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Infrared Spectroscopic Studies of Adsorption and Catalysis

V. Acetaldehyde on Silica-Supported Nickel

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An investigation has been made by infrared spectroscopy of the surface species obtained from the adsorption of acetaldehyde on a silica-supported nickel catalyst which is active in promoting the decarbonylation reaction. Techniques are described which are successful in separately assessing which features of the spectra arise from adsorption on the metal and which from adsorption on the silica parts of surface, respectively.

After evacuation of the gas-phase and physically adsorbed acetaldehyde the dominant surface species found on the metal through its infrared absorption bands is of the alkoxide type. Reasons are given for assigning the associatively adsorbed structure $CH_3 \cdot CH\mathbf{M}{-}O\mathbf{M}$ ($\mathbf{M}$ = surface metal atom) to this species. As bands from this species decay in intensity on heating, spectra from decarbonylation products increase in intensity. Bands are also observed from carbon monoxide and the CH_3COO^- ion chemisorbed on the metal; the latter probably arises from a slow oxidation reaction on the surface. No bands were observed which could be assigned to the surface acyl species $CH_3 \cdot CO \cdot \mathbf{M}$.

Infrared bands are also observed from C_2H_5OSi groups on the silica surface and from physically adsorbed paraldehyde which builds up on the surface more slowly. These species do not occur on the adsorption of acetaldehyde on silica alone and must also result from catalytic processes involving nickel.

The oxidation of acetaldehyde to $R \cdot COO^-$, and the reduction process which forms ethoxide groups on silica, may be initiated by dissociative adsorption of some acetaldehyde molecules on the metal surface.

INTRODUCTION

Infrared spectroscopy is now widely used in the structure determination of surface species, as it makes possible a comparison of the spectra of molecules in the adsorbed phase with those of suitable model compounds. We have already reported the results of spectroscopic studies of a series of aliphatic aldehydes and ketones adsorbed on pure silica (*1*, *2*), and of some preliminary experiments using a silica-supported nickel catalyst (*2*). One of our principal interests in this field has been the determination of the structures of surface species formed by the adsorption of such carbonyl compounds on catalytically active metal surfaces. If detailed information of this kind could be obtained, it should help to provide a clearer understanding of the nature of the catalytic reactions of these compounds. For example, in the course of a study of the carbonylation of olefins and the converse decarbonylation of aldehydes over metallic palladium, Tsuji *et al.* (*3*) have postulated a surface acyl species (formulated by them as $R \cdot CO \cdot \mathbf{Pd} \cdot H$ as derived from $R \cdot CHO$) as a likely catalytic intermediate. Such a surface species should be readily detectable by infrared spectroscopy because of the expected strong C=O stretching vibration. We report here results obtained from a spectroscopic study of acetaldehyde adsorbed on silica-supported nickel over a range of temperatures and pressures. As reported previously (*1*), this

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type of catalyst gives rise to a decarbonylation reaction with acetaldehyde even at 25°C. Gas-phase methane, carbon monoxide, and chemisorbed carbon monoxide can be detected by infrared means.

Blyholder and Neff (*4*, *5*) have recently reported infrared results from the chemisorption of acetaldehyde on iron (*4*) and nickel (*5*) suspended in paraffin oil. They conclude that the surface species on iron is the alkoxide group $CH_3CH_2O\mathbf{M}$ ($\mathbf{M}$ = surface metal atom). By contrast, they observe strong bands from chemisorbed CO on nickel, a weak band at 1720 cm^{-1} which they attribute to the surface acyl species $CH_3{\cdot}CO{\cdot}\mathbf{M}$, but no strong bands from surface alkoxide species. Although Blyholder and Wyatt (*6*) have studied the spectra resulting from adsorption of a number of alcohols on silica-supported metals, including nickel, they do not report any results using acetaldehyde. However in the experiments with alcohols on nickel/paraffin (*5*) a weak band was again reported at 1720 cm^{-1} and attributed to similar acyl species as reported from acetaldehyde. Alcohols on silica-supported nickel (*6*) did not give rise to C═O bands; however, on cobalt, bands were observed in the 1600–1570 cm^{-1} region and these were also assigned to surface acyl species (*6*). As these latter frequencies differ markedly from those attributed to the same species on nickel/paraffin, a further investigation is clearly called for.

EXPERIMENTAL METHODS

Commercial grade acetaldehyde was distilled under dry nitrogen and thoroughly degassed before use. The silica used was Cab-O-Sil H5 (kindly donated by the Cabot Corporation, Boston, Mass.), which was heated for 12 hr in air at 600°C; 2 g of Cab-O-Sil was then mixed with 1 g of nickel nitrate [$Ni(NO_3)_2{\cdot}6H_2O$, Analar grade] in about 30 ml of distilled water and the resulting paste was dried and crushed. A thin self-supporting silica–nickel nitrate disc 1 in. in diameter was prepared by pressing 150 mg of the powder for 2 min at 5 ton/in.^{2} in a hydraulic press. The disc was then mounted in the adsorption/infrared cell and reduced *in situ* to nickel metal in a stream of hydrogen at 350°C for 4 hr before evacuation to 10^{-5} Torr and subsequent cooling to room temperature. The double-beam infrared cell (*2*) enabled separate spectra to be obtained on the surface and in the gas phase.

A typical nickel/silica disc of 150 mg weight had a transmittance of about 30% at 3000 cm^{-1}. By operating the spectrometer at a fixed slit width of 0.4 mm, and with attenuation of the reference beam, spectra of very good quality and reproducibility were obtained. The infrared spectrometer was a Grubb-Parsons Model GS2 grating instrument. The adsorption cell used has been described previously (*2*). It was found that a stiff paste of silica powder and silicone high vacuum grease (*7*) afforded an excellent vacuum seal between the flanges of the cell ends and the potassium bromide windows used, making the cell suitable for work at elevated temperatures.

RESULTS AND DISCUSSION

1. *The Spectrum of the Stable Surface Species*

Acetaldehyde vapor at a pressure of 10 Torr was admitted to a freshly reduced nickel sample at 25°C and allowed to stand overnight before recording the spectrum (Fig. 1 and Table 1). This was considerably different from the spectrum observed over a pure silica sample [Fig. 5a, of Ref. (*1*)] in that strong νCH bond-stretching bands appeared at 2985, 2945, and 2911 cm^{-1} in addition to the aldehydic νCH bands. Broad bands of moderate intensity also appeared in the 2100–1800 cm^{-1} region showing that the decarbonylation reaction had occurred over the nickel catalyst [compare the results of Tsuji *et al.* (*3*) over palladium]. In addition to the strong aldehyde νC═O band at 1720 cm^{-1}, rather broad and ill-defined absorptions occurred near 1580 and 1445 cm^{-1}. In this work, considerably better quality spectra were obtained than previously reported (*1*) due to improvements in sample preparation and spectroscopic techniques. Slight differences in the quoted frequencies may be attributed to this. Evac-

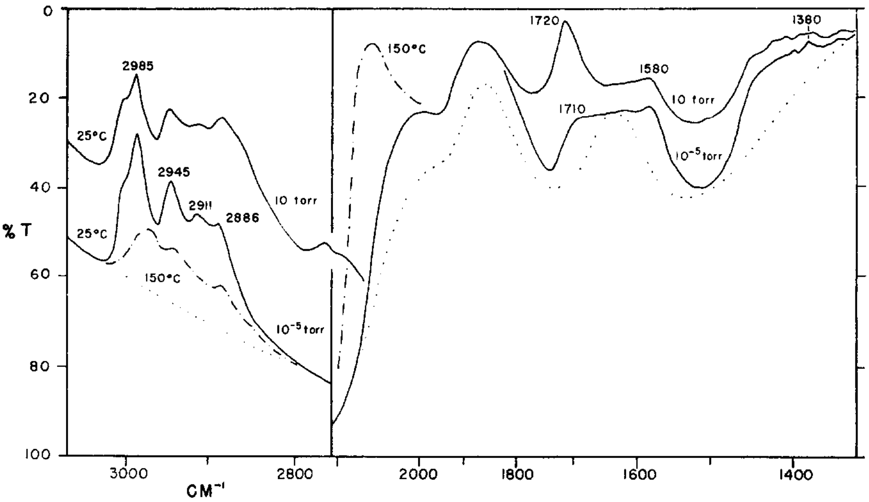

FIG. 1. Infrared spectra of acetaldehyde adsorbed overnight on silica-supported nickel (10% Ni, 150 mg) at 25° (10 Torr), after evacuation to 10^{-5} Torr, and after heating to 150°C.

uation at 25°C for 4 hr at 10^{-5} Torr removed nearly all the acetaldehyde that was physically adsorbed to silica, as shown by the disappearance of the aldehydic νCH and νC=O bands. The residual spectrum was therefore at first all attributed to material chemisorbed to nickel. However, the results of subsequent experiments described below showed a number of different surface species to be present, some adsorbed on the silica part of the disc. The assignment of bands to the various species is anticipated in Table 1.

TABLE 1
INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF ACETALDEHYDE ADSORBED ON SILICA-SUPPORTED NICKEL[a]

Type of vibration	Frequency (cm^{-1})	Intensity (OD)[b]	Surface species
	3000	(shoulder)	Paraldehyde
νCH	2985	0.35	RCHO/Ni[c]
	2945	0.23	
	2911	0.18	
	2886	0.18	
	2040	0.2	Ni/CO
	1870	0.3	
νCO	1710	0.10	RCHO---HOSi
	1580	0.18	R · COO⁻ on Ni
	ca. 1430	0.23	
δCH	1402	0.13	Paraldehyde
	1380	0.25	RCHO/Ni[c]

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[a] Acetaldehyde vapor at 10 Torr was admitted to 150-mg disc containing 10% by weight of nickel, allowed to stand for 15 hr at 25°C and then evacuated for 2 hr at 10^{-5} Torr.

[b] OD = optical density.

[c] These are assigned to $CH_3 \cdot CH\mathbf{M}\text{-}O\mathbf{M}$ (see text).

(a) Carbonyl absorption bands. The infrared spectrum of adsorbed carbon monoxide on nickel is known to show two strong bands near 2050 and 1900 cm^{-1} (*8, 9*). We assign to these species the ill-defined bands near 2040 and 1870 cm^{-1} (Fig. 1) observed in this spectrum superimposed on the silica background.

The weak band near 1710 cm^{-1} remaining after pumping at 10^{-5} Torr for 2 hr is ascribed to residual physically adsorbed aldehyde; it is shown in Sect. 2b that the species concerned is adsorbed to silica and not to nickel. Although virtually all physically adsorbed aldehyde must have been removed from pure silica after pumping for such a period it is conceivable that small amounts of aldehyde may slowly migrate from different parts of the cell or from the nickel to the silica surface over prolonged periods.

The broad band at about 1580 cm^{-1} was found in the earlier experiments with a range of aldehydes, but it soon became apparent that it was not associated with the same species that produced the absorptions in the νCH region because the relative intensities in these two regions varied markedly in different experiments. It was suspected that some oxidation of the aldehyde to acetic acid had occurred, resulting in the formation of acetate ion groups on the surface, and that this species was also responsible for the broad band near 1430 cm^{-1} (the two bands arising, respectively, from the antisymmetric and symmetric νCO modes of the surface $CH_3{\cdot}CO_2^-$ structure).

In confirmation of this hypothesis the same bands were obtained by a study of the spectrum of carboxylic acids adsorbed on silica/nickel. The adsorption of formic acid on nickel has previously been discussed by several authors (*10*, *11*), and shows two strong νCO bands at about 1580 and 1400 cm^{-1}. Propionic acid on nickel/silica gives absorption bands of $Et{\cdot}CO_2^-$ at 1562 and 1430 cm^{-1} (unpublished work). It has also been found (*12*) that when a carboxylic acid itself is adsorbed on silica, a strong band appears at about 1750 cm^{-1} corresponding to the νCO vibration of chemisorbed surface ester groups, $R{\cdot}CO{\cdot}O\mathbf{Si}$. These are formed by the reaction of the acid with surface hydroxyl groups and the elimination of water. No bands were ever observed at this frequency when aldehydes were exposed to a nickel/silica surface, or a silica surface alone, establishing that the acid responsible for the 1580 and ca. 1430 cm^{-1} bands was formed on the catalyst and was not due to acid contamination in the aldehyde sample.

It was also found that bands at these frequencies were still obtained when extended reduction procedures were carried out. Subsequent experiments (for which we are indebted to Dr. R.St.C. Smart) showed that the bands near 1580 and 1430 cm^{-1} did not occur on initial adsorption of acetaldehyde on nickel/silica but grew in intensity slowly as a function of time over a period of 40 hr when acetaldehyde was present in the gas phase. The intensity shown in Fig. 1 results from overnight adsorption before recording of the spectrum. We therefore consider that the bands near 1580 and 1430 cm^{-1} in the acetaldehyde case are caused by a slow oxidation reaction taking place on the metal surface rather than chemisorption on residual nickel oxide resulting from incomplete reduction. The necessary oxygen may be provided by some degree of dissociative adsorption of acetaldehyde on the metal, as is common with olefins on metals. Hydrogen released to the surface at the same time may be responsible for the detection of some ethyl groups attached to the silica part of the surface (see discussion in Sect. 2).

In considering the significance of the 1580 and 1430 cm^{-1} bands it must not be forgotten that these bands are of very high intrinsic intensity in the infrared spectrum, so that the proportion of CH_3COO^- species implied by Fig. 1 is very small in proportion to the chemisorbed species giving νCH bands in the 3000 cm^{-1} region.

We conclude that the spectra shown in Fig. 1 contain no bands that may properly be assigned to surface acyl species. The infrared spectra of a number of metal acyl complexes have been reported in solution. In all cases the ν$C{=}O$ frequency lies in the range 1685–1625 cm^{-1} (*13–19*) and values of about 1650–1630 cm^{-1} were observed for the acetyl complexes of platinum (*13*, *19*), iron (*15*), and manganese (*17*). No spectra of nickel acyl complexes appear to have been reported. These data suggest that the band observed at 1720 cm^{-1} by Blyholder and Neff (*5*) from acetaldehyde on nickel/paraffin is too high in frequency for attribution to a surface acyl group. Those obtained in the 1600–1570 cm^{-1} region by Blyholder and Wyatt (*6*) from alcohols on cobalt (but not on nickel) might more reasonably be assigned to such species on frequency grounds. However, accompanying bands of comparable intensity in the 1400–1450 cm^{-1} region raise the question whether these cannot also be attributed to oxidation products of the type $R{\cdot}COO^-$.

The absence of infrared evidence for the surface acyl species does not exclude the possibility that in small quantity this may play an active part in the catalytic reaction.

On the other hand, the decay of the saturated surface species on nickel discussed below does coincide with the growth of decarbonylation products.

(b) νCH and δCH absorption bands. νCH bands shown in Fig. 1 are of sufficient intensity that they can be ascribed to one or more major surface species. Since no accompanying νCO band appears in the 1680–1620 cm^{-1} region characteristic of acyl complexes, the most likely type of surface species seems to be alkoxide. Possible structures based on the acetaldehyde skeleton are therefore

$$\text{(I) } CH_3 \cdot CH_2 \cdot \mathbf{OM}, \qquad \text{(II) } CH_3 \cdot CH\mathbf{M} \cdot \mathbf{OM},$$
$$\text{(III) } CH_2\mathbf{M} \cdot CH\mathbf{M} \cdot \mathbf{OM},$$

where **M** = surface metal atom. Of these, the triadsorbed species (**III**) cannot be a predominant one because the spectrum shows strong bands characteristic of methyl groups attached to carbon.

(**I**) is a hydrogenation product of acetaldehyde, and requires either the presence of hydrogen atoms on the metal surface (which, by its method of preparation, is considered to be relatively hydrogen free) or the occurrence of self-hydrogenation processes on the surface. (**I**) is also the species favored by Blyholder and Neff (*4*) from observations of the skeletal region of the spectrum obtained from acetaldehyde on Fe/paraffin. Anderson and Kemball (*20*) have concluded from the rapid deuterium exchange of the hydroxyl hydrogen atom of alcohols observed over metal films, that the $RCH_2O\mathbf{M}$ species was short lived and should not be regarded as a stable surface species; however this may not be strictly relevant as their experiments, unlike ours, were carried out in the presence of excess hydrogen or deuterium.

The diadsorbed structure (**II**) could be formed on a completely bare metal surface merely by opening the C=O double bond. The νCH region of the spectrum certainly resembles that of a methyl group attached to a saturated (sp^3) carbon atom. It is difficult, however, to distinguish between structures (**I**) and (**II**), purely on the basis of the νCH bands, for Nolin and Jones (*21*) found rather similar νCH spectral profiles from $MeCH_2O$– and $MeCD_2O$– groups. We discuss in Sect. 2b which of the two species, (**I**) or (**II**), is to be preferred. That the species are, at least in part, chemisorbed to the metal is confirmed by the effect of heating to 150°C (Fig. 1), when a decrease in the intensity of these νCH bands is accompanied by decarbonylation. This results in the growth of the 2040 cm^{-1} band (Fig. 1) of chemisorbed carbon monoxide and the appearance of the gas-phase bands of carbon monoxide and methane.

It is shown in Sect. 2b that paraldehyde, the cyclic trimer of acetaldehyde, was also present and is identifiable by the sharp high frequency shoulder at 3006 cm^{-1} from a νCH vibration and the angle deformation mode at 1402 cm^{-1} (Fig. 1).

2. The Effect of the Silica Support on the Overall Spectrum of the Adsorbate

The observed alkoxide-type spectra are similar to those of ethoxide groups on silica surfaces as obtained by the reaction of ethanol with surface OH groups (Sect. 2b). Although the reaction of acetaldehyde with the nickel/silica catalyst was carried out with what is considered to be essentially a "bare," i.e., hydrogen-free nickel surface, there is the possibility that some of the aldehyde groups may dissociatively adsorb to form surface-carbide type species such as are postulated with hydrocarbons on silica-supported metals (*22, 23*). The hydrogen so released, together with acetaldehyde, could then give rise to ethoxy groups attached to metal atoms. Alternatively ethanol may be produced catalytically and then react with the silica surface to form EtO**Si** groups. This raises the question of the extent to which the silica support, which is necessary for the preparation of thermally stable and infrared transparent metal samples, may play a part in producing the observed spectra in conjunction with the nickel catalyst. Cab-O-Sil discs by themselves give rise to only physically adsorbed species when acetaldehyde is added at 25°C (*1*). We have therefore attempted to make allowance for the spectra of materials present on the silica support. These experiments are described below.

(a) Variation of metal concentration. If the spectrum is due to adsorbate on the metal, then the intensity of the bands should be proportional to the concentration of the metal in the sample (taking sample discs with the same silica weight, and assuming perfect dispersion of the metal, i.e., that the metal area is strictly proportional to the weight used). Acetaldehyde was therefore admitted to sample discs of 150 mg containing 10, 2, and 0.5% by weight of nickel. After standing at 10 Torr for 2 min, the samples were evacuated at 10^{-5} Torr for 2 hr and the spectra were recorded (top curves of Fig. 2A). A further dose at 10 Torr was then admitted and allowed to stand overnight at 25°C and spectra (upper curves in Fig. 2B) were taken after evacuation for 2 hr.

The four main bands in the νCH region at 2985, 2945, 2911, and 2886 cm^{-1} showed a consistent increase in intensity with increasing metal concentration. Typical values for the optical densities of the strongest 2985 cm^{-1} band after the shorter period of adsorption are 0.022 (0.5% Ni), 0.058 (2% Ni) and 0.102 (10% Ni). The lack of a linear relationship between the band strength and amount of metal is probably due to the formation of larger metal crystallites at higher metal concentrations, i.e., imperfect dispersion of the metal. These spectra are therefore consistent with the conclusion that the spectra are associated with the metal part of the sample. An alternative possibility, however, is that the bands could have arisen from products which have migrated from the nickel to the silica surface.

(b) "Half and half" discs. This latter possibility was explored by using discs of which one half was pure silica and the other silica-supported nickel, with a sharp boundary along a diameter. Any by-products formed on the metal, and subsequently adsorbed on the silica part of a silica/nickel disc, should also be able to migrate to the pure silica half of such a disc, where their spectra can be examined separately. Subtraction of this "silica" spectrum from the "silica/nickel" spectrum should give a better appraisal of the spectrum of the species adsorbed on the metal alone. It was only possible to use such a "half and half" disc

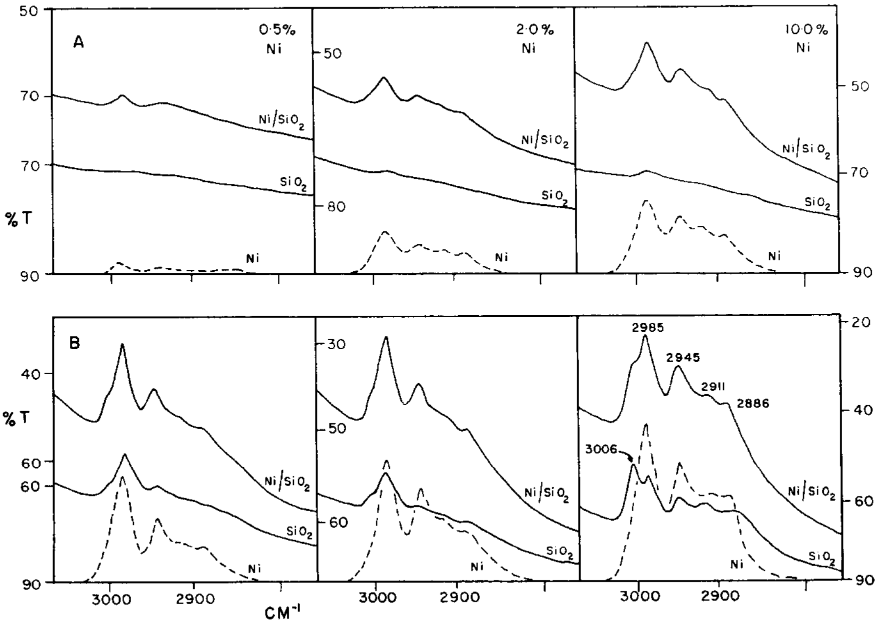

FIG. 2. Infrared spectra (νCH region) of acetaldehyde on "half and half" discs at various nickel concentrations (0.5, 2, and 10% Ni by weight): (A) 10 Torr admitted for 2 min; pumped 2 hr at 10^{-5} Torr; (B) 10 Torr admitted for 15 hr; pumped 2 hr at 10^{-5} Torr. Subtracted spectra (Ni/SiO$_2$ − SiO$_2$) are drawn (- - -) on the 90% transmission line.

technique because the sample could be placed in the spectrometer at a focus of the beam, where the image width from the light source was only a fraction of the width of the disc. Spectra could thereby be obtained from portions of the disc immediately on either side of the dividing line.

The spectra illustrated in Fig. 2A and B were in fact observed using "half and half" discs, where the other half consisted of the same weight of silica alone. The spectra observed from the silica half discs are shown as the lower spectra with sloping backgrounds in Fig. 2A and B.

The broken lines drawn on the base lines of Fig. 2A and B represent the difference spectra obtained by subtracting each spectrum on silica from that on Ni/silica. If the species adsorbed on the silica half of the disc are sufficiently mobile these broken line spectra should represent the species adsorbed on nickel itself. Each of these spectra has in fact a closely similar contour and, as expected, they increase in intensity with increasing nickel content of the catalyst, and with the time of adsorption.

After overnight adsorption the 10% nickel sample clearly showed prominent bands on silica (in particular at 3006 cm^{-1}) of an additional species, which was responsible for the ca. 3000 cm^{-1} shoulder previously observed in the spectrum of adsorbed acetaldehyde (Fig. 1). This was identified as paraldehyde, the cyclic trimer of acetaldehyde, as mentioned earlier (Sect. 1b). Since the formation of paraldehyde was not observed on discs of pure silica alone, and because more was formed on discs with a higher nickel concentration, it was concluded that the polymerization had occurred by activation on the nickel surface.

The spectra on the silica half-discs also showed the residual νC=O band at 1710 cm^{-1}, confirming that it should not be assigned to a nickel acyl species.

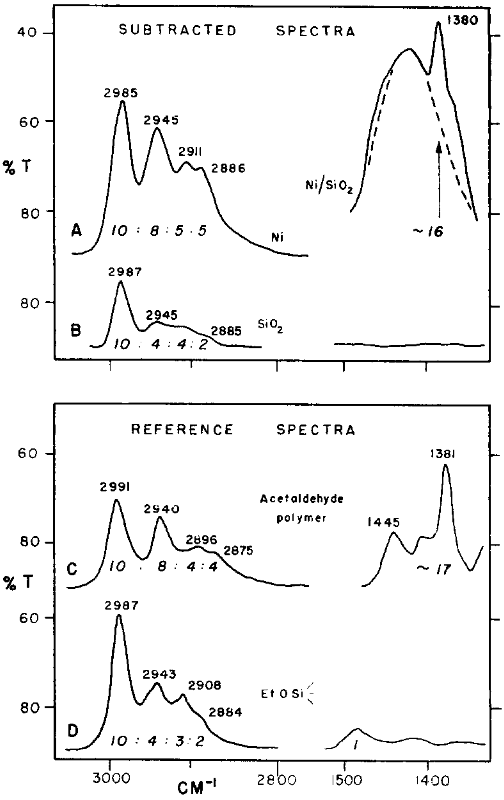

FIG. 3. Comparison of subtracted spectra with those of model compounds: (A) acetaldehyde chemisorbed on nickel (Ni/SiO$_2$ − SiO$_2$); (B) ethanol [by-product on silica from (SiO$_2$–paraldehyde)]; (C) acetaldehyde polymer (soln. in CCl$_4$) [Ref. (*24*)]; (D) ethanol chemisorbed on silica (R. P. Young, unpublished work).

3. The Nature of the Saturated Surface Species on Nickel

In Fig. 3A and C a comparison is made between the spectrum observed on nickel with that of a linear acetaldehyde polymer —[(CH$_3$)CH·O—]*n* prepared by the method of Novak and Whalley (*24*) while Fig. 3B and D compare the spectrum observed on a silica half-disc and that from surface EtO**Si** groups deliberately formed by the reaction of ethanol with a silica disc (10 Torr of ethanol admitted for 15 hr, and pumped for 2 hr at 10^{-5} Torr). The frequencies of the bands in all these spectra are very similar, but there is a significant difference in the relative intensities of the component bands, particularly in the greater strength of the 2940 cm^{-1} band of the first two spectra in comparison with the last two. This is taken to indicate a real difference in the nature of the two species and the intensity profile in Fig. 3B and C is closely similar to that described by Nolin and Jones (*21*) for CH_3CH_2O— groups. A strong CH deformation band at 1380 cm^{-1} is also present in the spectra shown in Fig. 3A and C, but not in the other two. On this basis the spectrum on silica (Fig. 3B) is assigned to CH_3CH_2OSi groups, and that on nickel to species closely resembling —$(CH_3)CH$—O—. The remaining question is whether the latter represents the diadsorbed alkoxide $CH_3 \cdot CHM \cdot OM$ or physically adsorbed linear polymer —$[(CH_3)CH$—O—$]n$ on the metal surface. The former interpretation is preferred for the following reasons:

1. The frequencies of the corresponding νCH bands in Fig. 3A and C are all slightly different (outside possible experimental error), as might be expected for the two slightly different structures.

2. Spectra identical to Fig. 3A (except in total intensity) were also obtained on the more dilute nickel discs (0.5 and 2% Ni) where there was virtually no evidence for the formation of the well defined polymer paraldehyde (see Fig. 2). It seems likely that paraldehyde would be one of the first polymers to be formed and if this is absent then the presence of higher polymers seems unlikely.

3. The surface species $CH_3 \cdot CHM \cdot OM$ would be a natural precursor of polymeric products.

We therefore conclude that acetaldehyde is most probably adsorbed on nickel as the diadsorbed alkoxide (**II**) $CH_3 \cdot CHNi \cdot ONi$ by addition across the C═O double bond. Additional evidence for this structure would be provided by the identification in the spectrum of both the νC—Ni and νO—Ni modes. It is unfortunate that observation in the

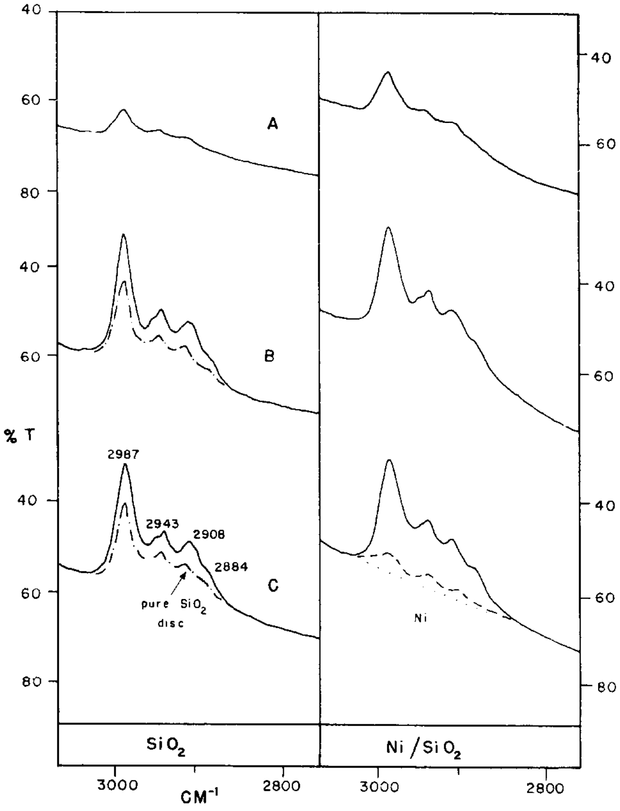

FIG. 4. Infrared spectra from the adsorption of ethanol on a "half and half" nickel–silica disc (150 mg, 10% Ni) at 25°C: (A) 10 Torr admitted for 2 min; pumped 2 hr at 10^{-5} Torr; (B) 10 Torr admitted for 15 hr; pumped 2 hr at 10^{-5} Torr; (C) 10 Torr admitted for 15 hr; pumped 6 hr at 10^{-5} Torr. Analogous spectra on a pure silica disc (· — · —); and the weak subtracted spectrum (Ni/SiO_2 − SiO_2) (- - -).

relevant region of the spectrum (about 500 cm^{-1}) is not possible by infrared means with these metal/silica samples on account of absorption by the silica support.

4. Spectra of Ethanol Adsorbed on Nickel/Silica

In their studies using nickel/paraffin Blyholder and Neff (*4, 5*) reported the observation of similar spectra from ethanol and acetaldehyde, but with nickel/silica Blyholder and Wyatt (*6*) studied the adsorption of only ethanol, and no comparative data were published for acetaldehyde. The latter authors assumed that their observed spectra resulted from adsorption of the alcohol on the metal, although they admitted the possibility of there also being adsorption on the silica support. In an attempt properly to assess the effect on the overall spectrum of species adsorbed on silica, we have examined the spectra obtained when ethanol was admitted to a half and half disc containing 10% nickel. The results are shown in Fig. 4.

Unlike our findings with acetaldehyde (Fig. 2), only a very weak residual spectrum (Fig. 4C) was found after subtraction of the νCH spectrum on the silica half of the disc from that obtained on the nickel/silica half. Nevertheless the nickel had catalyzed some decomposition of adsorbed ethanol as shown by the presence of absorption bands characteristic of chemisorbed CO on the nickel/silica half disc. This is in agreement with the work of Blyholder and Wyatt (*6*) and, like them, we find no evidence for $\nu C{=}O$ bands that could arise from surface acyl species on this metal. The spectra obtained on both silica and nickel/silica were of the same contour as those obtained by the adsorption of ethanol on a pure silica disc (Fig. 3D). Our experiments therefore indicate that even on nickel/silica the main surface species from the adsorption of ethanol is CH_3CH_2OSi rather than CH_3CH_2ONi.

These observations of the different behavior of acetaldehyde and ethanol are consistent with our conclusion that the former is adsorbed on nickel as a diadsorbed rather than a monoadsorbed alkoxide species. The results obtained in this paper show that, when interpreting the spectra from supported metals with active or polar adsorbates, care must be taken to make accurate allowance for species adsorbed onto the catalyst support, by using techniques such as those we have described.

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