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Infrared Spectra of Chemisorbed Molecules

V. Magnetic and Infrared Measurements on Methane, Ethane, Ethylene, and Acetylene Adsorbed on Silica-Supported Nickel

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Magnetic and ir measurements were made on methane, ethane, ethylene, and acetylene adsorbed on a silica-supported nickel catalyst. Adsorption of acetylene at −20 and 25°C and ethylene at −20°C at a low surface coverage on a bare surface did not give any ir absorption bands, although the presence of chemisorbed species followed from a decrease in magnetization. The number of bonds attached to the metal was estimated by comparing the magnetization-volume isotherms of the adsorbed hydrocarbons with that observed for hydrogen; this indicated the presence of the same surface species NiCH=CHNi for ethane, ethylene, and acetylene adsorbed at 25°C on a bare nickel surface. At a higher coverage, the spectra of adsorbed acetylene and ethylene indicated the presence of surface alkyl groups, which could not be derived from magnetic measurements. No ir spectra were obtained for methane and ethane. Hydrogenation of adsorbed acetylene was studied by magnetic and ir measurements at 25°C. At a low surface coverage, the first portion of the hydrogen that was admitted was chemisorbed; hydrogenation resulted from further additions of hydrogen. Adsorption of acetylene and ethylene was also studied on a hydrogen-covered nickel surface. Magnetic measurements indicated a surface reaction accompanied by a decrease in the number of bonds formed between adsorbate and metal surface. Adsorption of acetylene on such a surface gave rise to ir absorption bands at a low surface concentration; except that the intensity at a given surface concentration was higher, the spectrum did not differ from that obtained with a bare surface.

INTRODUCTION

Although there is much information on hydrocarbons adsorbed on metals available (*1–12*), the precise structure and composition of the adsorbed species are still obscure. To help in solving this problem, we carried out magnetic and ir spectroscopy measurements on methane, ethane, ethylene, and acetylene adsorbed on silica-supported nickel catalyst. ir spectroscopy was used to determine the structure of the adsorbed molecules, and magnetic measurements to reveal changes in the properties of the nickel caused by bonding of the hydrocarbons or their fragments (carbon deposition) to the metal surface. These measurements are limited to superparamagnetic, single-domain particles. The number of bonds formed between adsorbate and metal surface is derived from the decrease in magnetization as a function of the amount adsorbed (*13*). The initial slope of the magnetization-volume isotherm of the adsorbate is therefore compared with that observed for hydrogen at 25°C. In addition, it is assumed that each adsorbed hydrogen molecule after dissociation is attached to

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the surface by two bonds, so that the number of adsorbate bonds equals twice the ratio of the slopes. A complicating factor, observed by Martin *et al.* (*14*), is that the number of bonds of adsorbed hydrocarbons is dependent on the strength of the magnetic field, which they explained by a preferential adsorption on the small particles. The low-field approach, as applied in our investigation, is therefore valid only if a catalyst consisting of uniform nickel particles is used. To fulfill this condition as much as possible, a homogeneously precipitated nickel catalyst (*15*) was used which is known to have a fairly narrow particle-size distribution (*16*).

Other uncertain factors in the determination of the number of bonds are, for instance, hydrogen spill-over and back-donation of electrons from the metal to the adsorbed hydrocarbon, if π bonding should occur (*17*). Conclusions concerning the number of bonds should therefore be drawn with caution. It is clear that the information obtained from ir and magnetic measurements is supplementary. This combination of experimental methods applied to the same catalyst sample may therefore lead to a better understanding of the adsorption of hydrocarbons on a nickel-on-silica catalyst.

EXPERIMENTAL

Catalyst Preparation

Aerosil (surface area 170 m^2/g) was boiled in a urea/nickel nitrate solution (*15*). Decomposition of the urea increases the pH, causing precipitation of the nickel. The catalyst was superparamagnetic (*13*) as a linear relationship existed between the magnetization and the reciprocal value of the absolute temperature. The average particle size calculated from hydrogen adsorption data was 1.5 nm (cube root of mean volume) or 2.5 nm (diameter). X-ray line broadening gave 2.6 nm and magnetic susceptibility (*13*) 2.0 nm.

Powdered catalyst samples (1 g) were used for magnetic measurements, and pressed disks (pressure 5 ton, weight 60 mg, diameter 25 mm) for ir measurements. Reduction was carried out for 2 hr at 450°C under H_2 (30 liters/hr), followed by degassing for 2 hr at 400°C (degree of reduction 80%). The time between successive adsorption measurements was 15 min. Gas volumes were calculated under normal conditions (101 kPa, 0°C) per gram of nickel.

Magnetic Measurements

Magnetic susceptibility was measured in a two-coil system analogous to that described by Selwood (*13*) and Geus *et al.* (*18*). One coil contained the sample cell with catalyst, and the other was used to compensate for the induction voltage of the first coil. Each coil consisted of 1000 primary turns (height 29 cm, diameter 74 mm) and 2000 secondary turns (height 21 cm, diameter 55 mm). The field strength was 5251 A/m and the frequency 260 Hz to avoid influences of the 50 Hz mains. Considerable attention was paid to the stability of the compensation; the temperature of the coil systems was kept constant within 0.02°C, using a thermostatic bath filled with silicone oil. The compensation voltage—remaining after counterconnecting the secondary coils—was decreased as much as possible through

—an amplitude compensation, using small auxiliary coils on the outside of the primary coils short-circuited by a variable resistor;

—a phase compensation, by slightly modifying the position of the secondary coils in the magnetic field by means of tightening bars.

The sample cell could be removed from the coils during a gas-adsorption run to check the zero-point drift of the signal of the secondary coils. Stability was sufficient to detect changes well below 1% in the relative magnetization of the samples.

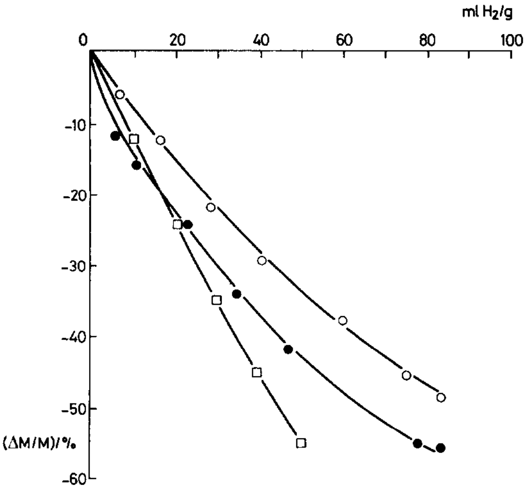


FIG. 1. Magnetization-volume isotherms of hydrogen at 25°C for two samples of nickel (●, ○) and theoretical curve (□).

Signal detection was via a lock-in amplifier (Princeton Applied Research, Model HR 8). For each experiment, the value of the magnetic field was checked by measuring the susceptibility of a sample of ferrous ammonium sulfate (Mohr's salt).

ir Measurements

ir spectra were run on a Grubb–Parsons GS4 double-beam spectrometer (spectral slit width 7 cm^{-1}). Details of the ir cell, which was specifically designed for obtaining spectra during volumetric measurements, have been described earlier (*19*, *20*). A small amount of helium was introduced into the cell to facilitate temperature equilibration of the nickel particles. Gas-chromatographic separations were carried out on a benzyl cyanide/$AgNO_3$ column.

Magnetic Measurements on Pressed Disks

ir measurements were carried out with self-supporting disks and magnetic measurements with powders. To detect any error in the results, comparative magnetic measurements on the adsorption of acetylene were carried out with pressed catalyst disks as well as powders. Hardly any difference was found between the adsorption of acetylene on either adsorbent, except at a surface coverage exceeding 10 ml/g, at which also the residual pressures differed.

RESULTS AND INTERPRETATION

Magnetic Measurements

The theoretical magnetization-volume isotherm (13) (Fig. 1) at 25°C is represented by:

$$\Delta M/M = -13.1 \times 10^{-3} V_{H_2} + 42.8 \times 10^{-6} V^2_{H_2}$$

where $\Delta M/M$ is the relative decrease in magnetization and V_{H_2} the amount of hydrogen adsorbed (ml/g of Ni). The difference between the curves obtained for two

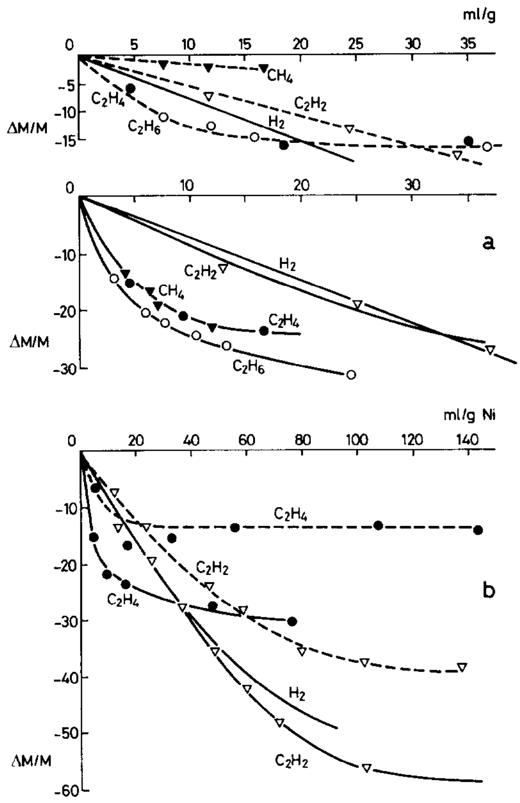


FIG. 2. (a) Initial magnetization-volume isotherms of methane, ethane, ethylene, and acetylene at −20°C (- - -) and 25°C (—). (b) Magnetization-volume isotherms of ethylene and acetylene at −20°C (- - -) and 25°C (—).

catalyst samples (Fig. 1) and the deviation of these curves from the theoretical one must be due to differences in particle-size distribution, although the mean nickel particle size of the catalyst hardly differed. To ensure that changes in magnetization could be ascribed to chemisorption and not to polarization of the adsorbate molecule, krypton was adsorbed onto a hydrogen-covered surface at −20°C ($\Delta M/M = -32\%$). In contrast with the measurements by Selwood (*13*), who observed a loss of magnetization of about 20% of that caused by hydrogen, we did not observe any change. Therefore, all changes in magnetization will be ascribed to changes in the number of bonds, i.e., to chemisorption effects.

Acetylene. The adsorption of acetylene at ambient temperature or lower has been studied by the magnetic method only to a very limited extent (*21, 22*). On determining the magnetization-volume isotherms at −20 and 25°C (Figs. 2a and b), we found that the decrease in magnetization at 25°C (101 kPa) exceeds that of hydrogen. Geus (*23*) has pointed out that the establishment of chemisorptive bonds leads to decoupling of the moments of the surface metal atoms from those of the other metal atoms. To explain the large magnetic effect of acetylene, a magnetic decoupling of nickel atoms in the subsurface layers must therefore be supposed. This requires penetration of species derived from acetylene into the nickel particle. For carbon atoms as such, penetration is difficult, but it is even more difficult for carbon atoms with one or more hydrogen atoms bonded. We therefore assume complete dissociation of at least part of the acetylene into carbon atoms, which penetrate into the bulk nickel, and into hydrogen atoms that either desorb or remain adsorbed on the surface. The self-hydrogenation of acetylene on nickel at −31°C also indicates carbon formation (*9*). Although it was expected that penetration of the carbon atoms would be a function of time, only a further small decrease in magnetization had taken place after 16 hr. We therefore believe that carbon formation hardly affects the number of bonds derived from the initial slope of the magnetization-volume isotherm. The number of bonds formed per molecule at 25°C is about 2.3, which can be ascribed to an associatively adsorbed species like NiCH=CHNi or dissociatively adsorbed HC≡CNi, together with one adsorbed hydrogen atom. In both cases, one would expect 2.0 bonds attached to the surface. At −20°C, 1.4 bonds were formed, whereas Martin and Imelik (*22*) reported 2.0 bonds. Since a species derived from acetylene with less than two σ bonds attached to the surface is difficult to imagine, part of the acetylene must be physically adsorbed, unless a π complex has been formed. Formation of a π complex could, however, not be substantiated by evidence from ir investigations (see below).

In an experiment in which the nickel surface was fully covered with hydrogen (Fig. 3a) and afterwards evacuated (roughly 62.5 ml/g remained), admission of acetylene slightly increased $\Delta M/M$ (from −44 up to −35%), indicating removal of part of the hydrogen by surface hydrogenation, presumably with immediate formation of ethane (cf. ir measurements). The decrease in $\Delta M/M$ to −78% at a higher surface concentration obviously indicates carbon formation as was the case with the adsorption of acetylene on a bare surface at 25°C (Fig. 2b). Adsorption of acetylene at −20°C on a surface partly covered with hydrogen (31.3 ml/g) also shows a maximum followed by a horizontal part near $\Delta M/M = -46\%$; the latter value was also found for hydrogen adsorption only. The total number of bonds formed with the nickel surface remains constant in this region, obviously pointing to physical adsorption of the acetylene; the surface is fully covered and no penetration of carbon atoms into the bulk nickel takes place.

Preadsorption of acetylene (23.1 ml/g) followed by hydrogen admission at 25°C

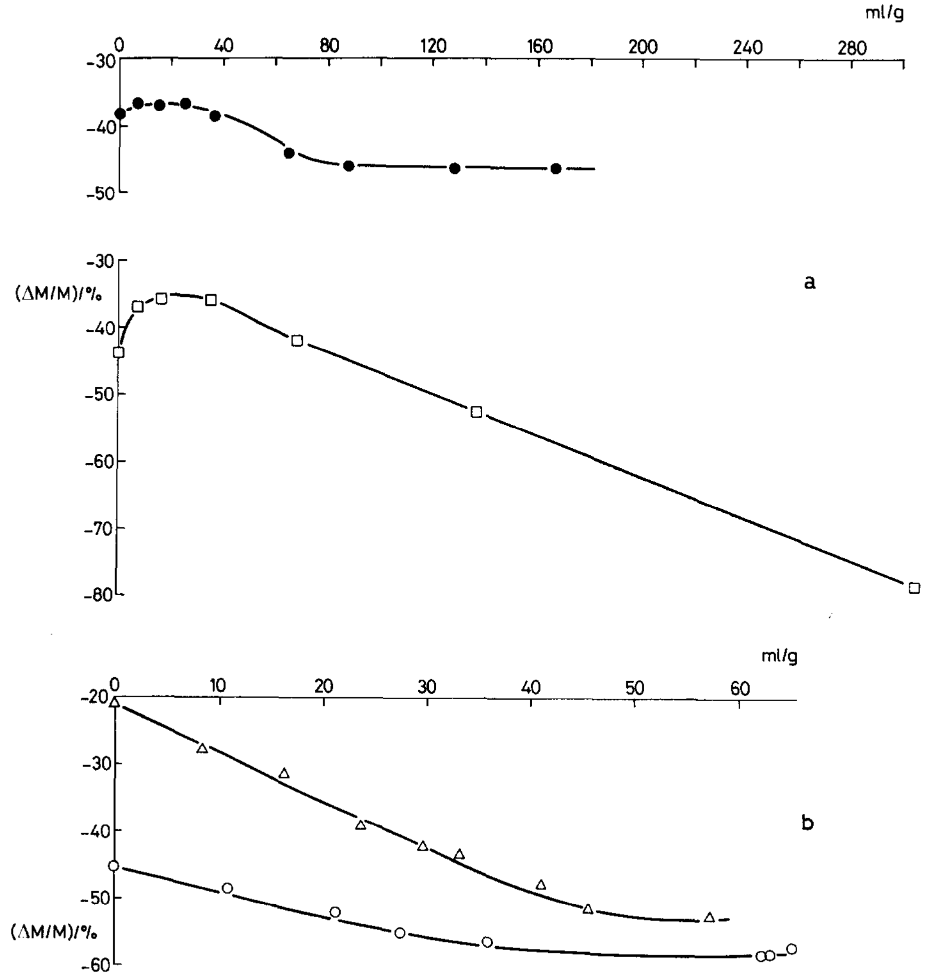


FIG. 3. (a) Magnetization-volume isotherms of acetylene over preadsorbed hydrogen at −20°C (●) and 25°C (□). (b) Magnetization-volume isotherms of hydrogen over preadsorbed acetylene at 25°C, 23.1 ml of acetylene/g (△), 51.9 ml of acetylene/g (○).

decreases $\Delta M/M$ to -53% followed by more adsorption not further lowering the magnetization (Fig. 3b). The initial slope of the magnetization-volume isotherm for hydrogen is somewhat smaller than that of the almost linear isotherm for hydrogen adsorption on a bare nickel surface. Obviously, part of the hydrogen is used for hydrogenation of the surface species, the rest being adsorbed on bare sites. At a preadsorption of 51.9 ml of acetylene/g, the initial slope of the magnetization-volume isotherm is further reduced, indicating that still more hydrogen was consumed for hydrogenation. This may simply be the result of increasing precoverage, so that between the hydrocarbon species less free space is available where hydrogen can adsorb without having an adsorbed hydrocarbon species in its immediate neighborhood, which seems necessary for surface hydrogenation. The magnetization-volume isotherm has no maximum, presumably because only surface hydrogenation of the dissociatively adsorbed and partly self-hydrogenated species occurs without considerable formation of gaseous products. The horizontal parts of the magnetization-volume isotherms indicate adsorption of hydrogen without changing the number of surface bonds, which can take place only when carbon–nickel bonds are replaced by hydrogen–nickel bonds. The differences between the maximum magnetization losses probably reflect the higher degree of carbonization occurring at higher acetylene precoverage.

Ethylene. The magnetization-volume isotherm for ethylene at 25°C (Fig. 2a) shows that the number of bonds formed with the surface is about four. At low surface coverage with ethylene, this is consistent with the presence of the same surface species as suggested for acetylene, i.e., NiCH=CHNi, in addition to two adsorbed hydrogen atoms. The smaller number of bonds formed at −20°C, viz. 2.8, points to physical adsorption or to a less dissociated species like $NiCH_2$–CH_2Ni.

Admission of ethylene to a surface completely covered with hydrogen at 25°C increases the magnetization (Fig. 4a), indicating that hydrogen atoms were removed from the surface. Further admission of ethylene decreases the magnetization to the initial value, proving that the surface is again fully covered. The horizontal part in the isotherm at −20°C indicates physical adsorption. Similar phenomena have already been discussed extensively for acetylene. Admission of hydrogen to preadsorbed ethylene (5 ml/g at 997 Pa) (Fig. 4b) caused an initial decrease in magnetization equal to that caused by hydrogen adsorbed onto a bare surface. This means that hydrogenation of ethylene did not take place at this low surface concentration which is in agreement with the observation by Martin *et al.* (*24*). A horizontal part in the isotherm, when roughly 6.3 ml of hydrogen/g was admitted, indicates hydrogenation without changes in the number of surface bonds so that each nickel–carbon bond is replaced by a nickel–hydrogen bond. Additional adsorption of hydrogen further decreases the magnetization.

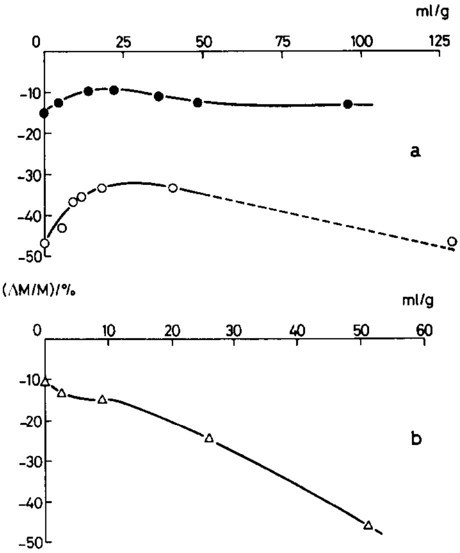


FIG. 4. Magnetization volume isotherms of: (a) ethylene over preadsorbed hydrogen at −20°C, 10.8 ml of H_2/g (●) and at 25°C, 72.5 ml of H_2/g (○), and (b) hydrogen over preadsorbed ethylene at 25°C, 5.0 ml of ethylene/g (△).

Methane. The magnetization-volume isotherm shows that at −20°C, 0.4 bonds are attached to the surface (Fig. 2a). Since in the case of chemisorption at least two bonds are formed with the surface (CH_3-group and H-atom), physical adsorption must in part have taken place. The occurrence of physical adsorption also follows from the isotherm being almost horizontal. At 25°C, four to five surface bonds are formed (Fig. 2a), from which it would follow that carbon deposition has taken place, provided that the loss of magnetization of nickel due to an adsorbed carbon atom equals the loss due to an adsorbed hydrogen atom. Since the maximum decrease in magnetization at 101 kPa and 25°C was only 23%, any penetration of carbon atoms into the bulk would not be observable.

Experiments with surfaces precovered with hydrogen showed that at −20°C, on admission of 3.1 ml of H_2/g, sufficient to decrease $\Delta M/M$ to −4%, further adsorption of methane (3.1 ml/g) did not change the magnetization, so that the active sites for methane chemisorption were obviously covered. At 25°C, however, after admission of 37.5 ml of H_2/g ($\Delta M/M = -22\%$), further adsorption of methane strongly decreased the magnetization.

Ethane. The magnetization-volume isotherm of ethane points to three and six surface bonds at −20 and 25°C, respectively (Fig. 2a). The latter number would again indicate surface species like NiCH=CHNi, in addition to four hydrogen atoms chemisorbed on the surface. Adsorption of ethane at −20°C on a surface precovered with hydrogen (44.4 ml/g) hardly changes the magnetization, so that physical adsorption probably takes place.

ir Measurements

To be able to compare ir data with those of magnetic measurements, the spectrum of the adsorbed species should be studied as a function of the surface concentration.

Acetylene. Acetylene is particularly suited for this study since the spectrum of the gas phase does not interfere with that of the adsorbed species; moreover, no spectrum of any gas phase was observed at a low surface concentration. At −20 and 25°C, roughly 9.4 ml of acetylene/g must be present before a weak spectrum can be observed (Fig. 5a and b). Above that amount, the intensity of the band at 2960 cm^{-1} ($\nu_{as}CH_3$) increases linearly as a function of the surface concentration (intensity-volume isotherm). At −20°C, the isotherm deviates from linearity at a surface coverage of about 62.5 ml of acetylene/g (Fig. 5b), possibly indicating physical adsorption. The 2960 cm^{-1} band was chosen arbitrarily as a measure of the intensity of the spectrum. The band near 2920 cm^{-1} showed a similar behavior.

The question whether the different types of spectrum of adsorbed hydrocarbons depend on the presence or absence of preadsorbed hydrogen has been discussed else-

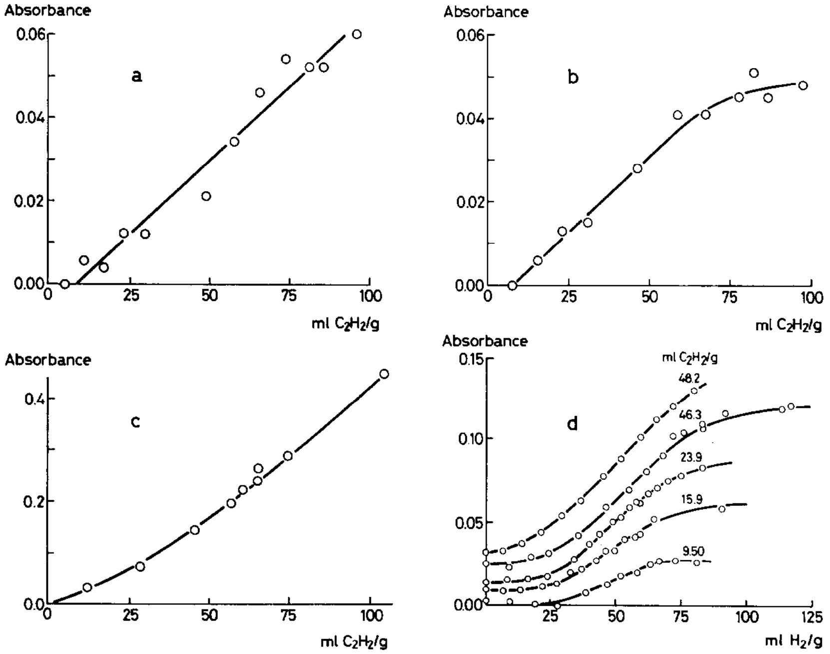


FIG. 5. Intensity-volume isotherm (band at 2960 cm^{-1}) of: (a) acetylene at 25°C, (b) acetylene at −20°C, (c) acetylene with change in background at 3333 cm^{-1} and 25°C, and (d) hydrogen over preadsorbed acetylene at 25°C.

where (*25–27*). We made some experiments at 25°C in which acetylene was adsorbed onto a surface precovered with hydrogen. At a precoverage of 18.2 ml/g the intensity-volume isotherm at 2960 cm^{-1} passes through the origin. This was also the case at a precoverage of 30.6 ml/g although a correction had to be made for the presence of bands due to gaseous ethane. These results indicate that adsorption of acetylene on bare or hydrogen-covered surfaces does not give different types of spectrum. The intensity of a spectrum of acetylene adsorbed onto a hydrogen-covered surface is, however, greater than on a bare surface at equal surface concentrations.

Adsorption of hydrocarbons is accompanied by a decrease in background transmission, which is usually corrected for by changing the setting of the beam attenuator. We also monitored the change in background as a function of the concentration of adsorbed acetylene at 25°C by measuring the background transmission ($T = I/I_0$) at 3333 cm^{-1} and plotting $\log I_0/I$ (absorbance) against the surface concentration, in which I_0 is the radiant intensity before and I after adsorption (Fig. 5c). The rise in absorbance now observed is ascribed (*28*, *29*) to a change in scattering characteristics of the solid with adsorption.

The spectra of adsorbed acetylene, recorded at 25 and −25°C as a function of the surface concentration (Fig. 6a–e) agree with those published by Sheppard and Ward (*30*); their interpretation of absorption bands will be used here. The bands at 2967 and 1440 cm^{-1}, assigned to the CH_3 group, indicate the presence of surface alkyl species, whereas the band at 3020 cm^{-1} is due to ν CH in ethylenic surface species. The latter band was particularly intense at a very high surface concentration, while also a weak band appeared at 3060 cm^{-1} (not shown in Fig. 6) indicating the presence of a $=CH_2$ group. Possibly, polymerization to, for example, butadiene had occurred. Further contributions to the spectrum are due to CH_2 and possibly to Ni_2CH, $NiCH_2$, and CHNi groups. The band at 1620 cm^{-1} (Fig. 6e) indicates the presence of water. In contrast with the findings of Sheppard and Ward (*30*) a band near 1684 cm^{-1} was observed. Rhandhava

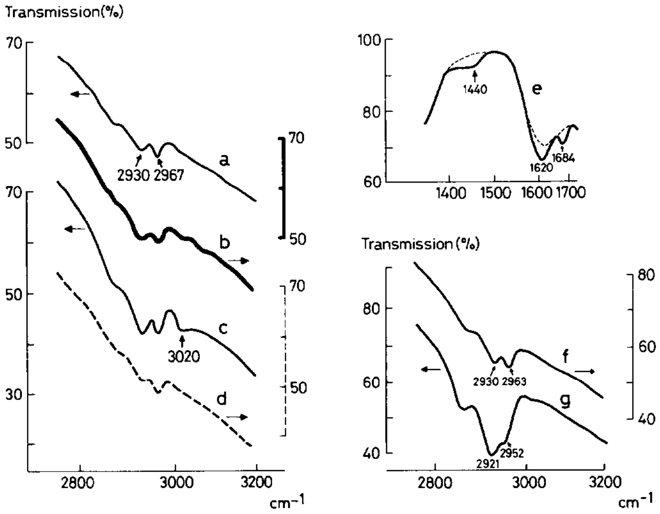


FIG. 6. ir spectra of adsorbed acetylene as a function of surface concentration (a) 36.3 ml/g, at 25°C, (b) 89.4 ml/g, at 25°C, (c) 170.0 ml/g, at 25°C, (d) 78.1 ml/g, at −25°C, and (e) 98.8 ml/g, at −25°C, and (e) 98.8 ml/g, at 25°C, and of preadsorbed ethylene (56.3 ml/g) after hydrogenation (f) 29.4 ml of H_2/g, and (g) 82.5 ml of H_2/g.

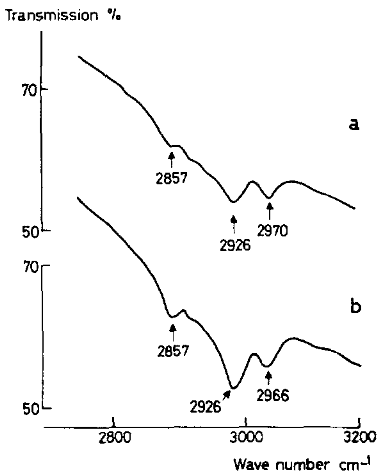
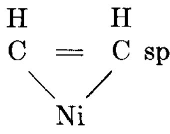


FIG. 7. ir spectra of adsorbed ethylene after evacuation: (a) 65.0 ml/g, at −20°C, and (b) 17.0 ml/g, at 25°C.

and Rehmat (*31*) also observed a band near that position (1690 cm^{-1}) in their study of the adsorption of acetylene on alumina-supported platinum, which they assigned to a ν C=C stretching vibration in an unsaturated surface species, such as PtCH=CHPt, rather than to an acetylene–platinum coordination compound. As an unsaturated surface species probably has a lower value for ν C=C than (*Z*) C–CH=CH–C (1660 cm^{-1}), we prefer to assign the 1684 cm^{-1} band to a  species, which is in agreement with such species known from organometallic chemistry (*32*).

The increase in absorbance of the 2960 cm^{-1} band (see Fig. 5a) was also used to monitor the progress of the hydrogenation reaction of preadsorbed acetylene at 25°C as a function of the surface concentration. The choice of the unresolved band seems justified, as computer-aided resolution of the overlapping bands at 2920 and 2960 cm^{-1} showed that both bands displayed the same behavior. The observed curves (Fig. 5d) consist of three regions, which is particularly clear at the lowest surface coverage. The first portion of admitted hydrogen (31.3 ml/g) is obviously adsorbed without any hydrogenation of the surface species taking place. Further admission of hydrogen up to 62.6 ml/g causes hydrogenation, reflected by enhancement of the band. Beyond this region, the intensity of the band remains more or less constant, although further adsorption of hydrogen took place. The separation between the three regions becomes less clear at increasing acetylene surface coverage, obviously indicating that the hydrogenation starts at an earlier stage and that, therefore, an increasing part of the admitted hydrogen is consumed for hydrogenation.

The changes in the spectrum during hydrogenation of preadsorbed acetylene are given in Figs. 6f and 6g. The bands due to unsaturated groups, such as 3020 cm^{-1} (ethylenic ν CH) and 1684 cm^{-1} (ν C=C), have disappeared. The 2970 cm^{-1} band also shifts towards lower wavenumbers; this effect has been described earlier (*33*, *34*).

Ethylene. Contrary to acetylene, the spectrum of the adsorbed phase of ethylene was overlapped by that of the gas phase. It was therefore impossible to establish whether any absorption bands due to the adsorbed phase were present at a low surface concentration. At higher surface concentrations (18.8 up to 37.5 ml/g cat) we found at −20°C an almost linear increase in intensity of the 2960 cm^{-1} band of the adsorbed species after subtracting the spectrum of the gas phase. Extrapolation showed that absorption bands appear only after a discrete amount has been adsorbed.

The spectra of ethylene adsorbed on a bare surface after pumping off the gas phase (Fig. 7) resemble those obtained after hydrogen admission by Morrow and Sheppard (*27*) (long adsorption time) and by Erkelens and Liefkens (*26*) and are consistent with those of surface alkyl groups. Also Whalley *et al.* (*11*) reported dimerization of ethylene on a nickel surface. The type of adsorbed species formed obviously depends on the experimental conditions.

Methane. No ir spectra of the adsorbed species could be obtained at −20 or 25°C, neither in the presence nor in the absence of the gas phase. This could be expected from the small amount of methane adsorbed (<12.5 ml/g at 25°C), which is the concentration range where no spectrum of acetylene or ethylene could be observed, and for the experiment at 25°C also from the strong dissociation which magnetic measurements had shown to take place.

Ethane. The adsorbed phase of ethane did not give a spectrum at 25°C either; only after hydrogen admission was a weak, poorly resolved spectrum observed, indicating the presence of chemisorbed species.

Gas-Chromatographic Analysis

Gas-chromatographic analyses of the gas phase were carried out after adsorption of various hydrocarbons on the reduced and evacuated nickel surface at room temperature. After adsorption of methane, no other compounds were found in the gas phase. Ethylenic hydrocarbons and traces of saturated products, mainly with even-numbered carbon chains, were observed after adsorption of ethylene. Adsorption of acetylene caused formation of products with odd- and even-numbered carbon chains as well as butadiene. After adsorption of ethane, various saturated products such as methane, propane, and isobutane were observed. Admission of hydrogen to adsorbed acetylene resulted in a large amount of heptane while, with ethylene, hexane was the predominant product. These results strongly point to polymerization of the adsorbed species on the surface. It is significant that Kokes and Bartek (*35*) observed butane and butene during catalytic hydrogenation of ethylene over nickel at room temperature. In the case of methane a range of saturated products was observed on hydrogen admission. The gas-chromatographic results agree with those of the ir investigations which also point to polymerization (surface alkyl groups), especially in the case of acetylene, the spectrum of which suggests the presence of butadiene at high surface concentrations.

DISCUSSION

Magnetic measurements suggest that at 25°C, the same surface species NiCH=CHNi is formed from ethane, ethylene, and acetylene at low surface coverage. This may be due to the species being stabilized by resonance, since a structure with double bonds to the nickel surface is also possible. The carbon atom in such a resonating structure causes loss of magnetization equal to one hydrogen atom. This follows from the considerations mentioned before and from the experimental fact that the magnetic effect of a multiple-bonded oxygen atom equals that of a single bond in an adsorbed hydrogen atom (*23*). A structure like Ni_2CH–$CHNi_2$ can be imagined (*30*) but is not probable since four carbon–nickel bonds would be necessary, which cannot explain our observations. Since ir absorption bands could not be obtained for methane and ethane, and only at a surface coverage >9.4 ml/g for acetylene and ethylene, the structure of the surface species derived from magnetic measurements can neither be confirmed nor denied. Bradshaw and Pritchard (*36*) reported that on adsorption of carbon monoxide on iron, nickel, and cobalt, the absorption bands occurred only at high coverage, which is in agreement with our observation.

At higher surface concentrations of adsorbed acetylene or ethylene, the presence of surface alkyl groups formed by self-hydrogenation of the adsorbed species can be deduced from the ir spectra. Since the presence of such groups can never be derived by simply counting the number of adsorbate bonds to the nickel surface, it follows that structures of adsorbed species derived from magnetic measurements at low surface coverages are not applicable to higher surface concentrations. Nevertheless, the presence of bands at 3020 and 1684 cm^{-1} suggests that part of the acetylene is adsorbed in the form of ethylenic surface species, possibly bonded to one nickel atom (*32*). The group intensity for an ethylenic group is, however, considerably lower than that for the CH_2 or CH_3 group (*37*), so that the amount of ethylenic species may be greater than would follow from comparison of band intensities only. There is no reason to postulate π bonding. Although such coordination complexes have been suggested by Erkelens (*38, 39*) and by Garnett and Sollich-Baumgartner (*40*) as intermediates in heterogeneously catalyzed reactions, they have so far not been observed by ir spectroscopy for acetylene, ethylenic hydrocarbons (*26, 27, 34*), or benzene (*41*) chemisorbed on nickel surfaces.

It was concluded from magnetic measurements that physical adsorption occurs at 25°C at high acetylene concentrations. At these concentrations, polymerized product —possibly butadiene—may be physically adsorbed as appears from the ir spectrum and gas-chromatographic analysis. Magnetic measurements also indicate carbon deposition at 25°C, which cannot be observed by ir spectroscopy. Physical adsorption at -25°C at a surface concentration above 62.5 ml/g was concluded from both the magnetic and ir measurements.

The dissociation of various hydrocarbons is counteracted on a hydrogen-covered surface. When acetylene or ethylene was adsorbed on such a surface, magnetic measurements indicate that part of the adsorbed hydrogen is used for the surface reaction, which is in agreement with the immediate appearance of ir absorption bands. The sites for dissociative adsorption of methane and ethane at -20°C were obviously covered with hydrogen, although we observed dissociative adsorption of methane at 25°C. Selwood (*13*) reports no adsorption of ethane over hydrogen at room temperature.

It is generally recognized (*25–27, 34*) that hydrogenation of adsorbed alkenes leads to species which can be successively hydrogenated and dehydrogenated by addition or removal of hydrogen. In order to obtain thermodynamic and kinetic data, Avery (*42*) studied the intensity of the spectra of various hydrocarbons on a palladium surface as a function of pressure and temperature. Detailed information on the hydrogenation of hydrocarbon species derived from adsorbed acetylene can be obtained by comparing our magnetic and infrared spectroscopic measurements (Figs. 3b and 5d). A certain amount of hydrogen, depending on the surface concentration of acetylene, is necessary to start the hydrogenation. The part of the hydrogen admitted for hydrogenation increases with increasing acetylene surface coverage, while the part used for mere adsorption consequently decreases. Beyond 52 ml of hydrogen admitted per gram, hydrogenation of the adsorbed hydrocarbon species takes place, while the number of surface bonds is maintained, so that each carbon–metal bond is replaced by one hydrogen–metal bond.

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