Infrared Spectroscopy and Catalysis Research

Infrared spectra of adsorbed molecules provide important information in the study of catalysis.

R. P. Eischens

The term *surface chemistry,* as used in the field of catalysis, refers to chemical reactions between the outermost layer of atoms of a solid and molecules brought to the solid surface in the liquid or gaseous state. The gaseous or liquid molecules which are involved in the surface reaction are referred to as chemisorbed (chemically adsorbed). In the catalytic process the chemisorbed layer is a reaction intermediate which may be formed and decomposed under a single set of experimental conditions. The decomposition regenerates the surface atoms of the solid and produces desorbed products which, it is hoped, will be more valuable than the initial reactants. The point emphasized here is that the nature of the desorbed products depends primarily on the nature of the chemisorbed reaction intermediate.

Surface chemists who are working toward an understanding of catalysis can gain knowledge of the chemisorbed intermediate from a study of the desorbed products. This classical approach has been outstandingly successful in the evolution of the concept of adsorbed carbonium ions (positively charged hydrocarbon ions) as the reaction intermediate in reactions involving cracking, polymerization, and isomerization of hydrocarbons over strongly acidic solids. Studies of reaction products which utilize isotopic tracers have also been successful in revealing the nature of the chemisorbed intermediate in several important, but more limited, cases.

Despite these successes there is a need to develop or adapt techniques which will provide more direct evidence on the nature of chemisorbed layers. A large proportion of the recent catalysis research effort has gone into this type of development. The use of infrared spectroscopy is an example of the adaptation of a previously well-established and widely used physical tool to the study of chemisorbed layers. The purpose of this article is to present several examples of the use of infrared spectroscopy in catalysis research to illustrate the reasons for the enthusiastic adoption of this technique by surface chemists.

Early Applications in Surface Research

The infrared region consists of radiation having a wavelength between 2.5 and 25 microns. In the more commonly used wave number units, this is the region between 4000 and 400 cm^{-1} (the wave number is the reciprocal of the wavelength, in microns, times 10,000). When infrared radiation is passed through a sample material, atomic vibrations within the sample cause absorption of energy from the beam at certain wave numbers. The wave number of the absorbed radiation depends on the energy changes associated with the atomic vibrations, and these energy changes depend on the mass of the vibrating atoms and the strength of the bonds between atoms. Thus, the pattern of the absorption of radiation in an infrared spectrum gives information on the nature and quantity of the atomic groupings in the absorbing material.

An extensive background in the interpretation of infrared spectra has been accumulated from studies of conventional chemical compounds. Interpretation of the spectra of chemisorbed molecules is based on analogy with spectra of conventional compounds. That the analogy method of interpreting spectra of surface compounds is valid is tacitly assumed by all chemists who use infrared spectroscopy in surface research. (This common acceptance of the analogy method, of course, does not preclude disagreement on how the method should be applied in any specific case.) Despite the many examples of the apparently successful use of the analogy method, the validity of this type of interpretation of spectra of chemisorbed molecules has been persistently questioned by many surface chemists. It is known that there are strong force fields at solid surfaces, and one of the basic questions of surface chemistry research is the question of whether surface compounds can be directly compared to conventional compounds. Use of the analogy type of interpretation, therefore, is burdened with a philosophical weakness—the assumption that this question, which many surface chemists believe is still to be answered, can be answered in the affirmative.

The analogy method may be illustrated by an example of its use in one of the earliest instances in which infrared spectra of adsorbed molecules provided information which was of continuing research interest (*1*). Figure 1 shows spectra with bands attributable to water adsorbed on montmorillonite under a variety of conditions. (These conditions are described in the legend to Fig. 1). Montmorillonite is a clay mineral whose composition may be expressed by the formula $(Ca,Mg)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$.

This work was carried out before convenient methods of determining the surface area of high-area solids had been developed (*2*). The surface area of the montmorillonite of Fig. 1 is not known, but it was probably about 50 square meters per gram. The high surface areas which are characteristic of these naturally occurring clays was an important factor in the ease with which Buswell and his associates were able to obtain these spectra. They passed the infrared beam through a thin layer of small particles of montmorillonite. The small particles were obtained by sedimentation. The sample was exposed to the ambient atmosphere while the spectra were being observed. In current work the sample is almost invariably kept in a cell, so that the atmosphere above the sample may be controlled.

Figure 1 shows two absorption bands.

The author is senior research associate in the Fundamental Research Division at the Texaco Research Center, Beacon, N.Y.

Both of these bands are attributable to oxygen-hydrogen stretching vibrations. One type of OH, which produced the band at the wave number of 3410 cm^{-1}, was easily removed, while the other, which produced the band at 3630 cm^{-1}, was tightly held. Buswell had previously studied the infrared spectra of the OH groups of alcohols dissolved in carbon tetrachloride. He had found that, in dilute solutions where there was no interaction between the hydroxyl groups of the alcohol molecules, the oxygen-hydrogen stretching band was observed at 3630 cm^{-1}. In more concentrated solutions the band was observed at 3410 cm^{-1}. This shift was attributable to hydrogen bonding whereby partial bonds are formed between the hydroxyl hydrogen atoms of one molecule and the oxygen atoms of another molecule. Hydrogen bonding has the effect of weakening the primary intramolecular oxygen-hydrogen bond, so the band shifts toward a lower energy region.

Because of this experience with alcohols in solution, Buswell attributed the OH band at 3630 cm^{-1} to a species, —OH, in which there was no hydrogen bonding effect, and the band at 3410 cm^{-1} to hydrogen-bonded hydroxyls similar to those of liquid water. Buswell did not speculate on whether the non-hydrogen-bonded species, which he indicated as —OH, was bonded to silicon or aluminum atoms on the montmorillonite surface. Recently studies have been made to determine the specific adsorption site for the non-hydrogen-bonded hydroxyl groups on the surface of synthetic silica-alumina catalysts (*3*). This work indicates that the most tightly held surface hydroxyl groups are attached to silicon. For the experiments of Fig. 1, the maximum drying temperature was 110°C. This temperature was far too low to affect the species producing the 3630 cm^{-1} band, since this band is often observed after drying at temperatures as high as 500°C.

An important advance in the application of infrared spectroscopy to surface studies was made by Russian workers who found that surface hydroxyl groups similar to those which produce Buswell's 3630 cm^{-1} band showed a spectral shift as a result of hydrogen bonding effects involving adsorbed layers on top of the surface hydroxyls (*4*). This effect is observed with almost all adsorbed materials, including rare gases (*5*). The hydrogen bonding effects which cause the shifts in hydroxyl bands are not commonly considered to be equivalent to chemisorption forces. Instead, they are related to physical attractive forces similar to the forces which cause condensation of vapors.

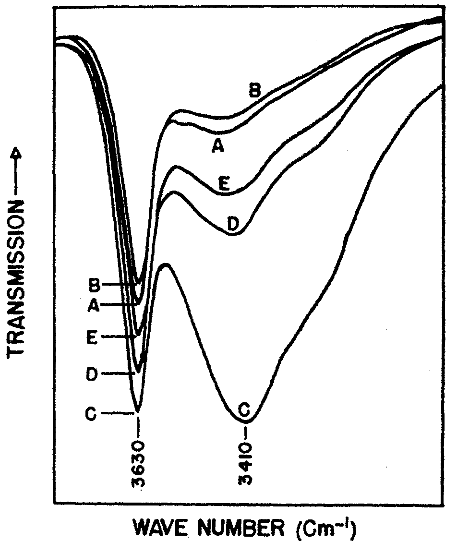


Fig. 1. Spectra of montmorillonite: *A*, dried at 100°C for 36 hours; *B*, dried at 100°C for 42 hours; *C*, after exposure to air saturated with water vapor; *D*, redried at 110°C for 6 hours; *E*, redried at 100°C for an additional 24 hours. [From Buswell, Krebs, and Rodebush (*1*), with permission]

I have described the work of Buswell to introduce this article because it is one of the earliest significant examples of infrared studies of adsorbed molecules. A more detailed description of the early development of spectral studies of adsorbed molecules would include the earlier work of de Boer, who observed the ultraviolet spectra of dyes and simple molecules such as I_2, and nitrobenzene adsorbed on CaF_2 and $BaCl_2$ (*6*).

Ultraviolet spectroscopy is currently making important contributions in studies of adsorbed molecules, even though the scope of its application is more limited than that of infrared spectroscopy. These contributions are mainly confined to studies of the electronic transitions in carbonium ions adsorbed on strongly acidic solid catalysts. This work has been reviewed recently (*7*).

Experimental Methods

Workers concerned with infrared studies of adsorbed molecules may justifiably ascribe the widespread interest in this type of research to the useful, stimulating data which can be obtained. However, it is also true that the easy availability of reliable, commercially developed infrared spectrophotometers has been a significant factor in the rapid expansion of this work. All of the experiments discussed in this article could be repeated with the hundreds of infrared spectrophotometers in use in laboratories throughout the world, even though some instruments are superior to others and sometimes advantages are gained through modification of commercial instruments.

This does not mean that all problems associated with observing spectra of adsorbed molecules have been solved, but it does mean that in many cases spectra of adsorbed molecules are easily observed. In any specific case successful observation of the adsorbed molecules depends on the transmission characteristics of the solid, the adsorptive capacity of the solid, and the specific absorption coefficient of the adsorbed molecules (*8*). All these factors are especially favorable for the case of carbon monoxide chemisorbed on platinum, which is dispersed on silica, and observation of the chemisorbed carbon monoxide could easily be carried out as a laboratory experiment in an undergraduate course on physical chemistry.

One of the inherent advantages of the infrared technique is the feasibility, with this technique, of conducting chemisorption experiments while the sample remains in the path of the infrared beam. The extent to which this advantage can be realized depends on temperature limitations imposed by the design of the cell. The infrared beam cannot be transmitted through pyrex glass, which is commonly used in constructing laboratory apparatus, and it is necessary to seal infrared transmitting windows onto the cell. These windows are commonly salts such as NaCl or CaF_2, which are difficult to seal to glass in such a way that the seal will withstand elevated temperatures, since the sealing material is a wax or resin. In some cases MgO windows have been sealed to glass by techniques which make these seals suitable for use at elevated temperature, but such seals are difficult to obtain (*9*).

In catalytic work it is often necessary to heat the sample. To avoid the difficulty caused by the poor high-temperature characteristics of the window seals, the most simple cells are designed so that the sample may be moved into a side arm when it is to be heated. This technique is satisfactory for many purposes, even though it imposes the limi-

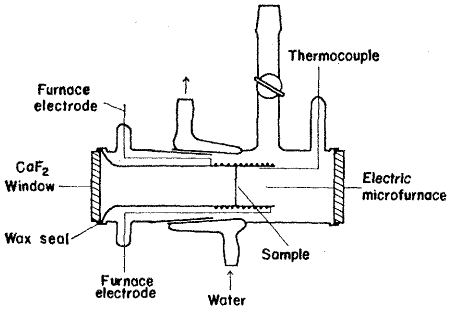


Fig. 2. Schematic diagram of cell for infrared study of chemisorbed molecules. [From Courtois and Teichner (*10*), with permission]

tation that the sample cannot be heated while the spectra are being measured. The sample space of most instruments limits the length of the cells to not more than 13 centimeters. With careful design it is possible to make a cell, within this length limitation, in which spectra can be observed while the sample is heated. A cell of this type is shown in Fig. 2 (*10*). The cell body is made from a water-cooled ground-glass joint. The sample is a powder, which has been pressed into a thin self-supporting wafer. The wafer is mounted inside the electric microfurnace.

Cells have also been made in which the sample may be either cooled or heated while it is in the infrared beam. However, these cells require modification of the optical system of the infrared spectrophotometer (*11*).

As may be seen from the work of Buswell, it is relatively simple to obtain a sample of oxide which is suitable for infrared spectroscopy studies. In many cases it is possible to use the oxidic material just as it is found in the laboratory. Samples suitable for infrared study of chemisorption on metals are prepared by dispersing small metal particles on an oxide carrier. In these cases the carrier, which is commonly silica or alumina, is impregnated with a solution of the salt of the metal. The mixture is dried, and the salt is converted to the metal by reduction with hydrogen at elevated temperature (*12*). Metal concentrations in the range of 0.5 to 25 percent by weight have been used. The diameters of the metal particles are usually in the range of 30 to 70 angstroms. In a metal particle 30 angstroms in diameter, about one-third of the total number of metal atoms are exposed on the surface of the particle; in a particle 70 angstroms in diameter, about one-seventh of the atoms are exposed on the surface. In the metal-on-carrier samples, carrier surface as well as metal surface is exposed. Thus, it is necessary to know whether the observed spectra are due to molecules adsorbed on the metal or to molecules adsorbed on the carrier. This is usually not a difficult problem because of the differences in the chemical properties of the two solids. However, it is common procedure to make blank runs on the carrier material.

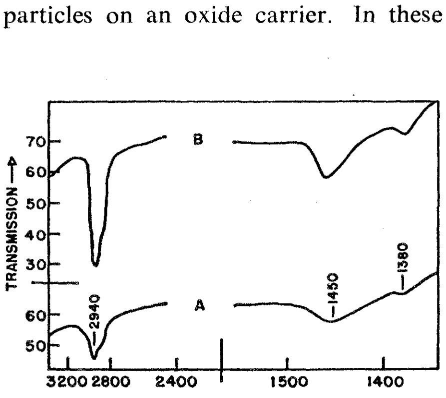


Fig. 3. *A*, Spectrum of acetylene chemisorbed on nickel; *B*, spectrum after treatment of chemisorbed acetylene with hydrogen at room temperature. [From Eischens and Pliskin (*13*), with permission]

Cells such as that illustrated in Fig. 2 are used with vacuum pumping systems which cannot reduce the pressure below 10^{-6} mm-Hg. This capability is far below the standards of currently available vacuum systems which easily reduce the pressure to 10^{-9} mm-Hg. These better systems are necessary for reliable adsorption studies on low-area samples. Simple calculations show that at 10^{-6} mm-Hg the surface of a low-area sample, such as a wire, would be covered by a monolayer of the residual gas within a few seconds. Despite this, catalytic chemists, who work with the type of sample used in infrared studies, carry out their experiments in a leisurely manner, without apparent concern for the modern developments in high-vacuum technology. This leisurely approach is justified by the high adsorptive capacity of the catalyst samples. A typical sample wafer will weigh about 0.1 gram and will chemisorb about 0.1 cubic centimeter of gas, at standard temperature and pressure, on its metal portion. For example, if one assumes a cell volume of 760 cubic centimeters, the 0.1 cubic centimeter of chemisorbed gas would be equivalent to the amount of gas present in the cell if the pressure were 0.1 millimeter. Thus, the gas retained in the cell after pumping to a pressure of 10^{-6} mm-Hg is only one-thousandth of 1 percent of the amount required to cover the metal surface. It is also necessary to consider the desorption of gases from the glass walls of the cell after the cell is cut off from the vacuum pumps. If this should give a pressure buildup of, say, from 10^{-6} to 10^{-4} mm-Hg in 1 hour—a higher-than-average buildup—this would still be equivalent to only one-tenth of 1 percent of the surface capacity.

Spectra of Chemisorbed Acetylene

In this section I discuss the infrared spectra of acetylene chemisorbed on nickel, on palladium, and on alumina, to show the variety of types of chemisorbed acetylene and to illustrate how infrared spectroscopy has been used to provide information on the structure of the various chemisorbed acetylenes.

Spectrum *A* of Fig. 3 was observed after chemisorption of acetylene on a nickel-on-silica sample (nickel, 9.1 percent by weight) at room temperature (*13*). This spectrum shows carbon-hydrogen bands at wave numbers of 2940, 1450, and 1380 cm^{-1}. The 2940 cm^{-1} band is due to the stretching vibrations of the carbon-hydrogen bonds. The appearance of the stretching band in this region indicates that the carbon is saturated. If the carbon-hydrogen

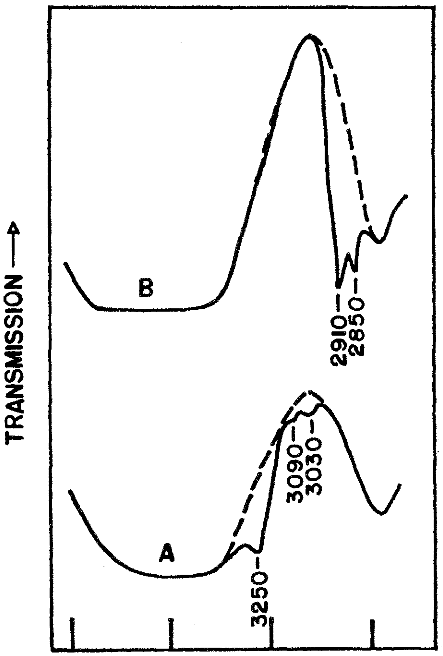
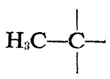


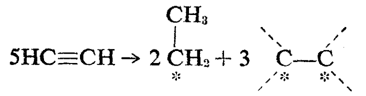
Fig. 4. *A*, Spectrum of acetylene chemisorbed on palladium; *B*, spectrum after treatment of chemisorbed acetylene with hydrogen at room temperature. [From Little, Sheppard, and Yates (*14*), with permission]

stretching vibration involved carbons which were doubly or triply bonded to other carbons, the bands would be expected at about 3050 and 3250 cm^{-1}, respectively. In spectra which are not shown, the 2940 cm^{-1} band was studied at higher resolution, and it was found that this band is actually due to two bands, at 2960 and 2910 cm^{-1}. The 2960 cm^{-1} band is characteristic of CH_3 groups, and the 2910 cm^{-1} band is characteristic of CH_2 groups. The 1450 cm^{-1} band is due to a scissors-like hydrogen-carbon-hydrogen bending vibration. This band shows that there are at least two hydrogen atoms bonded to the carbon. The 1380 cm^{-1} band is characteristic of another bending vibration, which is attributable to CH_3 groups attached to carbon,

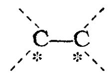


$$H_3C{-}\overset{|}{\underset{|}{C}}{-}$$

It was concluded that spectrum *A* was due to adsorbed ethyl radicals, Ni-CH_2CH_3. This raised a question concerning the source of the hydrogen atoms needed to convert acetylene to ethyl radicals. It was determined that these hydrogen atoms were produced by a self-hydrogenation reaction which may be expressed as



(the asterisk indicates a bond to the surface). The species

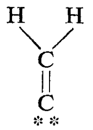


represents a surface carbide which has lost hydrogen to the ethyl groups. The dashed lines indicate that the bonding of this species is not known. There is some evidence for polymerization of C_2 units, and it is also possible that unsaturated bonds are present.

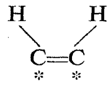
The surface carbide cannot be detected directly by the infrared method because the spectral region, where the bands might be expected, is obscured by bands of the carrier material. However, the presence of the surface carbide was confirmed by its reactivity with hydrogen. The addition of hydrogen leads to an increase in the number of carbon-hydrogen bonds, with a consequent increase in band intensities, as shown in spectrum *B* of Fig. 3.

Spectrum *A* of Fig. 4 was observed after chemisorption of acetylene on a palladium-on-silica sample (palladium, 2 percent by weight) (*14*). In Fig. 4 the absorption bands are indicated as displacements from the dashed portions of the curve. The dashed portions represent contributions of the background which was observed if no chemisorbed acetylene were present.

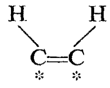
The most important difference between spectrum *A* of Fig. 3 and spectrum *A* of Fig. 4 is the fact that the latter does not show evidence of carbon-hydrogen bonds of saturated carbons. Thus, chemisorption of acetylene on palladium does not produce adsorbed ethyl radicals. Spectrum *A* of Fig. 4 shows bands at 3090 and 3030 cm^{-1} which are both attributable to the carbon-hydrogen stretching vibrations of olefinic species. Little and Sheppard ascribe the 3090 cm^{-1} band to the structure



and the 3030 cm^{-1} band to the structure



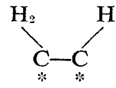
the latter being the predominant form. It is interesting to note that the



structure is the one which probably would be predicted for chemisorbed acetylene, since it is obtained simply by opening one of the carbon-carbon bonds.

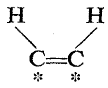
The band at 3250 cm^{-1} is due to an adsorbed species in which the triple bond has been retained. Most of this band is easily removed by pumping at room temperature, and the band may be partially due to acetylene which is merely condensed (physically adsorbed) on the silica. In this case the silica used as a support for the palladium was in the form of porous glass. Porous glass is made by dissolving B_2O_3 from a boron oxide-silica glass, and its surface area is constituted by the area of the small pores in the rigid silica matrix. This type of silica is not the same as the more conventional silica powder used to support the nickel of Fig. 3.

After removal of most of the 3250 cm^{-1} band by evacuation, the acetylene chemisorbed on palladium was exposed to hydrogen at room temperature. The resulting spectrum *B* of Fig. 4 has bands at 2910 and 2850 cm^{-1}. The species producing this spectrum is obviously rich in CH_2 groups. Little and Sheppard concluded that this spectrum was probably due to the species

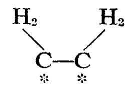


but that a polymer, Pd$(CH_2)nCH_3$, where *n* is large, could not be excluded.

There was an eightfold increase in band intensities in going from the 3090 and 3030 cm^{-1} bands of spectrum *A* to the 2910 and 2850 cm^{-1} bands of spectrum *B*. An olefinic carbon-hydrogen stretching vibration commonly has a specific absorption coefficient which is only about one-third as large as that of paraffinic CH. Thus, in going from



to



one might reasonably expect a sixfold increase in band intensities. The observed increase is about eightfold (*15*). This increase might indicate that the difference between the specific absorption coefficients of olefinic and paraffinic CH's is greater than anticipated. The slightly high increase in band intensities might also be due to the presence of some surface carbon of the type discussed in the case of acetylene on nickel. The presence of surface carbon is not precluded by the absence of adsorbed ethyl radicals, since a self-hydrogenation over palladium might produce ethane, which would desorb from the surface and not be detected in the infrared spectrum.

The chemisorption of acetylene on alumina has been the object of a thorough study which included work with deuterated acetylene, methyl acetylene, and dimethyl acetylene (*16*). This work is too extensive to be discussed in detail here. Part of it is related to the 3250 cm^{-1} band, whose status was not fully clarified in the studies of palladium on porous glass discussed above. Through use of high-resolution spectroscopy, Yates and Lucchesi found two bands in the 3250 cm^{-1} region. One species, which was strongly bonded to the surface, produced a band at 3300 cm^{-1}, while a weakly bonded species produced a band at 3220 cm^{-1}. It was shown that the 3300 cm^{-1} band was due to the carbon-hydrogen stretching in a species which was held perpendicular to the alumina surface,

$$\begin{array}{c} H \\ | \\ C \\ ||| \\ C \\ * \end{array}$$

The bonding of the species producing the 3220 cm^{-1} band was found to be similar to the bonding of physically adsorbed acetylene, and this species was lying parallel to the surface.

Detection of Reaction Intermediates

One of the ultimate objectives in infrared spectroscopy studies of adsorbed molecules is to gain an understanding of the rate-controlling intermediates in catalytic reactions. Simple observation of a chemisorbed species is not sufficient evidence to support a conclusion that the observed species is a rate-controlling intermediate. The latter conclusion requires supplementary evidence based on the kinetic behavior of the observed species. In a reaction of the type A + B $\rightarrow$ (AB) $\rightarrow$ C, in which the surface complex (AB) is the critical reaction intermediate, the overall reaction rate may be limited by either the rate at which (AB) forms or the rate at which (AB) is converted to C. Infrared studies of the (AB) complexes are not as easy to make as studies of chemisorbed molecules. In some cases (AB) decomposes so rapidly that quantities sufficient for detection are not accumulated. In other cases (AB) is stable and will be converted to C only if A and B are available to form new (AB) complexes. In these latter cases, if A and B are not available, (AB) will continue to exist in a form which is difficult to distinguish from an adsorbed reaction product. Ideally, an (AB) complex might be recognized by the fact that the complex produces a new infrared band while the reaction is in progress, and that this band fades away when the reaction ends. Let us consider a study of the (AB) complex in the oxidation of carbon monoxide to carbon dioxide. Spectrum *A* of Fig. 5 was observed after chemisorption of carbon monoxide on a nickel-on-silica sample (nickel, 9.1 percent by weight) at room temperature. The bands at wave numbers of 2070 and 1916 cm^{-1} are attributable to chemisorbed carbon monoxide. On the basis of analogy with spectra of metal carbonyls the 2070 cm^{-1} band was assigned to the linear structure Ni—C≡O, while the 1916 cm^{-1} band was assigned to the bridged structure

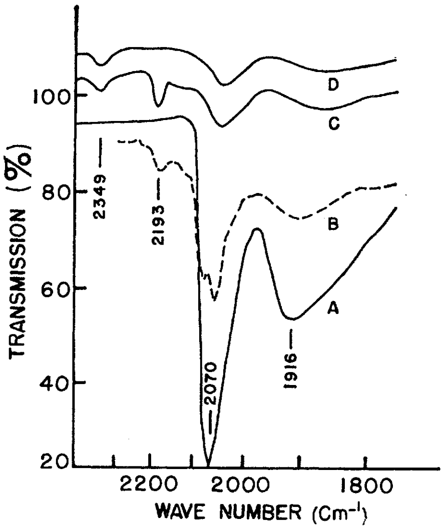
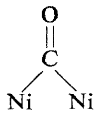


Fig. 5. Infrared spectroscopy study of the oxidation of CO: *A*, chemisorbed CO; *B* and *C*, intermediate stages after the addition of oxygen; *D*, spectrum after termination of the reaction. [From Eischens and Pliskin (*17*), with permission]



(see *17*). There is now some question concerning the latter assignment since a considerable body of later work has shown that certain substituents in metal carbonyls can cause the carbonyl band to be shifted to the 1900 cm^{-1} region even though the carbonyl group is not in the bridged form. For present purposes, the structure of the chemisorbed carbon monoxide is not as important as the observations made after oxygen was added. The effect of adding oxygen at room temperature is shown in spectra *B* and *C* of Fig. 5. The intensities of the 2070 and 1916 cm^{-1} bands decrease, and a new band appears at 2193 cm^{-1} which later disappears in spectrum *D*. New bands which persist in spectrum *D* are observed at 2349 cm^{-1}, 1560 cm^{-1}, and 1410 cm^{-1}. The band at 2349 cm^{-1} is due to gaseous carbon dioxide; the bands at 1560 and 1410 cm^{-1} (not shown in Fig. 5) are due to chemisorbed carbon dioxide.

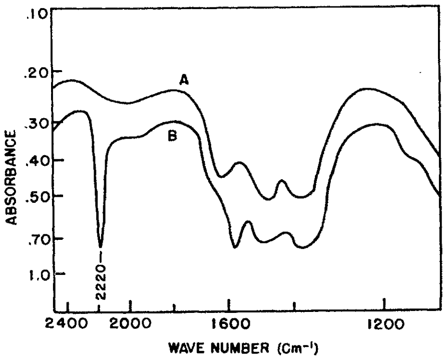
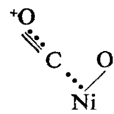


Fig. 6. *A*, Infrared spectrum of ZnO prior to reaction; *B*, spectrum 30 minutes after addition of 0.01*M* formamide to the reaction mixture in the presence of air and light. [From A. Nergaranian and M. C. Markham (*21*), with permission]

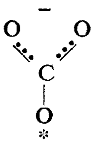
The 2193 cm^{-1} band is also observed when carbon monoxide and oxygen are added simultaneously and when oxygen is adsorbed prior to adsorption of carbon monoxide. Thus, the behavior pattern of the 2193 cm^{-1} band is consistent with the behavior which might be associated with an (AB) complex. Therefore, it is worthwhile to consider this band further to determine whether it can be assigned to a structure which is reasonable for the (AB) complex.

The 2193 cm^{-1} band was initially attributed to the structure $\mathrm{Ni}\cdots\mathrm{O}{=}\mathrm{C}{\equiv}\mathrm{O}$ (*17*). This structure represents carbon monoxide bonded to oxygen, with the oxygen adsorbed on nickel. The dotted lines represent weak bonds of order less than unity. Later Susz and his collaborators found the carbon-oxygen stretching band near 2200 cm^{-1} in addition compounds of aluminum chloride and methyl-substituted aromatic chlorocarbonyls (*18*). Susz represented the structure of these compounds as $(\mathrm{Ar{-}C{\equiv}O})^+(\mathrm{AlCl_4})^-$. If this information had been available at the time of our study of the 2193 cm^{-1} band we would have given more consideration to the possibility that this band is due to the carbon-oxygen stretching in the structure

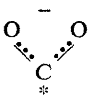


This structure implies that the reaction to form CO$_2$ takes place between two adjacently chemisorbed species. The $\mathrm{Ni}\cdots\mathrm{O}{=}\mathrm{C}{\equiv}\mathrm{O}$ structure implies that the reaction takes place with only the oxygen in contact with the surface. This is a significant difference. In catalysis research much attention has been devoted to the question of which of the general mechanisms represented by these alternatives is the most plausible.

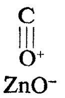
Recently a band equivalent to the 2193 cm^{-1} band was observed in an important study by Amberg and Seanor (*19*). In this case the band was found at 2174 cm^{-1} when CO was adsorbed on oxygen-rich ZnO at 30°C. The 2174 cm^{-1} band was found to attain a state of constant intensity, while bands in the 1300 to 1600 cm^{-1} region continued to increase with time. When the 1300 to 1600 cm^{-1} bands were very intense the 2174 cm^{-1} band was not detectable. The 1300 to 1600 cm^{-1} bands are attributable to adsorbed, oxidized CO. They are also observed when CO_2 is added directly to ZnO. These bands are due to carbonate



and carboxylate



species which, for simplicity, are referred to merely as chemisorbed CO_2. Amberg and Seanor consider the 2174 cm^{-1} band to be related to a species which may be described as an intermediate in the oxidation of CO to adsorbed CO_2, but they feel that it may be only a precursor to the critical rate-controlling intermediate for the complete oxidation to gaseous CO_2. They postulate that the 2174 cm^{-1} band is due to a dipolar, $^-C{\equiv}O^+$, which is attracted to the surface by the electrostatic force field provided by the oxygen ions in ZnO. They do not draw a structure to illustrate this concept, but it appears to be



$$\begin{matrix} C \\ ||| \\ O^+ \\ ZnO^- \end{matrix}$$

or

$$\begin{matrix} ^-C{\equiv}O^+ \\ ^+Zn{-}O^- \end{matrix}$$

A third interpretation for the carbon-oxygen stretching bands in the 2193 cm^{-1} region has been proposed by Gardner and Petrucci (*20*). They attribute the band to the $(CO)^+$ ion. This attribution represents the most straightforward application of the analogy type of interpretation, since the $(CO)^+$ ion is known to have a band at this position. The $(CO)^+$ concept differs from the $^-C{\equiv}O^+$ concept of Amberg and Seanor in that the latter concept visualizes only an increase in the normal charge separation of the CO molecule and does not imply a loss of an electron, as the $(CO)^+$ concept does.

In the foregoing discussion it has been shown that in some cases the band at wave numbers of 2174 to 2193 cm^{-1} may reasonably be associated with intermediates in the oxidation of CO. It is also evident that there are three different opinions concerning the nature of the species which produces this band. Taken out of context, these differences in interpretation might be discouraging. However, it should be remembered that even in conventional homogeneous reaction systems it is often difficult to get unambiguous evidence on the nature of reaction intermediates. The evidence already available of the catalyzed oxidation of CO is more specific than the evidence in many studies of reaction mechanisms, and there is good reason to believe that interpretation of the 2193 cm^{-1} band will be clarified by further work.

Inhibition of Peroxide Decomposition

In almost all recent infrared spectroscopy studies of adsorbed molecules, cells have been utilized in which the adsorbate molecules are transferred to the solid via the gaseous phase. Direct observation of reactions proceeding under aqueous conditions is not possible because the infrared beam cannot be transmitted through the aqueous medium. The work described in this section illustrates how significant information may be gained by infrared studies of the solid after it has been separated from the aqueous medium. The study was part of a program involving the decomposition and formation of hydrogen peroxide over zinc oxide by a photochemical reaction (*21*). In previous work Markham had found that the peroxide reactions were inhibited by small amounts of formamide ($HCONH_2$) or cyanide ions, and had postulated that the inhibition was due to chemisorption of formamide or cyanide ions on the zinc oxide surface. The work described here was designed to determine whether these substances were adsorbed on the zinc oxide under the pertinent experimental conditions, and to determine the nature of the adsorbed inhibitors if any were detected.

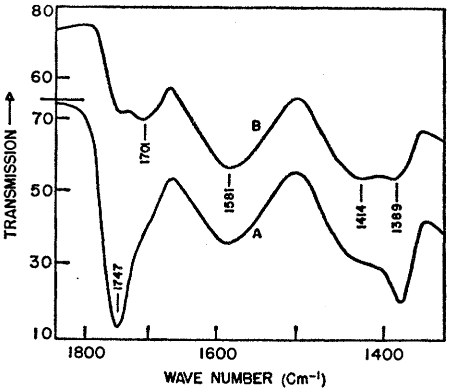


Fig. 7. Spectrum of acetic acid chemisorbed on $MgO–SiO_2$: *A*, at 70°C after drying of $MgO–SiO_2$ at 400°C; *B*, after admission of water vapor at 70°C.

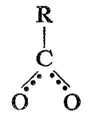
During the reaction the zinc oxide was kept in suspension by stirring. Prior to examination by infrared spectroscopy, the zinc oxide was separated from the water by centrifuging and drying.

Figure 6 shows results observed in an experiment in which there was a small quantity of formamide in the reaction mixture. Similar results were obtained when cyanide ions were present in the solution. The bands in the region of wave numbers 1600 to 1300 cm^{-1} are due to carbon dioxide chemisorbed in a form which is related to a carbonate or carboxylate. These bands are commonly found on zinc oxide which has been exposed to the atmosphere. They are not pertinent to the work under discussion. Spectrum *B* is the spectrum observed for zinc oxide which had been subjected to ultraviolet irradiation in the presence of oxygen and formamide. The band at the wave number of 2220 cm^{-1} [reported in (*21*) as the band at wavelength of 4.5 microns] is due to a cyanate ion. This interpretation is supported by the presence of the small band near 1200 cm^{-1}. The latter band shows up more clearly when more cyanate ion is present.

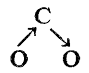
An interesting finding is the failure of adsorbed cyanate ions to inhibit the peroxide reactions if the cyanate ions are obtained by adding potassium cyanate to the water. Thus, the inhibiting effect is not simply due to blocking of the surface by adsorbed cyanate ions. Nergaranian and Markham (*21*) conclude that the inhibiting effect on the peroxide reactions is due to the competitive oxidation of formamide or cyanide at the electron-deficient sites created by irradiation of the zinc oxide.

Effect of Water on Chemisorbed Acetic Acid

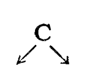
All carboxylic acids commonly produce carboxylate ions



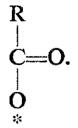
when chemisorbed on oxides. The carboxylate ion is detected by infrared bands near 1600 and 1400 cm^{-1} which are due to the asymmetric



and symmetric



carbon-oxygen stretching vibrations. Silica is an exception to the general pattern of oxide behavior, and carboxylate ions have not been detected on silica. Adsorption of carboxylic acids on silica is usually limited to physical adsorption, but in a few cases a small amount of a chemisorbed species is observed, which is bonded to the surface as an ester



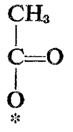
$$\begin{array}{l} R \\ | \\ C{=}O. \\ | \\ O \\ * \end{array}$$

This surface ester produces a carbon-oxygen stretching band near 1750 cm^{-1}.

Next let us consider chemisorption of acetic acid as a surface ester on a SiO_2–MgO catalyst (SiO_2, 74 percent; MgO, 26 percent). (This catalyst is important as a commercial cracking catalyst, but discussion of its use for that purpose is not pertinent here.)

Spectrum *A* of Fig. 7 was observed in our laboratory after the SiO_2–MgO had been exposed to acetic acid, at a pressure of 0.03 mm-Hg, at 70°C. Both the acid and the SiO_2–MgO had been carefully dried before the beginning of the experiment. The bands at 1581 and 1414 cm^{-1} have been attributed to carboxylate ions. These ions are probably on portions of the surface where MgO is exposed, since silica does not exhibit this type of chemisorption. However, this conclusion must be tempered with caution, since these catalysts are not simply mixtures of SiO_2 and MgO and the properties of either component may be profoundly influenced by the other.

Spectrum *A* also has bands at 1747 and 1389 cm^{-1}, which have been attributed to the ester



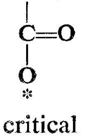
$$\begin{array}{l} CH_3 \\ | \\ C{=}O \\ | \\ O \\ * \end{array}$$

The 1389 cm^{-1} band is probably due to bending vibrations of the CH_3 group, but no attempt was made to confirm this interpretation by a study of chemisorbed deuterated acetic acid. As was mentioned earlier, ester groups, identified by carbon-oxygen bands near 1750 cm^{-1}, have been observed on pure silica. However, the bands on pure silica are so small, compared to the 1747 cm^{-1} band in spectrum *A* of Fig. 7, that the latter must be considered characteristic of the SiO_2–MgO rather than of SiO_2.

Spectrum *B* of Fig. 7 was observed after water vapor had been added. This brought about almost complete disappearance of the 1747 and 1389 cm^{-1} bands, but the 1581 and 1414 cm^{-1} carboxylate bands were essentially unaffected. In spectrum *B* there is also a band at 1701 cm^{-1}, which is due to physically adsorbed acetic acid. This band may be present in spectrum *A* as a shoulder on the 1747 cm^{-1} band, so it is not possible to determine whether the acetic acid was produced by hydrolysis of the surface ester or whether it was already present in spectrum *A*.

If either the acid or the SiO_2–MgO is not carefully dried prior to the initial chemisorption of the acid, spectra similar to *B* rather than to *A* are observed. The SiO_2–MgO is strongly hydrophilic, and water accumulates on the catalyst even though the concentration of water in the acid is small. Thus, if a relatively large volume of acid is passed over the catalyst, trace quantities of water will preclude formation of the surface ester.

Catalytic reactions are notorious for the difficulty of obtaining reproducible results. It is well known that some problems of reproducibility are caused by the introduction of small quantities of impurity with the reactant. The spectra of Fig. 7 illustrate how chemisorbed species may be affected by other molecules. It is obvious that the presence of traces of water would have a profound influence on a reaction in which the



$$\begin{array}{l} CH_3 \\ | \\ C{=}O \\ | \\ O \\ * \end{array}$$

species were a critical intermediate.

Summary

The examples discussed here represent only a small part of the published work relating to infrared spectra of adsorbed molecules. The publications in this field indicate that infrared spectroscopy is being used for surface chemistry research in about 50 laboratories throughout the world. This effort is mainly devoted to problems related to catalysis, and in this field infrared spectroscopy is the most widely used physical tool for surface chemistry studies. The general acceptance of infrared spectroscopy is primarily due to the fact that it provides information which is pertinent to the understanding of surface reactions on an atomic scale.

During the last decade significant progress has also been made in the classical chemical techniques of catalysis study and in utilization of physical tools which depend on phenomena of magnetism, conductivity, low-energy electron diffraction, and electron emission. Probably the most important progress has been in the field of inorganic chemistry, where dramatic advances have been made in knowledge of metal coordination compounds. Such knowledge is vital to the understanding of catalysis on metal surfaces.

I believe this progress has produced an attitude of sophisticated optimism among catalysis researchers with regard to eventual understanding of heterogeneous catalysis. This attitude is closely related to the realization that there is no "secret of catalysis" which places catalytic action beyond the limits of ordinary chemical knowledge (*22*). This view implies that the chemical aspects of heterogeneous catalysis are not unique and that the use of solid catalysts merely provides a highly effective exposure of catalytic atoms and facilitates separation of the products from the catalyst. Many capable catalysis researchers believe that studies of homogeneous catalysis provide the most direct route for the study of heterogeneous catalysis. Obviously homogeneous reactions catalyzed by compounds containing only one or two metal atoms do not leave room for effects associated with crystal parameters or with electronic band structure characteristic of the metallic state. At present, I believe, it is more reasonable to concede that these solid-state factors may play a role of secondary importance than to completely exclude them from consideration.

The view that catalysis involves

only conventional chemistry carried out under complicated conditions gives grounds for optimism, since it limits the boundaries of the problem. However, it also imposes a limitation on what might be expected from fundamental catalysis research. Most fundamental catalysis researchers do not rest their hopes on a single dramatic discovery which will make it possible to predict in detail the best catalyst for any specific reaction. The idea that catalysis researchers work with this goal in mind is as unrealistic as the idea that workers involved in practical catalysis development select constituents for catalysts by throwing darts at the periodic table. Although the fundamental catalysis researcher does not expect to advance ahead of general chemical knowledge, he does hope that he will not continue to lag behind. Infrared spectroscopy has provided a significant step toward closing the gap.

References and Notes

1. A. M. Buswell, K. Krebs, W. H. Rodebush, *J. Am. Chem. Soc.* **59**, 2603 (1937).
2. S. Brunauer, P. H. Emmett, E. Teller, *ibid.* **60**, 309 (1938).
3. M. R. Basila, *J. Phys. Chem.* **66**, 2223 (1962).
4. N. G. Yaroslavski and A. N. Terenin, *Dokl. Akad. Nauk SSSR* **66**, 885 (1949); L. N. Kurbatov and G. G. Neuimin, *ibid.* **68**, 341 (1949); ———, *ibid.* **85**, 1103 (1952).
5. R. S. McDonald, *J. Am. Chem. Soc.* **79**, 850 (1957).
6. J. H. de Boer, *Z. Physik. Chem. (Leipzig)* **B15**, 281 (1932).
7. H. P. Leftin and M. C. Hobson, Jr., *Advan. Catalysis* **14**, 115 (1963).
8. According to Beer's law, $\log I_0/I = kc$, where I is the transmission of the band peak, I_0 is the corresponding transmission of the background, k is the absorption coefficient, and c is a measure of the number of absorbing molecules in the beam path.
9. C. E. O'Neill and D. J. C. Yates, *J. Phys. Chem.* **65**, 901 (1961).
10. M. Courtois and S. J. Teichner, *J. Catalysis* **1**, 121 (1962).
11. R. P. Eischens and W. A. Pliskin, *Actes du Deuxième Congrès International de Catalyse* (1961), p. 789.
12. R. P. Eischens, S. A. Francis, W. A. Pliskin, *J. Phys. Chem.* **60**, 194 (1956).
13. R. P. Eischens and W. A. Pliskin, *Advan. Catalysis* **10**, 1 (1958).
14. L. H. Little, N. Sheppard, D. J. C. Yates, *Proc. Roy. Soc. London* **A259**, 242 (1960).
15. For present purposes a satisfactory indication of changes in band intensities may be gained by visual comparison of the bands in Fig. 4. However, quantitative intensity comparisons should be made on the basis of Beer's law (see *8*). To compare intensities the bands are replotted as $\log I_0/I$ versus wave number and the areas of the replotted bands are compared. The 8-fold increase was measured in this way.
16. D. J. C. Yates and P. J. Lucchesi, *J. Chem. Phys.* **35**, 243 (1961).
17. R. P. Eischens and W. A. Pliskin, *Advan. Catalysis* **9**, 662 (1957).
18. B. P. Susz and D. Cossimatis, *Helv. Chim. Acta* **44**, 395 (1961).
19. C. H. Amberg and D. H. Seanor, paper presented at the 3rd International Congress on Catalysis (1964).
20. R. A. Gardner and R. H. Petrucci, *J. Am. Chem. Soc.* **82**, 5051 (1960).
21. A. Nergaranian and M. C. Markham, *J. Phys. Chem.* **67**, 2679 (1963).
22. P. B. Weisz, *Advan. Catalysis* **13**, preface (1963).

Biomedical Science in Europe

Because of differences in their philosophies, Europe and America have much to offer each other in science.

R. P. Grant, C. P. Huttrer, C. G. Metzner

Modern science was born in Europe. Here, for 500 years, biological and medical research grew, and here its leadership has been, unchallenged by any other part of the world until the past generation. World War II was catastrophic for European science. In certain countries as much as 60 percent of the scientific manpower was lost—fled, killed, or exported. Hospitals and universities were destroyed. Virtually only a tradition was left intact. Now, nearly 20 years later, European science is approaching reconstitution, and its eminence is reemerging.

A rectangle in the middle of the map of Europe roughly outlined by lines connecting Rome, London, Stockholm, and Vienna has been the stronghold of European science. Here economic recovery has been most complete, cultural contact closest, and scientific restitution most rapid. In this article we attempt to study the patterns of scientific recovery in this part of Europe. This is an appraisal from an American point of view, in which developments in Western Europe are contrasted with those in the United States, for these two are the largest scientific communities in biomedicine.

European Scientific Community

The 12 countries of Western Europe (*1*) form an area barely one-fourth the size of the United States. Yet, 260 million people live there, as compared with 180 million in the United States. Together, they have 123 medical schools (the United States has 87), and in 1961 they turned out about 15,000 doctors, slightly more, per million of population, than the United States.

The relative size of the biomedical-research manpower pool in the two communities is difficult to determine. In 1960 the number of full-time medical faculty members in the United States was more than three times as large as the number in Western Europe. But the United States moved much more rapidly toward full-time staffing of its medical schools than Europe did. Furthermore, biomedical research is not confined to universities and medical schools in Europe, as it tends to be in the United States. For example, in Western Europe there are nearly 100 major "institutes" devoted to biomedical research which are independent of, although often situated near, universities. Some of them are government-owned and operated—for example, the Istituto Superiore di Sanità in Rome, which employs a thousand scientists and technicians. Others are mainly government-financed but are operated independently of the government or universities—for example, the 44 Max Planck institutes of West Germany, which together employ a thousand scientists. Still others are private, such as the Pasteur Institute of Paris, the Carlsberg Foundation in Copenhagen, and the Nuffield Institute in London. When we add the number of scientists in these institutes to the number on full-time staffs of the medical schools, we find that the biomedical manpower pool in Western Europe is very nearly as large as that in the United States.

But herein lies the largest single

The authors are affiliated with the European Office of the Office of International Research, National Institutes of Health, U.S. Public Health Service. The European Office is in Paris.