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Modifications of the Infrared Spectra from Chemisorbed CO as a Measure of Hydrogen Coverage of a Nickel Surface: Dependence of the Spectra of Chemisorbed Ethylene on Hydrogen Coverage

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The infrared absorption in the 2100–2000 cm^{-1} region from CO chemisorbed on silica-supported nickel is shown to be sensitive to the presence or otherwise of hydrogen co-adsorbed on the metal surface. A "hydrogen-covered" surface gives a νCO band near 2070 cm^{-1}; a "bare" or "hydrogen-free" surface gives a band near 2040 cm^{-1}. Using this criterion it is shown that a "hydrogen-covered" surface prepared at 25°C loses much of its hydrogen by pumping at 50°C.

Different spectra have been obtained (as previously by Eischens and Pliskin in 1958) from ethylene adsorbed on hydrogen-covered and bare nickel. The former spectra are stronger and show a particularly dominant band near 2890 cm^{-1} which is selectively removed by CO adsorption and also by hydrogenation. Closely similar spectra are obtained after hydrogenation of ethylene adsorbed on hydrogen-covered or bare nickel.

It is concluded that intervening reports of similar spectra from ethylene initially adsorbed on nickel surfaces prepared so as to be hydrogen-covered or bare may result, in part, from heating effects in the infrared beam which under certain experimental conditions can remove some of the hydrogen from the surfaces prepared as hydrogen-covered.

INTRODUCTION

Gas–metal interactions have been much used for the study of metal surfaces (*1*). Infrared studies have been particularly concerned with the adsorption of CO (*2*), but there has also been considerable interest in metal–hydrocarbon interactions with the aim of obtaining information about surface species which might play a part in catalytic reactions (*3,4*).

More recently, spectroscopic studies have been made of systems involving the co-adsorption of CO and hydrocarbons (*5–7*). Information about the mode of bonding of the hydrocarbon to the surface have been inferred from the effect of hydrocarbon adsorption on the CO spectra. In this paper we have applied this method to study the interaction of hydrogen and ethylene with the surfaces of silica-supported nickel catalysts.

EXPERIMENTAL METHODS

Nickel–silica samples were prepared by dissolving 2 g of nickel nitrate hexahydrate in about 80 ml of distilled water and adding 4 g of silica (Cab–O–Sil HS5) which had been previously calcined in air at 600°C. The water was removed by heating with stirring until a paste was obtained which was further dried at 110°C. After reduction the solid contained about 10% of nickel by weight.

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The resulting impregnated sample was ground up and then compressed under a pressure of 2–3 tons cm^{-2} so as to give discs of diameter 18 mm and of weight between 60 and 80 mg. A disc, placed in a quartz framework, was inserted into an infrared cell of a design that has been previously described (*8*). So as to minimize contamination the greased ground joint of the cell had been eliminated.

After an hour's evacuation at 200°C, hydrogen was introduced into the cell at progressively increasing temperatures up to 350°C; after evacuation at the same temperature the hydrogen was renewed two or three times. The reduction process was continued for about 6 to 8 hr overall. The sample was then cooled to 25°C in hydrogen in order to give a "hydrogen-covered" catalyst or evacuated at 350°C to give a "bare" surface.

During all the preceding treatment, and during all later introductions of gas, the infrared cell was protected from mercury from the vacuum pump by a trap immersed either in liquid nitrogen or in a mixture of solid CO_2 and acetone. Yates and Garland (*9*) have shown that traces of mercury can considerably affect the adsorption properties of metallic nickel.

The hydrogen used was taken from a cylinder provided by the British Oxygen Company, and any residual oxygen was removed by passing the stream of hydrogen through a DEOXO catalytic unit. The resulting water was removed by zeolite 5A, previously evacuated at 350°C and maintained at liquid nitrogen temperature. The hydrogen was stored over molecular sieves. The ethylene, of high purity, was obtained from the National Physical Laboratory, and CO from the British Oxygen Company; these two gases were used without further purification.

Infrared spectra were recorded using a Digilab FTS-14 Fourier transform interferometer. Spectra were measured at 25°C, with a resolution of 4 cm^{-1} over all wavenumber ranges. For each set of spectra a reference spectrum from the silica-supported metal sample was obtained at the beginning and stored in the 128 K disc that is auxiliary to the Nova minicomputer incorporated in the FTS-14 spectrometer. Subsequent spectra containing additional bands from adsorbed molecules were ratioed against the reference spectrum so that adsorbate spectra were obtained from which the adsorbent bands had been eliminated at the expense of a variable noise level. However, in some cases changes in the water vapor or CO_2 content in the spectrometer light path over a period of hours led to weak residual bands from these atmospheric constituents due to a slight degree of noncancellation. Different scale expansions of the intensity ordinate were automatically applied by the spectrometer so as to give an optimum presentation of the spectral data. The strengths of individual bands expressed in percentage absorption are indicated on the spectral diagrams.

I. INTERACTIONS OF CARBON MONOXIDE WITH SUPPORTED NICKEL

A. Introduction

Numerous studies have been made of the adsorption of CO on supported nickel. Eischens, Francis, and Pliskin (*10*) showed the importance of the degree of coverage of the surface on the frequencies and intensities of the νCO band. Effects due to the nature of the support were demonstrated by O'Neill and Yates (*11*) when the nickel was deposited on silica, alumina, and TiO_2. Van Hardeveld and Hartog (*12*) have demonstrated the influence of metal particle size on the relative intensities of the νCO bands on Ni/SiO_2.

As a preliminary to the study of the interactions of CO with other molecules, we measured the spectra of CO alone adsorbed on Ni/SiO_2.

B. Measurements Based on an Initially "Bare" Nickel Surface

A nickel/silica disc was evacuated for 4 hr at 350°C after reduction and hence corresponds to what earlier authors (*10*) have described as a "bare" or "hydrogen-free" surface.

The initial adsorption of CO at room temperature, in the presence of excess gas-phase CO at 10 Torr pressure, gave a very intense band at 2055 cm^{-1} with a well-defined shoulder near 2080 cm^{-1}. Another weaker band was centered near 1950 cm^{-1} with an extended absorption tail to lower wavenumbers. The precise wavenumbers are listed in Table 1.

After evacuation of the gas phase the band near 2055 cm^{-1} weakens very remarkedly and becomes broader, the high-frequency shoulder at 2080 cm^{-1} disappears, and the band at ca. 1950 cm^{-1} is displaced toward 1940 cm^{-1}. This latter spectrum is shown in Fig. 1a.

Evacuation for 30 min at 100°C (Fig. 1b) causes the maximum of the 2055 cm^{-1} band to move toward 2040 cm^{-1} with a further reduction in intensity; also the band at 1940 moves to near 1930 cm^{-1} with some reduction in intensity.

The addition of hydrogen at room temperature at this stage led to a displacement of the maximum of the high-wavenumber νCO band from ca. 2040 to ca. 2070 cm^{-1} with a somewhat enhanced intensity (Fig. 1c). A poorly resolved shoulder was left near 2040 cm^{-1}, and there was little change in the 1930 cm^{-1} absorption. Finally re-evacuation of hydrogen at room tempera-

TABLE 1

Wavenumbers and Intensities of the Absorption Bands of CO on Silica-Supported Nickel under Various Experimental Conditions[a]

Nature of treatment	Figure	Wavenumbers and intensities (% absorption) of absorption bands		
		"Linear" bands (>2000 cm^{-1})		"Bridged" bands (<2000 cm^{-1})
A. "Bare" nickel				
Adsorption of CO (gas present)	—	2080 (m, sh)	2057 (vs)	1948 (m)[b]
After pumping (room temperature)	1a	—	2055 (49, bd)	1940 (41)
After pumping (100°C)	1b	—	ca. 2065 (sh), 2038 (39)	1929 (29)
Addition of H$_2$ (room temperature)	1c	—	2069 (45), ca. 2035 (sh)	1930 (33)
B. "Hydrogen-covered" nickel				
Adsorption of CO (gas present)	—	2085 (m, sh)	2054 (vs)	1954 (m)[b]
After pumping (room temperature)	2a	—	2063 (56), 2040 (54)	1942 (62)
After pumping (90°C)	2b	—	ca. 2065 (sh), 2042 (60)	1940 (60)
Addition of H$_2$ (room temperature)	2c	—	2069 (65), ca. 2040 (sh)	1935 (60)
C. "Hydrogen-covered" and evacuation at 50°C				
Adsorption of CO (gas present)	3a	2083 (sh)	2053 (75)	1960 (45)
After pumping at 50°C	3b	—	ca. 2065 (sh), 2040 (32)	1953 (41)

[a] (sh), shoulder; (bd), broad; (m), medium; (vs), very strong.

[b] Only relative intensities are quoted for these bands as the spectra were not obtained on the same disc as the other spectra listed. However, in other series of experiments it was found that the strengths of the bands near 1950 cm^{-1} changed little on evacuation of the CO gas phase.

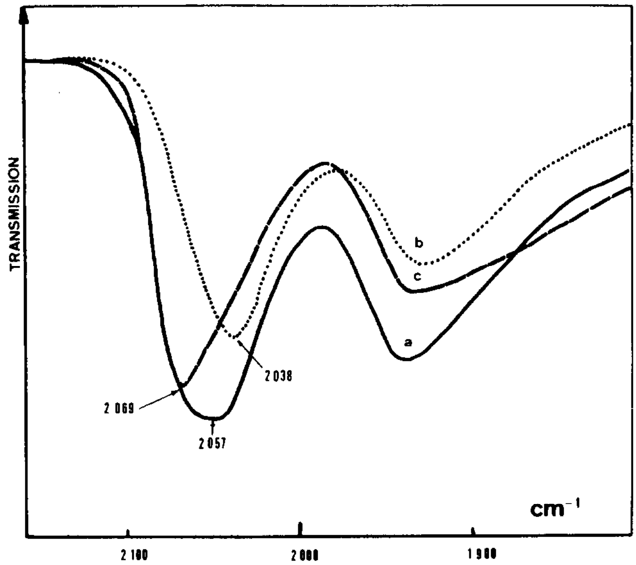

Fig. 1. νCO infrared absorption bands from carbon monoxide adsorbed on "bare" or "hydrogen-free" Ni/SiO_2. (a) CO retained on the surface after pumping at room temperature. (b) CO retained after further evacuation for 30 min at 100°C. (c) CO retained after 200 Torr of hydrogen had been in contact with the surface following spectrum (b).

ture gave once again a spectrum similar to that shown in Fig. 1b.

Evacuation for 1 hr at 200°C was sufficient to cause all the bands from adsorbed CO to disappear from the spectrum.

C. Measurements Based on an Initially Hydrogen-Covered Nickel Surface

In the presence of gas-phase CO at a pressure of 10 Torr the hydrogen-covered surface at 25°C gave a very similar spectrum to that on bare Ni as detailed in Table 1. However, evacuation of CO led to a rather different spectrum with two resolved bands above 2000 cm^{-1} near 2065 and 2040 cm^{-1} (Fig. 2a) and a relatively rather stronger band near 1940 cm^{-1}. Continued evacuation at 25°C led to some weakening of the 2065 cm^{-1} band relative to its neighbor at 2040 cm^{-1}, and pumping for 30 min at 90°C reduced the ca. 2065 cm^{-1} band to a weak shoulder (Fig. 2b). As before, subsequent readsorption of H_2 displaced the 2040 cm^{-1} band to near 2070 cm^{-1} (Fig. 2c), giving a very similar spectrum to Fig. 1c except for the continued relative weakness of the absorption bands above, compared with those below, 2000 cm^{-1}. The latter bands are little changed in position or in intensity by these various treatments (Table 1). Final evacuation at room temperature led once again to a spectrum very similar to that shown in Fig. 2b with some reduction in intensity at 2040 cm^{-1}.

Another experiment was carried out with an initially hydrogen-covered surface which had been evacuated at 50°C. Adsorption of CO at room temperature on this surface gave initially (Fig. 3a) a spectrum similar to that obtained on the other samples in the presence of gas-phase CO (Table 1). Evacuation of CO at 50°C left a much weaker band at 2040 cm^{-1}, but again with a high-frequency shoulder (Fig. 3b). In this series of experiments the absorption bands below 2000 cm^{-1} occurred at somewhat higher wavenumbers (1960–1950 cm^{-1}) and were relatively stronger than the ca. 2040 cm^{-1} band.

D. Discussion of the Results

The collected results summarized in Table 1 and illustrated in Figs. 1–3 show that the narrower absorption bands from adsorbed CO above 2000 cm^{-1} are much more sensitive to the state of the nickel surface than the broader bands below 2000 cm^{-1}. In accordance with earlier authors (*10,13*), and despite other possibilities (*14*), we shall refer to the bands above 2000 cm^{-1} as corresponding to "linearly adsorbed" species, and to those below 2000 cm^{-1} as corresponding to "bridged" species in which a CO molecule is bonded to two nickel atoms. Apart from a slight but consistent shift of the maxima of the latter bands to low wavenumbers after evacuation of the gas-phase CO, the bridged CO bands vary little in position or intensity during a set of experiments on a given metal disc (Table 1).

Above 2000 cm^{-1} very similar spectra were obtained in each case in the presence of CO in the gas phase, whether the nickel surface was prepared as hydrogen-covered or bare. Furthermore, in each case evacuation of the gas phase led to a loss of more than 50% of the intensity of the main band at ca. 2055 cm^{-1} and a disappearance of the weaker but substantial shoulder near 2080 cm^{-1}. The first of these changes could be caused by pumping away volatile nickel tetracarbonyl, which others have suggested is formed when CO is adsorbed on nickel at higher pressures (*12*). There is, however, little chance that any of this species remains after strong evacuation at 25°C (*15*). The band at 2085 cm^{-1} also arises from a weakly adsorbed species which Garland, Lord, and Troiano (*16*) have attributed to CO adsorbed on "amorphous parts" of the metal surface.

After evacuation of the gas phase the surface may not be completely covered with CO and so the reduction of intensity of the "linear" CO bands may also result from removal of a proportion of genuinely chemisorbed species. Measurements of ad-

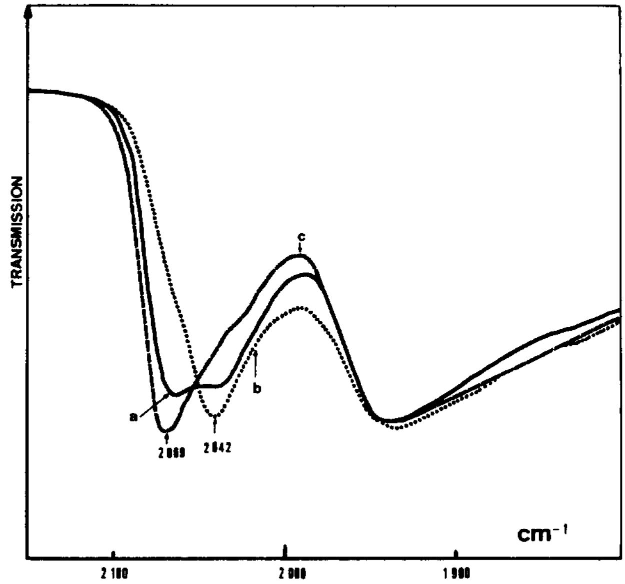

FIG. 2. νCO infrared absorption bands from carbon monoxide adsorbed on hydrogen-covered Ni/SiO$_2$. (a) CO retained on the surface after pumping at room temperature (25°C). (b) CO retained after further evacuation at 90°C for 30 min. (c) The spectrum obtained after 200 Torr of hydrogen had been in contact at 25°C with the surface that gave spectrum (b).

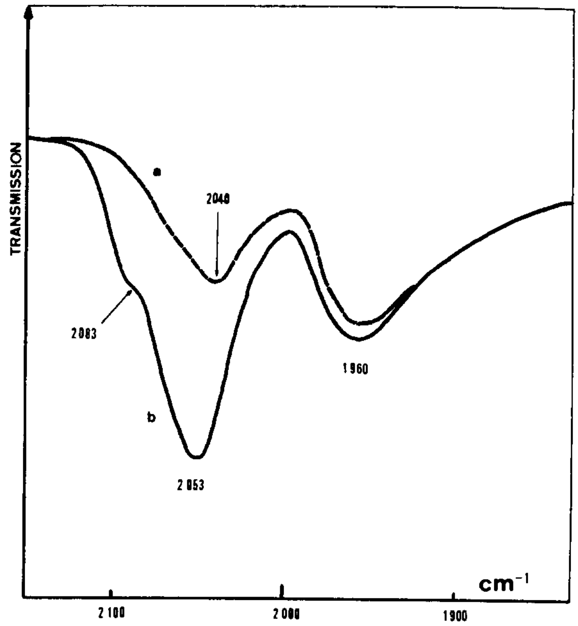

Fig. 3. (a) The spectrum from CO adsorbed on a hydrogen-covered Ni/SiO_2 surface after evacuation of hydrogen for 5 min at 50°C; the spectrum was obtained in the presence of gas-phase CO. (b) The spectrum obtained after evacuation of CO at 50°C.

sorption isotherms have shown that full monolayer coverage of CO on nickel is only to be expected for pressures of ca. 100 Torr at 25°C (*17*) and that after evacuation for 30 min at this temperature about one-third of the CO adsorbed under 1 Torr of gas-phase CO is removed from the surface (*11*).

Relative to the bridged CO bands in the 1940 cm^{-1} region, the linear CO bands that remain after pumping are rather stronger from the bare than from the hydrogen-covered nickel surface. It seems that in large measure all the spectra obtained above 2000 cm^{-1} after evacuation of CO can be interpreted in terms of two component absorption bands, near 2070–2065 and 2040 cm^{-1}, respectively, which vary in relative intensity according to the treatment of the surface. The terminal experiments in each series described under Sections IB and IC above leave no doubt that a hydrogen-covered surface gives the higher-frequency CO band, and that a bare surface gives the lower-frequency band. It seems, therefore, that these absorptions provide a most convenient method of at least qualitatively monitoring the amount of hydrogen on the surface of the nickel sample.

If this interpretation is also valid for the spectra at the beginning of the series shown in Figs. 1a and 2a, this implies (a) that there may be a degree of hydrogen coverage on the metal surface prepared according to the 'bare' recipe (because the broad flat-topped overall absorption near 2055 cm^{-1} may be caused in part by an unresolved contribution from the ca. 2070 cm^{-1} absorption) and (b) that there is very probably a proportion of hydrogen-free surface on the sample prepared so as to be 'hydrogen-covered' (the component band at 2040 cm^{-1}). The latter finding may only have been caused by displacement of a proportion of the original surface hydrogen by adsorbed CO. The former is more difficult to account for. However, as the CO coverage, to judge from the strength of the 2055 cm^{-1} absorption, is greatest in the case of Fig. 1a, it is possible that the observed frequency shift from 2040 to 2055 cm^{-1} may be related to this factor and not to hydrogen coverage.

Further experiments would be needed to understand completely the mutual interaction of CO and hydrogen on the nickel surfaces. Nevertheless, it is clear that heating to 90 or 100°C (Figs. 1b and 2b) removes most of the adsorbed hydrogen on a nickel surface, and that heating to even 50°C (Fig. 3b) has a similar effect. Toward the end of the cycles of treatment on each sample, even pumping at room temperature seems to be adequate to remove adsorbed hydrogen, but this is much less true on first pumping out CO. These findings imply both that the bonding of hydrogen atoms to the nickel surface is relatively weak, and that it may well occur in only a single form. The latter suggestion is consistent with the results of magnetic measurements (*18*).

It should be noted that, like earlier workers (*19*), we have been unable to detect any absorption bands associated with Ni-H bonds as such in the region expected for νNi-H vibrations near 2000 cm^{-1}, even when using the enhanced sensitivity of the Digilab spectrometer. We agree with Pliskin and Eischens (*19*) in supposing that any infrared absorption bands, perhaps arising from multicenter Ni_xH bonding, must occur in the silica blackout region below 1300 cm^{-1}.

Primet *et al.* (*5*) have previously shown that the position of the linear νCO infrared absorption on platinum can be correlated with the electron-donating properties of co-adsorbed molecules. High electron-donating power is correlated with low-frequency CO bands in accordance with theoretical concepts based on back-donation from filled *d*-orbitals of surface metal atoms to antibonding orbitals on the CO. If this picture remains valid for the co-adsorption of hydrogen, the higher frequency (2070 compared with 2040 cm^{-1}) in the presence of hydrogen suggests that the hydrogen is electron-attracting. This in turn is consistent with ferromagnetic resonance results from adsorption of hydrogen on nickel film at 20°C (*20*) which are interpreted to show a shift of the *d*-electrons of nickel to adsorbed hydrogen; this implies that the polarity of M–H bonds is of the type $M^{\delta+}$–$H^{\delta-}$. The concept of back-donation of *d* electrons into antibonding CO orbitals is not so readily applicable to bridged CO species, and hence it is not surprising that the infrared absorption bands from the latter are virtually unaffected by hydrogen coverage of the surface.

In their early work on the adsorption of hydrocarbons on nickel, Eischens and Pliskin (*21*) reported different results obtained on bare or hydrogen-covered surfaces, but later workers (*22–24*) did not observe marked differences. These contradictions have been attributed to the difficulty of reproducibly obtaining a surface that is hydrogen-free or hydrogen-covered. During the course of the studies reported in this paper, using the Digilab infrared interferometer, we were able to obtain once again different spectra from ethylene on bare and hydrogen-covered samples (see Section III below). The monitoring of the degree of hydrogen coverage from the linear CO absorption bands described in this section helped us to understand these findings.

II. INTERACTIONS OF ETHYLENE WITH NICKEL SURFACES UNDER DIFFERENT CONDITIONS

A. *Results*

(*1*) *The bare surface.* Several samples of bare nickel samples were studied in which the sample had been evacuated for 4 hr at 350°C after reduction with hydrogen. The spectra obtained after adsorption and then evacuation of ethylene were rather variable in overall intensity and in intensity profile. At one extreme very weak spectra were obtained such as is shown in Fig. 4a. This spectrum is very similar in profile and

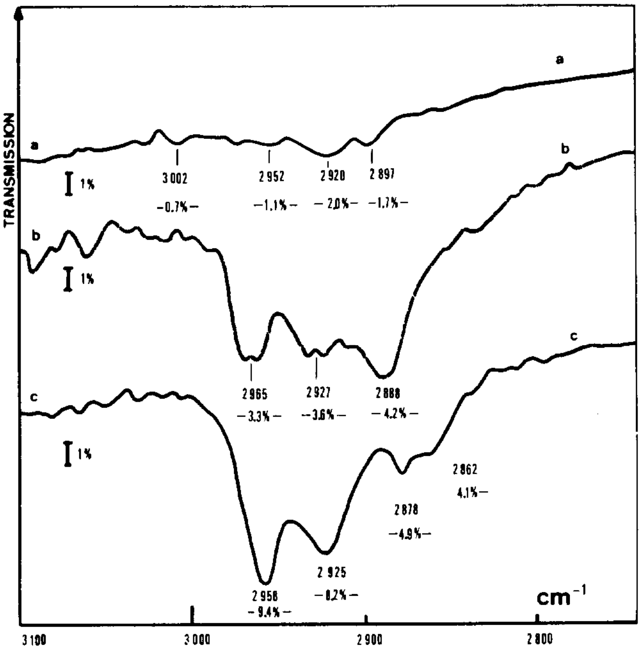

FIG. 4. Infrared spectra obtained at 25°C after adsorption of ethylene on samples of bare Ni/SiO$_2$. (a) A weak spectrum obtained on one sample after introduction of C_2H_4 (20 Torr) and evacuation. (b) A stronger (and more typical) spectrum obtained after contact with C_2H_4 (20 Torr) for 30 min and evacuation, obtained on another sample of bare nickel. (c) The spectrum obtained from the sample which gave spectrum (b) after addition of hydrogen in the gas phase (200 Torr) and without evacuation.

strength to that shown by Eischens and Pliskin (*21*) for a bare surface.

More typically, the spectra were somewhat stronger, such as the one shown in Fig. 4b. After 30 min of contact with ethylene at 25°C, followed by evacuation to remove physically adsorbed species, this spectrum showed bands at ca. 2965, ca. 2925, and 2888 cm^{-1} with weak shoulders near 2840 cm^{-1}. All the bands are weak on an absolute scale; the actual intensities are indicated. The noise levels were high relative to these weak spectra and, for example, it is not clear whether the apparent weak absorptions near 3060 and 3090 cm^{-1} are real or not.

On addition of hydrogen at room temperature to this sample, the 2888 cm^{-1} band disappeared immediately and the resulting spectrum (Fig. 4c) showed bands at 2958 (s), 2925 (s), 2878 (m) and 2862 cm^{-1} (m). The ratio of the absorbances of the 2925 and 2958 cm^{-1} bands, assignable to the asymmetric bond-stretching modes of CH$_2$ and CH$_3$ groups, respectively (*21*,*25*), was near 0.88.

(*2*) *Metal samples precovered with hydrogen at 25°C.* Again the results obtained after ethylene adsorption were somewhat variable, although they all conformed to a closely similar pattern of absorption bands. Spectrum 5a shows a typical spectrum obtained after adsorption and subsequent evacuation of ethylene. Well-defined bands were obtained at 2966 (m), 2936 (m), 2889 (vs) with a substantial shoulder at 2875 cm^{-1}, and 2835 cm^{-1} (w). These are at frequencies similar to those obtained on a bare surface (Fig. 4b), but the ca. 2890 cm^{-1} band is three times as intense, and the other twice as intense, as in the latter spectrum. In all spectra obtained on hydrogen-covered surfaces the ca. 2890 cm^{-1} band was dominant, but sometimes rather

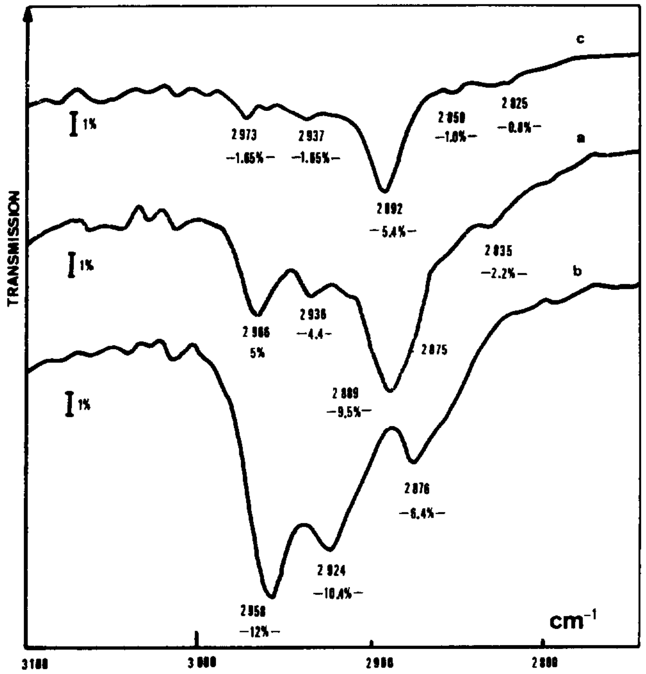

FIG. 5. Infrared spectra obtained at room temperature after C_2H_4 had been adsorbed on hydrogen-covered Ni/SiO_2. (a) after adsorption for 1 hr 15 min from 15 Torr of C_2H_4 in the gas phase, followed by evacuation; (b) after addition of 250 Torr H_2 at room temperature (and before evacuation). (c) Upper spectrum: another less typical spectrum obtained after adsorption of C_2H_4 followed by evacuation showing greater relative intensity of the 2890 cm^{-1} band.

weaker bands than usual (by a factor of about 2) were obtained near 2965 and 2935 cm^{-1}. Such a spectrum is shown in the upper spectrum (Fig. 5c). It is notable that in earlier work by Morrow and Sheppard (*23*) the ca. 2965 and 2935 cm^{-1} bands were found to grow relative to absorption in the 2890–2880 cm^{-1} region as a function of time of adsorption.

Addition of hydrogen to the same sample as gave the spectrum illustrated in Fig. 5a gave a spectrum (Fig. 5b) which was very similar in the frequencies and relative intensities of its bands to that obtained after hydrogenation on the bare surface (Fig. 4c). The wavenumbers of the bands are indicated in the figure, and the ratio of the intensities of the ca. 2925 and 2960 cm^{-1} bands was 0.87, i.e., very similar to the value for Fig. 4c. After pumping out the cell, and then reintroducing hydrogen, the ratio of intensities of these bands changed slightly to 0.94.

Those spectra which had relatively weaker bands near 2965 and 2935 cm^{-1} on initial addition of ethylene, also gave weaker absolute intensities (although similar frequencies and relative intensities) in the spectra measured after hydrogenation.

In another experiment the adsorption of CO, after the type of spectrum shown in Fig. 5a had been obtained, also led to the elimination of the 2889 cm^{-1} band while the others remained essentially unchanged.[1] Clearly more than one species contributes to the spectrum in Fig. 5a. Subsequent addition of hydrogen after the CO treatment led to the same "hydrogenated" spectrum as is shown in Fig. 5b.

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[1] We are indebted to Dr. H. A. Pearce (*7*), who told us of similar informative experiments involving the addition of CO to C_2H_4/rhodium samples.

When analogous experiments were carried out in reverse, i.e., CO was adsorbed first on the hydrogen-covered nickel surface (it was pumped at 25°C so as to leave only the irreversibly adsorbed gas; cf. Fig. 2a) and then ethylene added, again a spectrum was obtained that was similar to Fig. 5a without the 2889 cm^{-1} band. Nevertheless, in this case the other νCH bands were much weaker than in the spectrum from ethylene adsorbed directly onto hydrogen-covered nickel. The spectrum is in this respect similar to that obtained on the bare surface. This is not surprising, because the CO may restrict the sites available to ethylene.

In contrast to what has been observed when benzene and CO are co-adsorbed on platinum (*5*), the band from the linear CO species on nickel is not initially affected by the action of ethylene at room temperature. However, in the course of time a new shoulder develops at ca. 2065 cm^{-1} on the side of the 2035 cm^{-1} absorption.

(*3*) *Adsorption on a hydrogen-covered surface that had been evacuated at 50°C.* When ethylene was adsorbed at 50°C on a hydrogen-covered surface that had been subsequently evacuated at 50°C the spectra shown in Figs. 6a and 6b were obtained before and after hydrogenation. In terms of the absolute intensities in the initial spectrum, and the relative intensity of the 2890 cm^{-1} band, this falls in between those observed (Figs. 4a and 5a) for adsorption at 25°C on bare and hydrogen-covered surfaces but lies considerably closer to the former. The spectra after hydrogenation at 50°C are somewhat weaker in absolute intensities than those observed at 25°C (Figs. 4b and 5b) and significantly show an increased 2925/2960 absorbance ratio (1.14 compared to ca. 0.9 previously).

B. Discussion

(*1*) *Spectra from initially adsorbed ethylene.* We have once again observed substantial differences between the infrared spectra of ethylene adsorbed on bare and hydrogen-covered nickel, i.e., results similar to those previously reported by Eischens and Pliskin (*21*). The spectra reported more recently by Morrow and Sheppard (*23*) and Erkelens and Liefkens (*24*) seem to fall in between

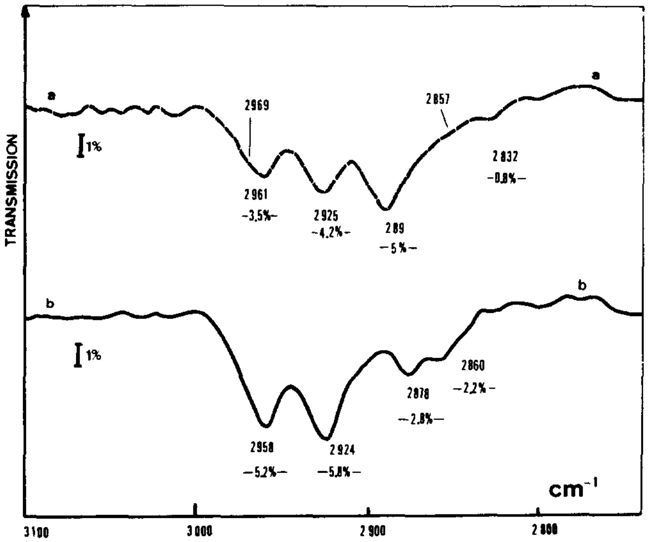

FIG. 6. Infrared spectra obtained after adsorption of C_2H_4 on hydrogen-covered Ni/SiO_2 evacuated at 50°C. (a) after addition of gas-phase C_2H_4 to the Ni/SiO_2 sample at 50°C, followed by evacuation at the same temperature; (b) after addition of 150 Torr H_2 at 50°C (before evacuation).

those that we have observed typically on bare and hydrogen-covered surfaces, particularly as concerns the intensity of the absorption near 2890 cm^{-1}. This suggests that their surfaces were partially hydrogenated at the time of the spectroscopic experiments.

We do not at this time wish to comment in detail on the interpretation of the spectra from initially adsorbed ethylene. This is because we shall later be reporting on the interpretation of these and additional results obtained by low-temperature measurements and by experiments with deuterated ethylene. Nevertheless, we have firm evidence, from the different results with bare and hydrogen-covered surfaces, and from the displacement experiments involving CO mentioned above, that the broad band in the 2890 cm^{-1} region is of a different origin from those above 2900 cm^{-1}. Earlier workers have variously attributed this band to $-CH_2M$, $-CHM_2$, or $-CHM-$ groups, where M denotes a surface metal atom, and one or other of these assignments is likely to be correct.

The greater overall strength of the spectrum, and in particular the greater strength of the 2890 cm^{-1} band, obtained on the hydrogen-covered surface, suggests that the initially adsorbed hydrogen either leads to hydrogenation of the adsorbed ethylene or, as is more consistent with earlier results (*26,23*), reduces the extent to which dissociative adsorption of the ethylene can occur by the breaking of CH bonds to form MH. The latter hypothesis is also consistent with the observation that, on a hydrogen-free surface with CO, adsorption of ethylene gave a growth of the νCO band near 2070 cm^{-1} which we attribute to a hydrogen-covered surface.

We have not reliably observed bands of measurable intensity above 3000 cm^{-1} which could indicate the presence of $=CH-$ or $=CH_2$ groups such as would be expected for a π-bonded ethylene–nickel complex. However in inorganic transition–metal complexes of this type such bands are weak (*27*) and therefore the infrared method is not ideal for the detection of such species. On the other hand the fact that, unlike the case of benzene + CO on platinum (*5,6*), adsorption of ethylene did not cause any appreciable change in the CO spectrum from a surface partly covered with that gas argues against π-electron donation from ethylene to nickel. These two, admittedly both negative, findings support the earlier conclusions (*21–24*) that the main surface species are σ-bonded to the metal surface. Of course a π-bonded species may occur as a reactive intermediate in the formation of the σ-bonded species.

(*2*) *Spectra obtained from adsorbed ethylene after hydrogenation.* Spectra of similar intensity and similar profile were obtained after hydrogenation on bare or hydrogen-covered nickel. The bands near 2960 and 2925 cm^{-1} may be attributed to νCH_3 (as) and νCH_2 (as) vibrations respectively; the weaker bands near 2875–80 and 2860 cm^{-1} are caused by the corresponding νCH_3 (s) and νCH_2 (s) vibrations (*28*). However, in using these bands to assign structures to the adsorbed species it has to be borne in mind that CH_2 groups attached directly to surface metal atoms do not absorb at the same positions (*25*).

The ratio of absorbances of the methylene and methyl 2925 and 2960 cm^{-1} bands obtained for the hydrogenated species at room temperature (ca. 0.9) appears to suggest their attribution to surface ethyl groups (or possibly, but much less likely for chemical reasons, surface *n*-propyl groups if the $-CH_2-M$ bands do not strongly overlap the 2925 cm^{-1} position). Indeed, Pliskin and Eischens (*21*) attributed the corresponding spectrum first obtained on a hydrogen-covered surface to an ethyl group; they obtained a somewhat different spectrum after adsorption and hydrogenation on a bare surface. The main difficulty with this assignment is that Morrow (*29*) has obtained recent infrared results from coordination complexes of known structure containing Pt–CH_2CH_3 groups which suggest that a surface-attached M–CH_2CH_3 group would have a substantially different profile from that predicted on the basis of analogies with the spectra of saturated hydrocarbons.

The spectrum obtained after hydrogenation following adsorption of ethylene at 50°C (Fig. 6b) has a different profile which is recognizable as that of a surface *n*-butyl group (*23*). Another possibility is that the other hydrogenated spectra are made up from overlapping contributions from surface *n*-butyl groups plus selectively physically adsorbed *n*-butane, which has a higher CH_3/CH_2 ratio (*23*). However, this seems unlikely, as it is expected that hydrogenation will give mainly ethane in the gas phase which will not be physically adsorbed at ambient temperatures (*30*).

III. CONCLUSIONS

The infrared results from linear CO species chemisorbed on nickel surfaces with different amounts of hyrogen demonstrate that bands near 2070 and 2040 cm^{-1} can be used to show whether hydrogen is present or not, respectively, on the metal surface, or to assess intermediate situations. It has been deduced by this means that a metal sample prepared as hydrogen-covered very readily loses much of its hydrogen on heating and pumping to the relatively modest temperature of 50°C.

We have found pronounced differences between the infrared spectra from ethylene adsorbed at room temperature on metal samples prepared as bare or hydrogen-covered, such as were originally described by Pliskin and Eischens (*21*). In the intervening period Ward (*22*), Morrow and Sheppard (*23*), and Erkelens and Liefkens (*24*) failed to obtain very different spectra from the two types of surface. Our present results indicate that their spectra correspond probably to nickel surfaces only partially covered with hydrogen under the conditions of the spectroscopic measurements. A rational explanation can be advanced for these differences in that the latter workers (*23,24*) used Grubb–Parsons infrared spectrometers in which the infrared beam is focused on a small part of the sample being measured. Heating effects on supported-metal catalyst samples are well known (*31*) and would be particularly pronounced under the above conditions. Indeed, Morrow and Sheppard (*23*) were well aware of heating effects in their spectra at low temperatures. Both Pliskin and Eischens (*21*), in their earlier work, and ourselves, using the Digilab FTS-14 infrared interferometer, measured spectra under conditions in which the infrared beam is spread more uniformly over a much wider area of the sample. Furthermore, with the interferometer a considerable fraction of the high-energy part of the infrared emission from the source is removed on passage through the beamsplitter.

Morrow and Sheppard (*23*) also obtained spectra from ethylene on nickel which varied with time in a more pronounced manner than those measured in the present work, leading to the increasing formation of surface *n*-butyl groups. We obtained similar results with ethylene adsorbed deliberately at 50°C (Fig. 6b) and conclude that sample-heating effects can account for most of the differences obtained in the different infrared studies of ethylene adsorbed on the same type of silica-supported nickel samples.

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