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Infrared Study of the Adsorption of Methanol, Ethanol, Ether, and Water and the Interaction of Carbon Monoxide and Hydrogen on a Nickel Surface

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Stable surface complexes formed by the interaction of methanol, ethanol, water, and diethyl ether with a nickel surface at 20°C were investigated. Exposure of the nickel surface to methanol gives infrared bands for surface species at 2040 and 1900 cm^{-1}. These bands are attributed to chemisorbed CO. Ethanol produced bands for surface species near 2960 cm^{-1} and 2030 and 1850 cm^{-1}. These bands are interpreted as indicating that ethanol decomposes on the clean surface to give chemisorbed CO and a hydrocarbon residue. H_2O and diethyl ether produced no detectable surface species and did not poison the surface to CO chemisorption. Surface compounds formed by the interaction of CO and H_2 on nickel at temperatures up to 180°C were looked for but not found even though products of the reaction of CO and H_2 were readily detected. In all cases studied the gases do not react with the silica support.

INTRODUCTION

In the considerable body of literature dealing with heterogeneous catalytic reactions, the presence and structure of many active adsorbed intermediates formed through the bonding of the reactants to the catalyst surface have been proposed. Such surface intermediates may be formed by dissociative adsorption, where a single bond is broken in the reactant to give two adsorbed species, by adsorption involving the opening of a multiple bond of the reactant, or by formation of a coordination bond of the reactant with the surface. Most proposals for surface structures have been made on the basis of observed products and reaction kinetics but unfortunately these considerations seldom give an unambiguous picture of reaction intermediates. The literature giving direct experimental evidence for surface structures is relatively small. Infrared spectroscopy has proven to be one of the most powerful tools for determining chemical structure. Eischens and co-workers have demonstrated the feasibility of applying infrared techniques to the study of adsorbed species on metals. In this study infrared spectroscopy is used as a tool to study stable surface structures on silica-supported nickel.

Due to their relatively short lifetimes genuine reaction intermediates are usually species that exist only while a reaction is going on and then only in relatively low concentrations. This makes intermediates difficult to observe. However, intermediates should have structures related to stable compounds. Since very little is even known about stable surface compounds we believe the determination of stable surface structures is an important first step in understanding heterogeneous reactions. It is also possible that surface species which are stable at one temperature but unstable at higher temperatures are reaction intermediates at the higher temperatures.

The catalytic cracking of alcohols at high temperatures on metals has long been recognized (*2*). R. Paul (*3, 4*) reports the principal reaction of ethyl alcohol over

Raney nickel catalysts to be dehydrogenation to aldehyde at room temperature with some decomposition to give CO at 80° to 90°C. At high pressures, 100 to 240 kg/cm^2, and high temperatures, 225° to 280°C, ethyl alcohol and Raney nickel are reported (*5*) to react to give considerable gaseous product, mostly CH_4 with only 4% CO, as well as dehydrogenation products. More recently Zderic, Bonner, and Greenlee (*6, 7*) have demonstrated that alcohols containing aromatic substituents on the number 2 carbon atom undergo cleavage of the carbon–carbon bond between atoms 1 and 2 under the relatively mild conditions of refluxing in ethyl alcohol with Raney nickel. Upon drying and heating the catalyst the carbon atom which had been split off was removed from the Raney nickel mostly as methane. However, since digesting the catalyst with sulfuric acid gave CO as the gaseous product, they believed the alcohol cleavage gave adsorbed CO as the principal by product. They also reported ethyl alcohol gave little gaseous product when it alone was refluxed with the Raney nickel.

The reaction of aliphatic alcohols with D_2 over evaporated nickel at moderate temperatures results (*8*) in the exchange of only one hydrogen atom of the alcohol with deuterium with no apparent cracking of the alcohols. Above 170°C methyl alcohol slowly decomposed to give CO.

In order to gain insight into the surface process of these and related reactions we decided to investigate the stable surface complexes formed by the interaction of methyl and ethyl alcohol and the related compounds, water and diethyl ether, with a nickel surface.

A reaction which may in a sense be considered the reverse of alcohol decomposition is the catalytic synthesis of hydrocarbons, alcohols, etc., from CO and H_2, known as the Fischer-Tropsch synthesis. Moreover it has been suggested (*9*) that alcoholic-type surface complexes are intermediates in the Fischer-Tropsch synthesis. We therefore decided to look for surface compounds formed by the interaction of CO and H_2 on nickel at temperatures up to 200°C. Eischens (*1*) has previously reported that he observed no interaction of CO and H_2 on silica-supported nickel at 35°C.

EXPERIMENTAL

The experimental technique, cells, sample preparation, and reduction procedures have previously been described (*10*) in detail. Essentially, $Ni(NO_3)_2 \cdot 6H_2O$ is dispersed on silica (Cab-O-Sil, donated by Godfrey L. Cabot, Inc., Boston, Mass.) pressed into a disk, and the disk placed in a vacuum cell. After evacuation (which took 6–9 hr to assure complete evacuation and removal of any contaminants), hydrogen, at 1 atm pressure, was passed through the purification system, into the vacuum system, and then through the cell. The initial flow rate was about 500 ml/min. After the hydrogen was allowed to flow for 1–2 min the heating coils were warmed up to about 280°C. This flow rate and temperature were used for about the first hour. After the first hour, the flow rate was reduced to about 100 ml/min and the temperature increased to about 320°C. Then after another 2 hr, the flow rate was reduced to 20–50 ml/min and the temperature increased to 380°C. This process was continued for about 15 hr. After the reduction process was completed, the sample was cooled in a hydrogen atmosphere and then evacuated. After cooling, the cells were completely evacuated, removed from the vacuum system, and then placed in the spectrophotometer. After this was accomplished, a vacuum system for handling gases was attached to the sample cell via a movable arm. Then background spectra of the two samples were recorded using the "differential" technique described earlier. Because the silica only transmits infrared radiation from 4000 to 1300 cm^{-1} only this range can be used. After the background spectrum was recorded, the gas was introduced into the cell. Then, depending on what information was desired, the cells were kept at room temperature or heated up to 180°C. By recording spectra at various time intervals, the desired information was obtained.

Reagent grade methanol, ethanol, and

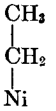
diethyl ether were used without further purification. The H_2O was distilled twice and pasesd through a 5-ft ion exchange column. All liquids were degassed by pumping on them while subjecting them to several freeze-thawing cycles. The CO and H_2 were purified as previously (*10*).

Results

Adsorption on pure silica. In order to be sure that effects due to adsorption on the nickel surface could be separated from effects due to adsorption on the silica support surface, adsorption experiments with pure silica disks were performed. It has been previously shown (*10*) that CO and H_2, either separately or together, at temperatures from 20° to 180°C produce no observable interaction with silica disks. When H_2O, methyl alcohol, or ethyl alcohol vapors are admitted to the cell containing only a pure silica disk at 20°C the infrared spectra show gas-phase bands for the respective gases and a broad band near 3300 cm^{-1}. The broad band near 3300 cm^{-1} is ascribed to an associated OH group, indicating physical adsorption of these gases on the silica surface with a hydrogen bond forming the main attachment to the surface. Separate experiments were performed for each vapor. Upon evacuating the cell, in all three cases the band at 3300 cm^{-1} does not immediately disappear. In the case of methyl and ethyl alcohols bands near 3000 cm^{-1} representing C—H stretching frequencies also do not immediately disappear on evacuation of the cell. However, evacuation for one-half hour at 20°C returns the spectra to the original background result. Likewise diethyl ether vapors leave no bands that persist after one-half hour of evacuation. Therefore we conclude that any bands that remain after a silica-supported nickel disk has been exposed to any of these vapors and then evacuated for one-half hour or more are due to species adsorbed on the nickel surface. It should be noted that since all vapors considered here except CO and H_2 do adsorb on the silica when the vapors are in the cell, any work which might be done with these vapors in the cell would be subject to some ambiguity in interpretation due to gases being adsorbed on both the metal and the silica support.

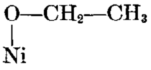
Methyl alcohol. When silica-supported nickel is exposed to 5 mm pressure of methyl alcohol vapor at 20°C and then the cell evacuated for 30 min, the infrared spectrum from 4000 to 1300 cm^{-1} shows intense bands at 2040 and 1900 cm^{-1}. These bands have been assigned (*1*) to chemisorbed CO. Thus it appears that the only stable surface species produced by the interaction of methyl alcohol and the nickel surface is chemisorbed CO.

Ethyl alcohol. The infrared spectrum recorded after silica-supported nickel is exposed to 2 mm of ethyl alcohol at 20°C and the cell then evacuated for 20 min is shown in Fig. 1. From the intense bands at 2030 and 1850 cm^{-1} it is evident that the principal reaction of the ethanol with the surface is to break the carbon–carbon bond, thereby producing an adsorbed hydrocarbon fragment and chemisorbed carbon monoxide. Using Bellamy's (*11*) assignments the band at 2960 cm^{-1} is assigned to a CH_3 group motion while the weak band at 2920 cm^{-1} is assigned to a CH_2 group. The spectrum of the surface complex indicates that it is largely made up of CH_3 groups, presumably bound to the surface in the structure CH_3—Ni. The fact that there is a weak band in the region where CH_2 groups are expected to absorb suggests that some of the alcohol interacted with the surface to produce a small amount of material with the structure



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ Ni \end{array}$$

or



$$\begin{array}{l} O\text{—}CH_2\text{—}CH_3 \\ | \\ Ni \end{array}$$

or both.

H_2O. No bands which stayed after evacuation of the cell were observed when the silica-supported nickel was exposed to amounts of water vapor varying from 50 μ to 5 mm in pressure. After the water vapor

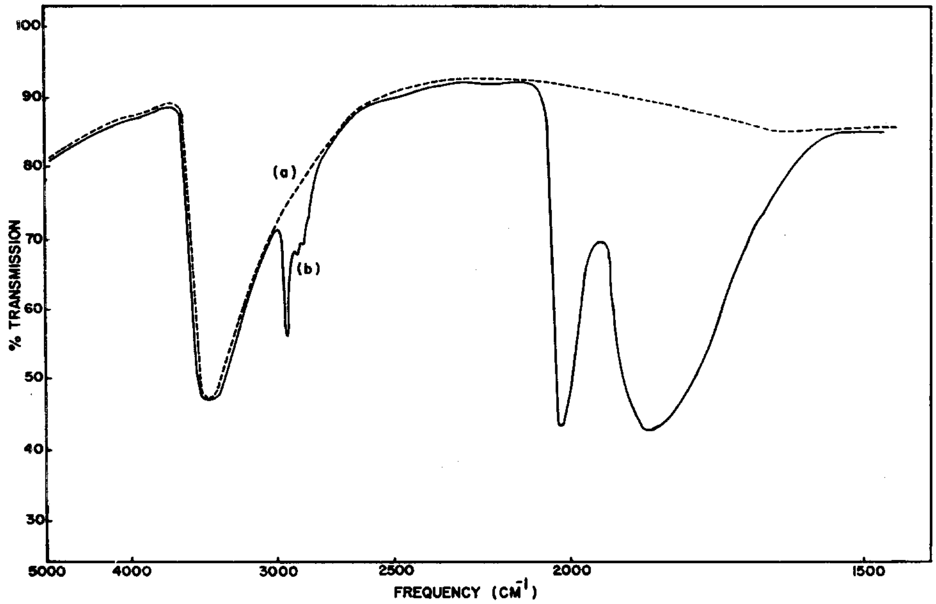


FIG. 1. Infrared spectrum of ethyl alcohol adsorbed on silica-supported nickel: (a) background; (b) spectrum recorded after removal of gas phase alcohol.

was pumped out of the cell, the addition of 5 mm of CO to the cell produced intense permanent bands for chemisorbed CO. This indicates that the water vapor not only did not permanently adsorb in any structure with OH groups, which would have been detected by a band near 3300 cm^{-1}, but it also did not leave any appreciable number of residues such as oxygen atoms on the surface which would poison the surface to CO chemisorption. Exposure of the surface to oxygen at pressures as low as one micron completely poisons the surface to CO chemisorption.

Diethyl ether. Exposure of the sample to 9 mm of diethyl ether vapor pressure followed by evacuation of the cell for 20 min produced no appreciable infrared bands which were not in the background spectrum. There appeared to be a little change in the spectrum near the carbon–hydrogen stretching region but the change was so small that it would not represent much chemisorbed ether. Upon subsequent exposure of this sample to 4 mm of CO gas, intense, permanent bands for chemisorbed CO were observed. This indicates that after the ether treatment the surface is still largely free.

Interaction of CO and H_2. No interaction between H_2 and CO on silica-supported nickel at 20°C was observed. Various amounts and ratios of the two gases were admitted to the cell and no interaction was observed even when the gases were allowed to stand in the cell for several hours. The only infrared bands observed were the two at 2060 and 1900 cm^{-1} for chemisorbed CO. It made no difference in the intensity or position of the bands for chemisorbed CO whether CO or H_2 was admitted to the cell first or both together from a bulb of premixed gases.

Upon heating the cell containing CO and H_2 the initial interaction was observed as an increase in the intensity of the OH band at 3500 cm^{-1}. This slight increase was noted before anything else was observed. The intensity of the OH band begins to increase after the first 15 min of heating with the gas mixture in the cell. Figure 2 shows three spectra recorded at different times. The spectrum denoted by (a) was recorded upon initial introduction of the

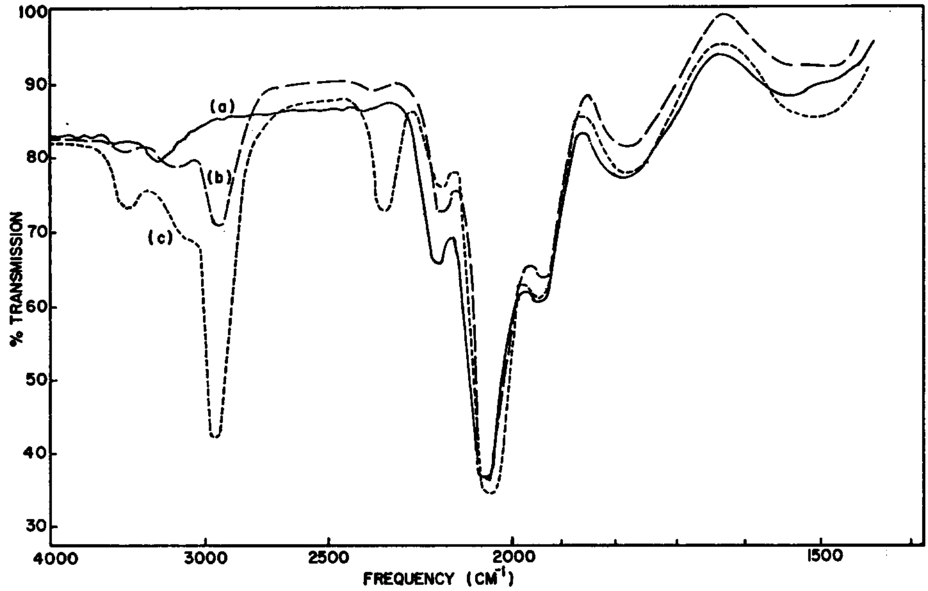


FIG. 2. Interaction of CO and H_2 on silica-supported nickel: (a) infrared spectrum just after admission of CO and H_2 at 180°C; (b) 2½ hours later; (c) 23 hours later.

gas mixture of 12 cm of CO and 18 cm of H_2 to the cell while it was at 180°C. The bands at 3260, 1800, and 1500 cm^{-1} are due to the silica support not being perfectly compensated for. The band at 2180 cm^{-1} is due to gas phase CO while the bands at 2060 and 1950 cm^{-1} are due to chemisorbed CO. Spectrum (b) of Fig. 2 was recorded 2½ hr after (a). Here the development of an OH band at 3500 cm^{-1}, a band at 3100 cm^{-1} which is assumed due to a carbon–hydrogen stretching mode of an unsaturated carbon atom, and a carbon–hydrogen stretching vibration at 2940 cm^{-1} for a mixture of CH_2 and CH_3 groups belonging to saturated carbon atoms are noted. Spectrum (c) was recorded 23 hr after (a). As well as the enlargement of the bands ascribed to OH groups and carbon–hydrogen stretching vibrations, a band at 2320 cm^{-1} which is assigned to a CO_2 vibration is noted. When the cell is evacuated, either hot or cooled to room temperature with the gases still in it, the only bands which remain are those ascribed to the silica support and chemisorbed CO. From this it is concluded that the observed OH and carbon–hydrogen groups belonging either to gas phase molecules or to molecules very loosely held to the surface. No species other than chemisorbed CO could be called a stable surface complex.

An attempt was made to see if chemisorbed CO without any gas-phase CO present would react with hydrogen. To this end 2 mm of CO was added to a cell containing a freshly reduced nickel-on-silica disk and then the cell was evacuated at 10^{-5} mm pressure for one-half hour. The spectrum of this sample shows intense bands at 2060 and 1900 cm^{-1} for chemisorbed CO. We have stored cells like this one for several weeks with no change in the spectrum of the chemisorbed CO, thereby demonstrating the great stability with respect to desorption of the chemisorbed CO at 20°C. After the spectrum was recorded 14 cm of hydrogen was added to the cell and the cell heated to 240°C. Within one hour the bands at 2060 and 1900 cm^{-1} disappeared but no other changes were observed in the spectra. Upon cooling the cell the bands for chemisorbed CO reappear, although they are not quite as intense as previously. This experiment was repeated with the cell at 180°C. The only change in result was that it took close to 2 hr for the CO to completely desorb. As a result of these experiments we are unable to say that CO while chemisorbed in the structures that produce the bands at 2060 and 1900 cm^{-1} will react with hydrogen.

DISCUSSION

The above experiments suggest that at room temperature the most stable surface structure formed by the C, H, and O compounds studied here is chemisorbed CO. It has often been suggested that many molecules chemisorb by coordinate bond formation of the adsorbate with the *d* orbitals of the metal surface. This may well be true for many reaction intermediates and for chemisorbed CO, although the structure or structures of chemisorbed CO have not been satisfactorily determined. However, in the compounds studied here oxygen did not appear to form stable bonds with the surface by coordinating its lone pair electrons with the surface. This is consistent with our previous finding (*12*) that sulfur compounds do not in general chemisorb on a silica-supported nickel surface by coordination of the sulfur atom with the surface. It might have been expected that water would interact more strongly with the surface than it did. Again the behavior of water is the same (*12*) as its sulfur analog, H_2S. While our experiments indicate that certainly the bulk of the surface did not interact with water, it is possible and perhaps probable that the water does interact strongly with high energy surface sites which could be as much as 5% of the surface without our detecting the interaction.

The ready cleavage of C—C and C—H bonds when one of the carbons has an OH group attached to it is noted. The rapid exchange of the hydroxyl hydrogen with deuterium on metal surfaces suggests that the first step of the alcohol decomposition is the dehydrogenation of the alcohol to produce an aldehyde. The aldehyde then breaks the C—C and C—H bonds to produce chemisorbed CO and other fragments. The failure of the diethyl ether to dissociate on the surface is then presumably due to the fact that the easy first step of forming a carbon-oxygen double bond cannot occur so readily in the ether as in the alcohol, so that little or no decomposition occurs.

This work would also seem to indicate that workers who have previously studied reactions of alcohols on nickel surfaces were working with nickel surfaces that were mostly covered with tightly chemisorbed decomposition products. Thus, whereas Bonner and co-workers (*6, 7*) report no decomposition of their reflux medium, ethyl alcohol, we would expect the ethyl alcohol to decompose on the surface until it is mostly covered with tightly chemisorbed CO and hydrocarbon fragments. This reaction would stop when the surface was mostly covered, so that no gaseous products would be observed. The rather stringent conditions that Zderic, Bonner, and Greenlee (*6*) find for cleavage on Raney nickel, i.e. a hydroxyl or aldehyde group on carbon atom 1 and an aromatic group on carbon atom 2, would appear to reflect the fact that the observed reaction is occurring only on the lowest energy sites on the surface which have not interacted with the ethyl alcohol.

Perhaps the most important chemical feature of the chemisorbed CO is its unreactivity at room temperature. In fact our experiments show no reaction of CO with hydrogen until temperatures high enough, i.e. over 180°C, to desorb the chemisorbed CO are reached. It should be noted that while 180°C is a high enough temperature to desorb CO, also at 180°C if one mm or more of gas phase CO is present, the bands at 2060 and 1900 cm^{-1} are about as intense as they are at lower temperatures. Thus we are unable to tell just which CO species does react at the higher temperatures.

For the Fischer-Tropsch synthesis nickel catalysts are in general considered to be poorer than iron catalysts. These experiments together with our previous work (*13*) on the interaction of CO and H_2 over an iron catalyst suggest some specific differences. In order to build up a moderately long chain it is necessary that the reacting species be firmly enough anchored to the surface that a number of chain-building steps can occur before desorption. In the case of a silica-supported iron catalyst it was found (*13*) that evacuation of the cell at 180°C left carbon- and hydrogen-containing species on the iron surface, whereas here evacuation at 180°C or even 20°C completely cleans the carbon–hydrogen species off the surface. This suggests that the reaction species are much less firmly bonded to the nickel than to the iron catalyst. Also, since alcoholic-type intermediates are believed (*9*) to be important in Fischer-Tropsch synthesis the great facility shown here by nickel for decomposing alcohols would seem to work against it as a Fischer-Tropsch catalyst.

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REFERENCES

1. EISCHENS, R. P., AND PLISKIN, W. A., *Adv. Catalysis* **10,** 1 (1958).

2. SABATIER, P., "Catalysis in Organic Chemistry." van Nostrand, New York, 1922.

3. PAUL, R., *Bull. Soc. Chim. France* **8,** 507 (1941).

4. PAUL, R., *Compt. rend.* **208,** 1319 (1939).

5. PATY, M., AND DESCHAMPS, J., *Compt. rend.* **234,** 2291 (1952).

6. ZDERIC, J. A., BONNER, W. A., AND GREENLEE, T. W., *J. Am. Chem. Soc.* **79,** 1696 (1957).

7. BONNER, W. A., AND GREENLEE, T. W., *J. Am. Chem. Soc.* **81,** 2122 (1959).

8. ANDERSON, J. R., AND KEMBALL, C., *Trans. Faraday Soc.* **51,** 966 (1955).

9. EMMETT, P. H., ed., "Catalysis," Vol. IV. Reinhold, New York, 1956.

10. BLYHOLDER, G., AND NEFF, L. D., *J. Phys. Chem.* **66,** 1464 (1962).

11. BELLAMY, L. J., "Infrared Spectra of Complex Molecules." Methuen, London, 1958.

12. BLYHOLDER, G., AND BOWEN, D. O., *J. Phys. Chem.* **66,** 1288 (1962).

13. BLYHOLDER, G., AND NEFF, L. D., *J. Phys. Chem.* **66,** 1664 (1962).