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# Infrared Spectroscopic Studies of Adsorption and Catalysis

## IV. Aliphatic Ketones on Silica-Supported Nickel

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The adsorption and decarbonylation of acetone, acetone-$d_6$, and diethylketone on silica-supported nickel have been studied between 25 and 200°C using infrared spectroscopy. After a short period of adsorption, two surface species were observed spectroscopically at 25°. The main one is considered to be the associatively adsorbed ketone $R_2C\mathbf{M}\text{–}O\mathbf{M}$ ($\mathbf{M}$ = surface metal atom). The minor one is a carbonyl-containing species possibly involving a complete acetone molecule held to a metal site through a relatively weak $\sigma$-bonded interaction with the carbon atom of the carbonyl group, or a $\pi$-bonded interaction with the carbonyl group as a whole. Over longer periods of time, bands were observed which are attributable to $R_2CH{\cdot}O\mathbf{Si}$ groups ($\mathbf{Si}$ = surface silicon atom of the support). These probably result from the reduction of the ketone to $R_2CHOH$ molecules which then react with OH groups of the silica surface. The hydrogen needed for the reduction process may arise from disproportionation of some of the dissociatively adsorbed species.

At higher temperatures (~180°C) acetone was decomposed to methane and carbon monoxide, the latter appearing both in the gas phase and chemisorbed to metal; at 200° diethylketone was decarbonylated to only a minor extent to give carbon monoxide and methane.

On adsorption of acetone-$d_6$, deuterium exchange with silica OH groups occurred rapidly, probably via the dissociatively adsorbed surface intermediate $CD_2\mathbf{M}\text{–}(CD_3)C\mathbf{M}\text{–}O\mathbf{M}$.

## 1. INTRODUCTION

The surface species formed by the chemisorption of ketones on nickel are of considerable interest from the point of view of the mechanism of the hydrogenation and deuterium exchange reactions on such catalysts. Bond (*1*) has reviewed much of the work in this field. Kemball and Stoddart (*2*) have made valuable contributions to the understanding of the reaction of acetone and deuterium over transition metals. They concluded that the most important single exchange process over nickel involved only one of the methyl groups at a time. This could be formulated in terms of the following surface species ($\mathbf{M}$ = surface metal atom):

$$(CH_3)_2C\mathbf{M}\text{–}O\mathbf{M} \xrightarrow{\mathbf{M}} \mathbf{M}CH_2\text{–}(CH_3)C\mathbf{M}\text{–}O\mathbf{M} \xrightarrow{D_2} CH_2D(CH_3)C\mathbf{M}\text{–}O\mathbf{M}.$$

They also discussed the results of deuteration reactions leading to the formation of isopropanol-$d_2$. The rate-determining step, which is also the slow step in the exchange of isopropanol, was considered to be

$$(CH_3)_2C\mathbf{M}\text{–}OD + D\mathbf{M} \rightarrow (CH_3)_2CDOD + 2\mathbf{M}.$$

Galwey and Kemball (*3*) have reported that slight dissociative adsorption occurs with acetone over silica-supported nickel and that at 100°C this was often accompanied by cracking.

All of the above conclusions were reached by analysis of gas-phase reaction products. It is clearly of interest to study the infrared spectra of the chemisorbed species formed

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when ketones interact with a nickel catalyst with a view to obtaining information about their structure. The spectra from acetone, and in less detail from acetone-$d_6$ and diethylketone, on silica-supported nickel are presented here. We have previously reported some very weak spectra from acetone on nickel (*4*) but improvements in spectroscopic and sample preparation techniques (*5*) have led to better results and warranted a more extensive investigation. Blyholder and Wyatt (*6*) have also briefly reported results from acetone on silica-supported nickel at a single temperature.

## 2. Experimental Methods

The apparatus and general procedures followed were as described before (*4, 7*). Acetone and diethylketone were stored over molecular sieves and distilled under dry nitrogen before use; acetone-$d_6$ was obtained from Ciba Ltd. (99.6% isotopic purity) and used without further purification. All adsorbates were thoroughly degassed before admission to the adsorption cell. The spectra obtained were of higher quality than before (*4*) because (a) sample discs of 150 mg were used, which effectively doubled the available catalyst area resulting in a corresponding increase in the intensity of the spectral bands of the adsorbate, and (b) operation of the Grubb-Parsons GS2 infrared grating spectrometer at a fixed slit width of 0.4 mm and with attenuation of the reference beam produced a lively pen response and a high signal-to-noise ratio. Spectra were generally recorded at 25°C after various periods of standing, evacuation or heating of the sample. In some cases use was made of a second infrared gas cell attached to a cold finger [the trap cell (*5*)], to enable the recording of the spectra of small amounts of material evacuated from the adsorption cell.

"Half-and-half" discs were pressed from silica and silica/nickel nitrate so as to have a sharp dividing diameter (*5*). Reduction to nickel/silica was done *in situ* in the infrared cell. The sharp image of the Nernst source obtainable with the Grubb-Parsons infrared spectrometer enabled spectra to be obtained from parts of the disc immediately on either side of the dividing line. This enabled spectra to be obtained of species on the silica surface which result from migration of products from the nickel particles; by this means spectral bands from species specifically adsorbed to nickel could be more reliably identified.

## 3. Results and Discussion

### 3.1. *Acetone*

Figure 1A shows the infrared spectra obtained when acetone was adsorbed overnight on silica-supported nickel (150 mg;

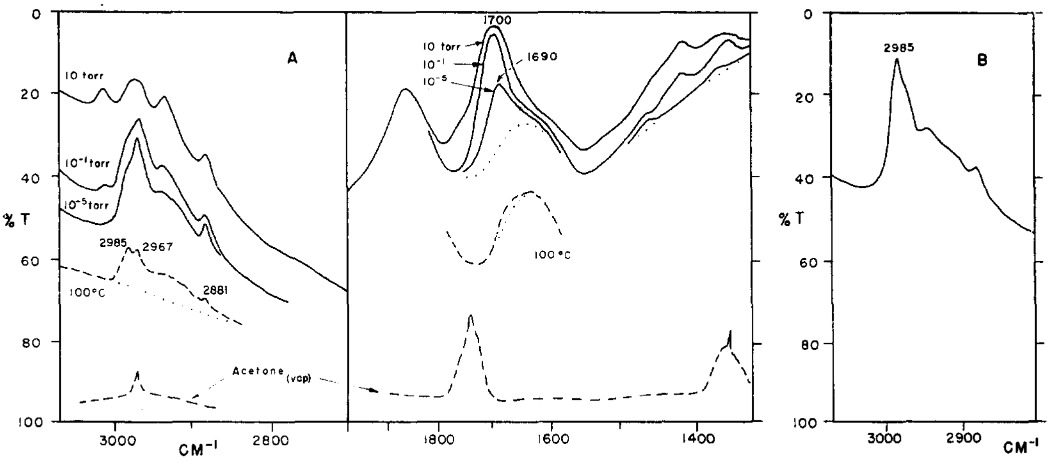


Fig. 1. Infrared spectra of acetone adsorbed on silica-supported nickel (150 mg, 10% w/w Ni): (A) at 25°C at 10, $10^{-1}$, and $10^{-5}$ Torr followed by heating to 100°C for 20 min (---); (B) $\nu$CH spectrum obtained on silica after an acetone/$H_2$ mixture had been in contact with the catalyst at 90°C for 15 hr followed by evacuation at $10^{-5}$ Torr for 3 hr at 25°C.

10% w/w Ni) at 25°C followed by evacuation from 10 to $10^{-1}$ and $10^{-5}$ torr. The evacuation process led to the removal of background absorption in the 3000 $cm^{-1}$ region which is caused by hydrogen bonded OH groups on the silica surface $[Si{-}OH \cdots O{=}C(CH_3)_2]$ and of the bands near 3010 $cm^{-1}$, 2960 and 2920 $cm^{-1}$ (partly obscured), 1410, 1370, and 1700 $cm^{-1}$ from the physically adsorbed acetone. Residual absorptions remained in the 3000 $cm^{-1}$ ($\nu CH$), 1690 $cm^{-1}$ ($\nu C{=}O$) and 1400 $cm^{-1}$ ($\delta CH_2$ or $\delta CH_3$) regions. The band at 1690 $cm^{-1}$ is clearly due to a carbonyl-containing species. However, as the intrinsic intensities of such bands are very high, the major part of the absorption remaining in the $\nu CH$ bond-stretching and $\delta CH_3$ or $\delta CH_2$ angle bending regions must arise from a different surface species.

Evacuation of the sample at 100°C for 20 min led to the removal of the 1690 $cm^{-1}$ band (upper broken line in Fig. 1) and unchanged acetone was recovered in the trap cell (lower broken line). Heating to 100°C also led to a general weakening of bands in the $\nu CH$ region so that a shoulder observed at 2985 $cm^{-1}$ at 25°C became relatively more prominent in the residual spectrum. As the $\nu CH$ bands decayed on heating, other bands from chemisorbed carbon monoxide appeared near 2070 and 1900 $cm^{-1}$, and methane and CO appeared in the gas phase.

In a separate experiment a sample of acetone was reduced to isopropanol in excess hydrogen (50 Torr at 90°C) over an identical nickel/silica catalyst. The product from this reaction interacted with the silica support to form chemisorbed isopropoxy groups $(CH_3)_2CH{-}O\mathbf{Si}$ (**Si** = surface silicon atom), with the absorption bands shown in Fig. 1B. It therefore seemed likely that the observed band at the same frequency from acetone alone (Fig. 1A, broken line) corresponds to the $\nu CH$ band at 2985 $cm^{-1}$ of the isopropoxy group. Analogous results have been obtained in the case of the adsorption of acetaldehyde on Ni/silica, where ethoxy groups were identified on the silica support (*5*). In that case it was considered that ethanol was formed on the nickel surface as a by-product (by the hydrogenation of small amounts of acetaldehyde), which subsequently migrated to the silica support and became chemisorbed as surface ethoxy groups.

The use of the "half-and-half" disc (see Sect. 2) confirmed that the original 2985 $cm^{-1}$ band in Fig. 1A was caused by a species predominantly (probably entirely) present on silica. In Fig. 2B the broken line represents the approximate spectrum on nickel alone (obtained by the subtraction $Ni/SiO_2 - SiO_2$) redrawn on the 90% transmission line. The bands have similar frequencies and relative intensities to those reported by Blyholder and Wyatt (*6*) on silica-supported nickel. We assign all three bands in this spectrum to a methyl-rich species (*8*), probably the associatively adsorbed species $Me_2C\mathbf{M}{-}O\mathbf{M}$. It is possible that the band at 2930 $cm^{-1}$ may be caused by a small proportion of $CH_2$ as well as $CH_3$ groups. The $Ni/SiO_2$ spectrum observed immediately after the admission of acetone to the surface followed by evacuation, Fig. 2A, was virtually identical to the "subtracted" spectrum on nickel, although rather weaker. The isopropoxide absorption bands on silica were only observed with any significant intensity (Fig. 2B) after adsorption for a number of hours.

It was mentioned above that a $\nu C{=}O$ band near 1690 $cm^{-1}$ persisted after room temperature evacuation, although it was removed at 100°C. Figure 2 also shows the spectra from nickel/silica and silica alone in the 1850–1600 $cm^{-1}$ region. As shown in the initial spectrum, Fig. 2A, the 1690 $cm^{-1}$ band arises from some species present on nickel, although a band of less intensity appeared between 1710 and 1700 $cm^{-1}$ on silica after standing overnight (Fig. 2B) but was readily removed by pumping. The subtracted "nickel" spectrum (broken line) shows an absorption maximum at 1685 $cm^{-1}$. The band on silica is probably due to acetone physically adsorbed to silica (*4*), i.e., $Me_2CO \cdots HOSi$. The band at 1685 $cm^{-1}$ on nickel is also due to a carbonyl-containing species which is not very strongly adsorbed, to judge from the fact that it is relatively easily removed at 100°C. We consider that the large frequency shift of the $\nu CO$ band [54 $cm^{-1}$, compared with 30 $cm^{-1}$ for hydro-

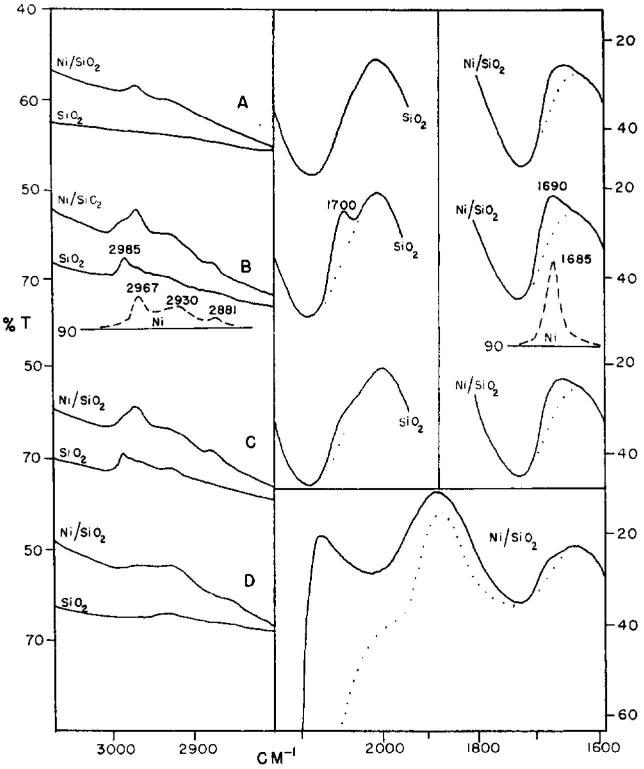
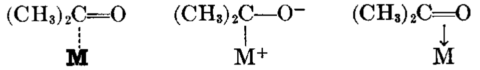


FIG. 2. Infrared spectra of acetone adsorbed on "half and half" nickel–silica/silica discs: (A) 25°C, 10 Torr for 2 min and pumped to $10^{-5}$ Torr for 2 hr; (B) 25°C, 10 Torr for 15 hr and pumped to $10^{-5}$ Torr for for 2 hr; (C) as (B) but pumped for 6 hr; (D) as (C) heated for 15 hr at 180°C, and pumped for 2 hr at 25°C.

gen bonding to HOSi (*4*)] implies that it interacts with the surface through the carbonyl group. A possible surface species may be formulated in electronic structure as partway between σ-complexed species (**I**) and



$$\underset{\mathbf{M}}{\overset{}{(CH_3)_2C{=}O}} \qquad \underset{M^+}{(CH_3)_2C{-}O^-} \qquad \underset{M}{(CH_3)_2C{=}O\downarrow}$$

(**I**) (**II**) (**III**)

(**II**) (closer to **I** rather than **II** to judge by the νCO frequency) or as a π-complexed species (**III**).*

We do not favor Blyholder and Wyatt's (*8*) alternative assignment of this band to a surface acyl species, presumably of type $CH_3 \cdot CO \cdot \mathbf{M}$. This is because we have not observed any methane under these experimental conditions (this might have been expected if acetone is dissociatively adsorbed in the above manner) and because the frequency is high, relative to the range 1650–1630 $cm^{-1}$ normally found for transition-metal acyl compounds (*9*). We have also identified unchanged acetone after removal of this species suggesting that the carbon skeleton is not broken on adsorption, i.e., as shown in our formulation. The νCH bands of acetyl groups are always much less intense than νCO absorptions so it is not considered that this species contributes appreciable intensity to the νCH region shown in Fig. 2B, and that the surface coverage by this species must be rather small.

Figure 2D shows the decay of νCH bands at 180°C and the growth of those associated with carbon monoxide chemisorbed on nickel at ~2070 and ~1900 $cm^{-1}$. Methane (rather than ethane) also appeared in the gas phase concurrently with the growth of the latter bands. The additional hydrogen atom may originate from some dissociative adsorption of acetone on nickel. A similar hypothesis is needed to account for the production of the

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* We thank a referee for suggesting this possibility.

surface $(CH_3)_2CH\cdot OSi$ groups via isopropanol that has been mentioned above. Blyholder and Wyatt (*6*) observed some weak bands from chemisorbed CO at room temperature on their nickel catalysts.

### *3.2. Acetone-$d_6$*

The spectra obtained from the adsorption of acetone-$d_6$ on silica–nickel are presented in Fig. 3. After the surface had been exposed to a pressure of 5 Torr at 25°C for only 2 min, a considerable amount of deuterium exchange with surface SiOH groups had occurred, as shown by the production of a broad $\nu$OD band at about 2600 $cm^{-1}$ representing acetone-$d_6$ physically adsorbed on silanol OD groups. No such exchange was observed at room temperature between pure silica and samples of the same batch of acetone-$d_6$; only by heating for several hours at 250°C could any be detected. The exchange reaction must therefore have taken place via chemisorption on the metal surface; the deuterium atoms, presumably initially produced as surface **Ni**D groups, must have subsequently interacted with the silica OH groups. A similar effect was observed during the decomposition of propionaldehyde-$d_1$ (*5*).

The amount of exchange increased considerably after standing overnight at 10 Torr at 25°C, and a weak $\nu$CH band also then appeared at about 2940 $cm^{-1}$ confirming that slight exchange had occurred into the methyl group. It seems probable that the exchange mechanism involves the triadsorbed intermediate $CD_2\mathbf{M}\text{–}(CD_3)C\mathbf{M}\text{–}O\mathbf{M}$ as suggested by Kemball and Stoddart (*2*). Pumping to $10^{-5}$ Torr revealed the 1690 $cm^{-1}$ band discussed for acetone; heating to 200° as before gave rise to bands of CO chemisorbed on nickel. Sharp bands in the region 2250 to 2150 $cm^{-1}$ are caused by $\nu$CD vibrations.

### *3.3. Diethylketone*

Diethylketone was examined to determine whether decarbonylation would lead to the formation of ethylene, ethane, or butane by analogy with the similar reaction with propionaldehyde [EtCHO (*5*)], since acetaldehyde and acetone both give carbon monoxide and methane. Figure 4 shows the $\nu$CH region of the spectrum recorded after evacuation at 25°C; a weak band at about 1690 $cm^{-1}$ was also observed (as in the case of acetone) and is attributed to the presence of a very small amount of an analogous species. The fairly strong $\nu$CH spectrum is again assigned to the associatively adsorbed surface species $(Et)_2C\mathbf{M}\text{–}O\mathbf{M}$. The bands are of very similar frequency and relative intensity to those of pentan-3-ol, $(Et_2)CHOH$.

Heating to 200°C for 15 hr at 10 Torr

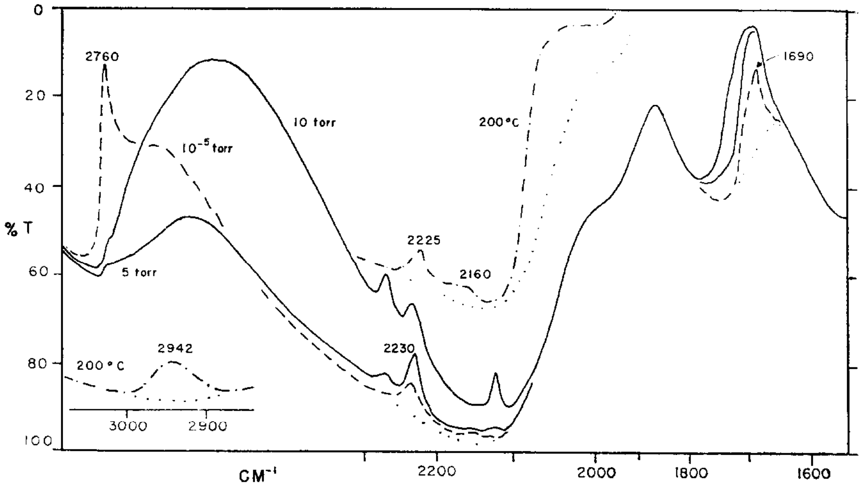

FIG. 3. Infrared spectra of acetone-$d_6$ adsorbed on silica–supported nickel (150 mg, 10% w/w Ni) at 25°C for 5 Torr for 2 min; for 10 Torr for 15 hr; after evacuation to $10^{-5}$ Torr (---); and after heating to 200°C (· — · —).

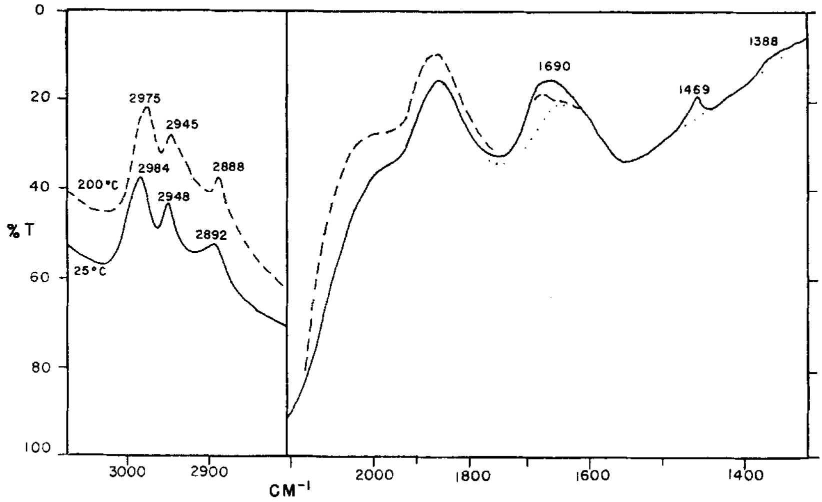

FIG. 4. Infrared spectra of diethylketone adsorbed on silica–supported nickel (150 mg, 10% w/w Ni) at 25°C for 10 Torr for 2 min, followed by evacuation at $10^{-5}$ for 2 hr, and after heating to 200°C for 15 hr (---).

caused only a relatively small amount of decarbonylation in this case to judge by the continued strength of the $\nu$CH spectrum and the weak bands in the 2100–1800 cm$^{-1}$ region from chemisorbed CO. The gas phase consisted of a small amount of methane and CO; no ethane or ethylene could be detected but the sensitivity of detection was not high.

## 4. CONCLUSIONS

We conclude that the adsorption of acetone on silica-supported nickel gives rise to three spectroscopically detectable surface species. The spectroscopically dominant one appears to be the associatively adsorbed species $(CH_3)_2CM{\cdot}OM$. Very small amounts of a carbonyl-containing species are also present; this possibly represents the adsorption of complete ketone molecules to metal sites in the manner depicted above. After a considerable period of time $(CH_3)_2CH{\cdot}OSi$ groups appear on the silica surface, which possibly originate in a small amount of reduction of the ketone to the alcohol followed by reaction with surface SiOH groups. The hydrogen required for this reduction process (and for the production of methane as a decomposition product at higher temperatures) may originate in some degree of dissociative adsorption. The experiments with $(CD_3)_2CO$ show ready exchange with silica SiOH groups, which does not occur in the absence of metal. This must also involve dissociative adsorption, at least in the reaction intermediate. The surface species obtained from diethylketone appear to be very similar to those described for acetone.

On heating to 180°C the $\nu$CH bands of the associatively adsorbed species from acetone, described above, were greatly reduced in intensity; a decarbonylation reaction occurred with CO and methane appearing as the only gas-phase products (no ethane was detected) and CO chemisorbed to nickel as a surface product; as we have previously reported (*4*), this reaction also occurs in the presence of hydrogen. By contrast only a very small amount of decarbonylation of diethylketone occurred at 200°C. As acetaldehyde also decarbonylates more readily than acetone (*2*), i.e., even at 25°C, the order of ease of this reaction MeCHO > $Me_2CO$ > $Et_2CO$ may possibly result from steric effects from the bulkier alkyl groups.

## ACKNOWLEDGMENTS

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