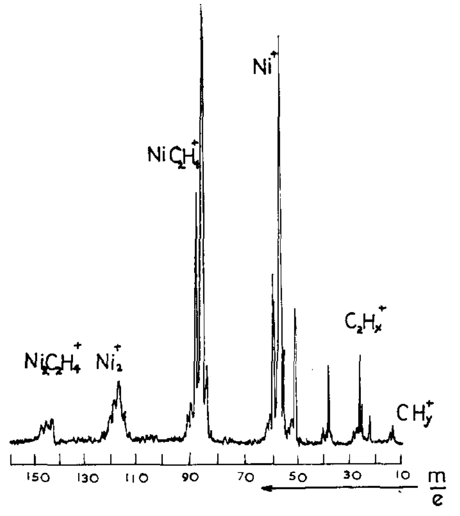

FIG. 3. SIMS spectrum of nickel foil after admission of a saturation dose of ethylene at 77 K.

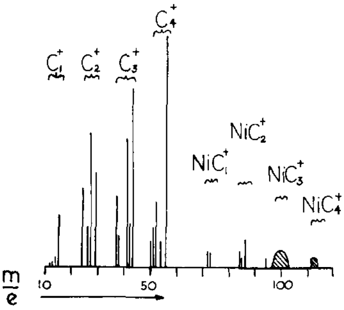

FIG. 4. Diagrammatic SIMS spectrum showing only hydrocarbon species which appeared in the spectrum after exposing the nickel sample to ethylene at 10^{-6} Torr for 1.5 hr at 295 K.

Admitting ethylene to the sample at 295 K caused peaks to appear in the spectrum at mass numbers 86 and 88 which, again, were assigned to $NiC_2H_4^+$. The intensities of these peaks were very much smaller than at 77 K. There were no peaks which could be assigned to $Ni_2C_2H_x^+$ even after flowing ethylene over the surface at 10^{-6} Torr for 1.5 hr.

However, there were peaks which could be assigned to hydrocarbon species and to hydrocarbon species associated with nickel. The diagrammatic spectrum showing the mass numbers and relative intensities of the peaks due to these species is shown in Fig. 4.

A similar experiment was carried out at 350 K but the appearance of the spectra obtained was very similar to that at 295 K; there were no new species and the relative intensities of the peaks were similar.

DISCUSSION

At 77 K two ethylene-containing species were observed in the spectrum. One is due to ethylene associated with one nickel atom and the other is due to ethylene associated with two nickel atoms. It is important to decide whether these are due to two distinct surface species or whether the one is derived

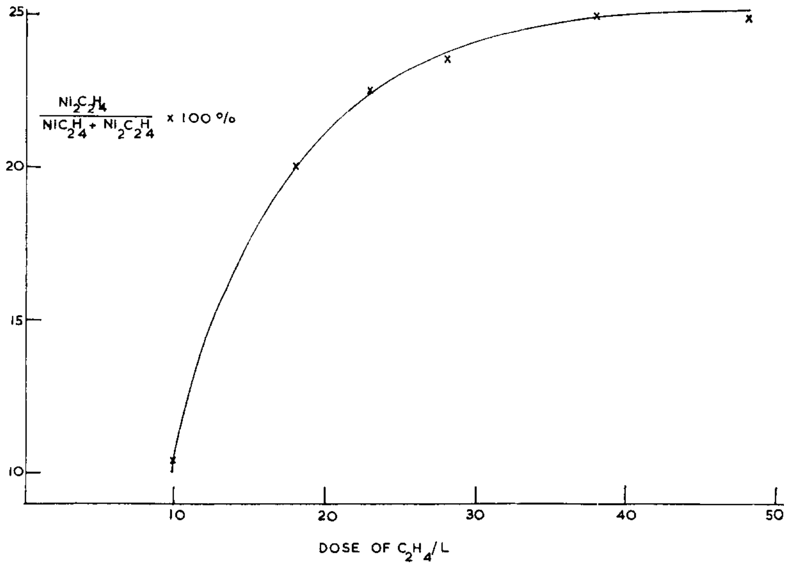

FIG. 5. Variation of the proportion of $Ni_2C_2H_4$ on the surface with dose of ethylene at 77 K.

in some way from the other. It could be argued that the smaller species is due to fragmentation of the larger species caused by the ion bombardment. If this were the case the ratio of the intensities of each of these spectral peaks would be expected to remain constant under all conditions. This is not the case. First, the relative intensity varies with dose at 77 K. Making certain assumptions about the sputtering coefficients, which are outlined elsewhere (*10*), it is possible to make a rough estimate of the relative abundances of each of the two species. Figure 5 shows how, with increasing dose, the amount of C_2H_4 which is adsorbed as $Ni_2C_2H_4$ increases relative to that adsorbed as NiC_2H_4. If the appearance of $NiC_2H_4^+$ in the spectrum were due to fragmentation of $Ni_2C_2H_4^+$ the relative abundances would be independent of dose. Second, adsorption at 295 K does not cause the appearance of $Ni_2C_2H_4^+$. Thus, it is unlikely that framentation is occurring, which implies that there are two distinct types of adsorption.

The type of surface structures formed must now be considered. Although SIMS cannot give direct evidence for this we would suggest that the species $NiC_2H_4^+$ is derived from a structure in which ethylene is bonded to a surface nickel atom by means of its π electrons, as suggested by photoemission (*4*). The $Ni_2C_2H_4^+$ species is derived, we suggest, from a structure in which each of the carbon atoms is bonded to a different nickel atom by means of σ bonds, the structure implied by ir experiments (*2*).

Returning now to Fig. 5, some reason must be suggested for the variation in the abundances of each of the ethylene-containing species with dose at 77 K. The following three possibilities are suggested:

i. There is an equilibrium concentration of each species on the surface and the curve represents the approach to equilibrium, but the rate of adsorption to form NiC_2H_4 is greater than that to form $Ni_2C_2H_4$.

ii. The NiC_2H_4 is decreased due to another surface reaction to which the $Ni_2C_2H_4$ is inert. In order to account for the leveling-off of the curve, this reaction must be reversible.

iii. The adsorption is reversible and the curve represents the ratio of the rates of adsorption to form each species.

Obviously, more work is required on this system to obtain a clear answer to this problem.

It is possible to explain the nonappearance of $Ni_2C_2H_4^+$ in the spectrum at 295 K by invoking thermodynamic arguments. A tentative explanation is that $Ni_2C_2H_4$ is just favored on enthalpy grounds but is disfavored on entropy grounds and, at the higher temperature, where the entropy term has a greater effect, the equilibrium between NiC_2H_4 and $Ni_2C_2H_4$ is very much on the side of the NiC_2H_4. This may be checked by carrying out adsorption studies at intermediate temperatures.

From our spectra it is evident that the adsorbed ethylene undergoes various surface reactions to form other hydrocarbon species.

Even at 77 K there is a small amount of self-hydrogenation and breakage of the C–C bond. This is evident from the peaks observed at mass numbers 84 and 90 and those at 13, 14 and 15. At higher temperatures it appears from our spectra that both C–C and C–H bond breaking and making can occur.

The C_1 and C_2H to C_2H_3 species could have been formed by fragmentation of the ethylene by the argon ion beam. Although the results contained here do not provide incontrovertible evidence that there is no induced fragmentation, two facts indicate that the species observed are those which are present on the surface. First, the hydrocarbon peaks indicate larger, as well as smaller, species than the parent, ethylene-containing, species and they form a fairly continuous series. If fragmentation were occurring only smaller species would be observed. Second, although not strictly comparable, adsorption of ethylene on silver (*11*) produces a SIMS spectrum in which only C_2 species are observed. If ion bombardment caused the appearance of C_1, C_3 and C_4 species in the spectrum obtained from nickel then it is likely that it would cause the appearance of these species on silver as well.

Further evidence to suggest that C_1 and C_4 species occur on the surface comes from hydrogenation experiments (*2*) over nickel in which butane is a major component in the gas phase at 293 K and methane is observed at 373 K. Evidence for self-hydrogenation comes from deuterium exchange work (*7*).

Assuming then, that these hydrocarbon species are present on the surface they must be due to surface reactions of the type

$$2C_2H_{4\,\mathrm{ads}} \rightarrow C_2H_{2\,\mathrm{ads}} + C_2H_{6\,\mathrm{ads}},$$

$$2C_2H_{4\,\mathrm{ads}} \rightarrow C_3H_{6\,\mathrm{ads}} + CH_{2\,\mathrm{ads}},$$

$$2C_2H_{4\,\mathrm{ads}} \rightarrow C_4H_{8\,\mathrm{ads}}, \text{ etc.}$$

Thus it is seen that a brief study by SIMS has provided a good deal of information on the adsorption of ethylene on nickel. Further work is planned to explain the phenomena observed here more fully and to extend the study to one of hydrogenation.

Although there is evidence to suggest that the ion beam does not interfere with the system under investigation it is necessary to undertake several detailed experiments to ensure that the surface is not significantly damaged by the flux of argon ions (10^{-9}–10^{-10} A cm^{-2}). The reproducibility of our results indicates that no real damage occurs but further work is required to ensure that this is the case.

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