ADSORPTION OF OLEFINS ON ZnO AND ZEOLITE CATALYSTS:
STUDIES BY NUCLEAR MAGNETIC RESONANCE

by

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Adsorption of Olefins on ZnO and Zeolite Catalysts: Studies by Nuclear Magnetic Resonance

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ABSTRACT

Nuclear magnetic resonance has been used to study the mode of interaction and the catalytic hydrogenation of ethylene on pure and doped ZnO. It was found that Li weakens and Ga strengthens the chemisorption of ethylene. The hydrogenation reactions were all first order with respect to adsorbed ethylene. Li doping decreases the rate, while small amounts of Ga increase it. Large amounts of Ga, however, decrease the rate of hydrogenation.

The adsorption of cyclic and acyclic olefins was studied by C-13 NMR. The chemical shifts of the adsorbed olefins on ZnO are compared to those of the corresponding ones on silica gel. It is likely that these olefins donate electrons to the ZnO surface, while maintaining their olefinic character; i.e., are \( \pi \)-bonded to the surface. In addition, the \( \pi \)-complexes are formed by the interaction between ethylene and the Zn ions. This has been confirmed by studying the successive adsorption of testing gases such as acetylene and CO by means of proton and C-13 NMR respectively.

The C-13 chemical shift measurements of adsorbed ethylene on Zn- and Cd-exchanged zeolite types X and A, revealed that the adsorption occurs via the formation of \( \pi \)-complexes with the cations in the lattice. Also, the hydrogenation of ethylene over these catalysts was studied by proton NMR. The
isomerization of butene-1 over the catalysts mentioned above supports the view that the active sites for this reaction are the acidic centers on the zeolites.
DEDICATION

to my wife Melanie Fridleifson
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I. INTRODUCTION

Adsorption of Gases

In heterogeneous catalysis, at least one of the reactants is somehow attached to the solid surface. Since this attachment is essential for the catalytic reactions, it is imperative that our major concern is the understanding of the mode of gas adsorption.

Atoms at solid surfaces, whether they are active catalysts or not, are unsaturated. Hence, whenever a solid is brought into contact with gas molecules a higher concentration of the gas molecules will result on the surface relative to that in the gas phase. This is called adsorption. The forces involved in the adsorption and the extent of adsorption may vary from one system to another. It is possible, however, to divide all adsorptions into two main types: physical and chemical.

Physical and Chemical Adsorption

Physical adsorption is caused by Van der Waals forces between the adsorbent and the adsorbate. Chemisorption on the other hand, involves electron sharing between the interacting
molecule and the underlying surface with consequential formation of a bond. In physical adsorption, electrons may be displaced away from or to the adsorbed molecules, but without sharing electrons with the surface.

There are certain experimental criteria by which the two types of adsorption can be identified. These are: the heat of adsorption, the rate of adsorption and the rate of desorption. However, each of these criteria may not be used solely to distinguish between chemisorption and physical adsorption.

It is frequently possible to differentiate between the two types of adsorption by the heat of adsorption. The heat of adsorption of physically adsorbed gases is usually less than 10 kcal/mole, whereas the heat evolved when one mole of a gas is chemisorbed on a solid is in the range of 10 to 100 kcal. Caution is required in applying this method to identify the type of adsorption, since in some cases the chemisorbed gases give a low heat of adsorption(1), and also some gases which are physically adsorbed produce a high heat of adsorption(2).

As a consequence of the high heat of chemisorption, the amount of gas adsorbed is large, even at a pressure as low as 0.01 of the saturated pressure. Thus, the adsorption isotherm of most chemisorbed gases reaches a plateau at low pressure. This indicates that the surface is covered by a monolayer of adsorbed molecules. On the other hand, the amount
adsorbed of physisorbed gas is small at low pressure, and the formation of a monolayer is seldom complete at a pressure lower than 0.1 of the saturated pressure. In addition, physically adsorbed gases tend to form multilayers such that the amount adsorbed increases with the increase of equilibrium pressure.

Another criterion is the rate of adsorption. Since physical adsorption simulates condensation, no activation energy is needed in the adsorption process, therefore the rate is fast. On the other hand, chemisorption of gases resembles a chemical reaction wherein an activation energy may be required. Accordingly, the rate of adsorption increases to a certain extent with the increase in temperature.

The rate of adsorption proves to be a useful guide in the distinction between the two types of adsorption. Just as for the heat of adsorption, it can, however, be misleading if it is the only criterion. For example, physical adsorption takes place at temperatures near the boiling point of the adsorbate, and chemical adsorption often occurs at or above room temperature. Interestingly, oxygen chemisorbs quickly on metals at liquid nitrogen temperature while physical adsorption of some gases takes place slowly on porous solids, if the diffusion of the molecules is the rate determining step. Obviously, the former and latter cases can be mistaken for non-activated and activated processes respectively.
The rate of desorption is a useful guide in identifying the type of adsorption. Physically adsorbed molecules are weakly attached to the surface, therefore no activation energy is required for their removal and degassing at room temperature is sufficient. On the other hand, chemisorbed molecules are strongly bound to the solid surface, hence heating the sample at high temperature is necessary for their removal. We must stress herein, caution is necessary in using the rate of desorption as a guide for the distinction between the two types of adsorption. For example, the removal of physically adsorbed molecules on microporous solids needs activation energy.

**Adsorption Isotherms**

When solid surfaces are brought into contact with a gas phase, some of the gas molecules hit the surface and may stay on for a time \( \tau \) (adsorption), and then return to the gas phase (desorption). \( \tau \) can be a fraction of a second or even years. Equilibrium is reached when the rate of adsorption is equal to the rate of desorption. The former is a function of the bare surface and the pressure of the gas, whereas the latter depends on the fraction of the surface covered by the adsorbed molecules.

The adsorption isotherm is by far the most convenient method of determining experimentally the adsorption characteristic.
of a solid. In the discussion that follows, a brief summary of the Langmuir model will be presented. The Langmuir equation is important in heterogeneous catalysis since it is used in numerous kinetic interpretations. Then the BET (3) theory will be summarized. The importance of this theory, in surface chemistry and heterogeneous catalysis, lies in its ability to make reliable measurements of the specific surface areas for solids.

Langmuir Model

Langmuir(4) proposed that gas molecules adsorb on localized sites and that these sites are energetically the same. The Langmuir isotherm is often expressed by the formula:

\[ \theta = \frac{bP}{1 + bP} = \frac{V}{V_m} \]  

[1]

where \( V_m \) is the volume of the gas required to cover the entire surface with only one layer of adsorbed molecules, \( V \) refers to the volume of the adsorbed gas at equilibrium pressure, \( \theta \) is the fraction of the monolayer at pressure \( P \), and \( b \) is a constant equal to the ratio of the adsorption rate to that of desorption. At low pressure, equation [1] reduces to \( \theta = pb \). The constant \( b \) is proportional to \( \exp( -H_a/RT ) \); \( H_a \) is the heat of adsorption,
k is Boltzmann's constant, and T is Kelvin's temperature. Thus, chemisorbed gases (large $H_a$) on a given catalyst result in steeper isotherms than physically adsorbed ones. On the other hand, at a higher pressure, equation [1] predicts that the surface is covered by a monolayer i.e., $V$ approaches $V_m$. Figure (1), shows the general shape of the isotherms as predicted by Langmuir's equation.

The B.E.T. Theory

Brunauer, Emmett and Teller (BET) (3) extended Langmuir's model to allow for multilayer adsorption. This theory has received prodigious attention by surface chemists who are interested in the surface area determination of solids, and in the heat of adsorption. It was considered as a turning point in the history of surface chemistry and heterogeneous catalysis.

The BET theory was made on the assumption — as in the Langmuir model — that the surface is an array of energetically equivalent sites, and each site can accommodate only one molecule. Langmuir postulated that molecules from the gas phase might condense onto molecules already condensed (i.e., forming multilayers), then re-evaporate. However, he focused only on the first layer where the adsorbed molecules are attached directly to the surface. In 1938, Brunauer, Emmett and
General shapes of isotherms which conform to the Langmuir equation.

1. Isotherm of a typical chemisorbed gas.
2. Isotherm of a typical physisorbed gas.
FIG. 1
Teller showed how to extend Langmuir's approach to multilayer adsorption. Their equation has become known as the BET equation. The derivation of this equation can be found in many surface chemistry books, or in reference 3.

The basic assumption in the BET theory is that the Langmuir equation is applied to each layer, with the new postulation that the heat evolved in the formation of the first layer is equal to the heat of adsorption, whereas that evolved in the formation of the second and the successive layers is equal to the heat of liquefaction. This postulate and the assumption that the surface is energetically uniform became a source of criticism (5) for the BET model.

The BET equation which is used frequently to express the adsorption isotherm takes the form

\[
\frac{P}{V(P_0 - P)} = \frac{1}{C V_m} + \frac{C - 1}{V_m C} \frac{P}{P_0}
\]

where \( C \) is proportional to \( \exp\left(\frac{H_a - H_L}{kT}\right) \), \( H_L \) is the heat of liquefaction and \( P \) is the saturation pressure.

The plot of \( P/V(P_0 - P) \) vs \( P/P_0 \) gives a straight line in the range between 0.05 and 0.35 \( P/P_0 \). The monolayer capacity \( V_m \) can be calculated from the slope \( S \) and the intercept \( I \) of the line viz:

\[ V_m = \left( S + I \right)^{-1} \]
This is probably the most simple method in determining the monolayer capacity of a solid. The surface area of a solid can be readily determined from the relationship:

\[
S_{\text{BET}} = \frac{V_m \ (\text{cc})}{22414} \times \sigma \times N \times 10^{-20}
\]  

where \( N \) is Avogadro's number and \( \sigma \) is the cross section area of the adsorbed molecules (for \( N_2 \), \( \sigma = 16.2\AA^2 \) (6)).

The surface area is by no means the only physical property which determines the extent of the catalytic reaction on solid catalysts. Equally important is the pore structure of the catalyst. Knowing the pore size distribution gives insight into the accessibility of the catalyst to the adsorbed molecules. In some cases, a portion of the catalyst is inaccessible to large reacting molecules, therefore it may decrease the rate of conversion by impeding the diffusion of the molecules into the pores.

There are many methods available for the determination of the pore-size distribution(7-10). The simplest and most frequently used ones that give reasonable results are those proposed by Mikhail(7, 8). Using these methods, the adsorption data of \( N_2 \) are used for the determination of the pore-size distribution, provided that \( N_2 \) condenses in the pores of interest (5-100\( \AA \) in diameter) at a pressure less than the
Activity of Solid Catalysts

So far the different types of adsorption and the basic models for adsorption isotherms have been briefly discussed in the previous sections. Now, however, the reader may be anxious to receive a simple account of the activity of solid catalysts. Let us assume that the following reaction is catalyzed by a solid S.

\[ G_2 + P_2 \]

The reactant molecules \( G_2 \) chemisorb rapidly on the surface forming intermediates. These intermediates form the products, \( P_2 \), which in turn are rapidly desorbed to regenerate vacant surface sites. This reaction may be schematically represented as:

\[
G_2 + S-S \xrightarrow{K_2} S-S \xrightarrow{K_1} S \xrightarrow{K_3} S-S + P_2
\]

Examining this reaction without going through kinetic expressions tells us that the number of active sites determines the catalytic activity, hence, larger surface area may bring about a larger activity. However, it was found that in most cases there is no correlation between the catalyst surface area
and the number of active sites and, therefore the catalytic activity. For this reason, it has become customary in heterogeneous catalysis to express the activity of a given solid by the number of active sites per unit area. It must be stressed that a large number of active sites per unit area is not enough to produce a large activity. Of equal importance, is the kinetics associated with these sites in that $K_3$ must be large and the ratio $K_1/K_2$ should be optimal. This simply means that the bond between the product and the active centers must be easily ruptured and the chemisorption is reversible.

The question now is how to describe relative activities. Since the chemisorption of at least one of the reactants is the precursor of the catalytic reaction, the catalyst decreases the formation energy of the surface intermediates, and therefore decreases the activation energy of the reaction relative to the uncatalyzed one. Accordingly, it seems logical that the activation energy can be taken as a quantitative measure of the catalytic activity of a given solid. In other words, the smaller the activation energy, the better the catalyst. However, caution is necessary in adopting this approach. This is because of the compensation effect (11) which can be explained in terms of the variation of the activation energy with the pre-exponential factor. The activation energy of a given reaction on catalyst A could be lower than that on catalyst B. However, the rate on B may be
greater than that on A, because the pre-exponential factor with B may be correspondingly larger.

Comparing the activities of various catalysts can be done in one of two ways: either (i) by comparing the rates at a fixed temperature or, (ii) by comparing the temperature at which fixed rates can be obtained. The drawback of the second method is that it is a qualitative one. Reporting that catalyst B is 60 °C more active than A may have some practical importance, but it is useless in fundamental investigation. Therefore, the first method is more practical since the comparison of activities is on a quantitative basis.

Deactivation of The Catalyst

Catalysts suffer a decline in potency with time. The sources of this deactivation may be one of the following: poisoning, fouling, sintering, or a combination thereof.

Poisoning of the surface occurs as a result of the chemisorption of entities on the active sites otherwise available for catalytic reaction. These poisoning compounds can be impurities in the gas phase, reactant molecules, or even the products. The impurities in the gas feed can easily be removed. However, if the poisoning results from the reactant molecules or the product, their removal is impossible, and the effect decreases the conversion.
Fouling can result from the deposition of some compounds from the reaction products, or from nonremovable products of a surface reaction (e.g., coke in cracking reactions). In both cases these species plug the pores, or may cover the active sites, hence denying access of the reactant molecules to these sites.

Sintering may occur after heating the catalyst at a high temperature, or may be due to the existence of oxidizing or reducing agents. As a result, the catalyst suffers a reduction in the surface area. This is because some – if not all – of the pores are sealed off, and this reduces the number of the active sites.

In the preceding paragraphs a summary of some principles of the adsorption on solid surfaces, the nature of the active sites and their role in determining the catalytic activity and finally, the sources for catalytic deactivation was presented.

In the next chapter the electronic structure of semiconductors and the mechanisms of chemisorption on n-type semiconductors, notably ZnO, will be briefly discussed.
II. CHEMISORPTION ON SEMICONDUCTORS

The catalytic activity of semiconductors resides at the interface between the solid and the reactants, thus, at least one of the reactant molecules must chemisorb on the surface. Therefore, it is worthwhile to discuss the theories of chemisorption on semiconductors. These theories are based firmly on the band theory (see ref. 12). A summary of the electronic theory of semiconductors, the boundary-layer theory, and the electronic theory of the Russian School will be presented in this chapter.

As we will see there is much experimental evidence to support these theories, but most of it is qualitative in nature and not precise.

Electronic Theory of Semiconductors

The band theory provides a good model to distinguish between semiconductors, metals and insulators. This theory proposed that in a pure crystal there are two important bands. One is called the valency band, and the other is the conduction band. These two bands are separated to a greater or lesser extent by what is named the forbidden gap. The Fermi level, is
defined as the energy state for which the probability of the electron occupation is equal to 0.5. It is located in the forbidden gap. The position of the Fermi level depends on the concentration of impurities in the semiconductor, and on temperature. For intrinsic semiconductors, the Fermi level is in the middle of the forbidden gap at any temperature. However, its location in extrinsic semiconductors can be near the valency band (p-type), or near the conduction band (n-type).

The forbidden gap in insulators is large compared to \( kT \). Therefore, it is difficult for electrons to be promoted from the valency band to the conduction band. In metals, both bands overlap so that there is a continuous flow of electrons from the valency band to the conduction band.

Zinc oxide is a non-stoichiometric compound. It contains excess Zn metal or ions at interstitial positions in the lattice (n-type)\(^{(13)}\). These metal atoms can be easily ionized to give electrons and ions upon the absorption of heat. The generated electrons go to the conduction band, thus, contributing to the conductivity of the oxide. In other words, the conductivity can be described by the number of electrons in the conduction band.

The conductivity of the semiconductor may be altered by replacing Zn in the lattice sites by foreign ions \(^{(14)}\). For example, a small amount of Ga ions in ZnO lattice increases the number of electrons in the conduction band, and thus increases the conductivity. This is because replacing Zn by Ga is
accompanied by the release of electrons in order to maintain the neutrality of the oxide. On the other hand, the incorporation of monovalent Li ions into ZnO lattice suppresses the conductivity by decreasing the concentration of free electrons in the conduction band (14).

These free electrons are likely to be involved in the chemisorption of acceptor gases whereby electrons leave the surface to the adsorbed molecules. On the other hand, ZnO can accept electrons from donor molecules upon adsorption. Hence, the conductivity in the former case decreases and, in the latter case increases.

The following theories explain qualitatively the mechanism of chemisorption on ZnO.

The Boundary Layer Theory

Early work on this theory was done by Aigrain and Dugas (15), Hauffe and Engell (16), and Weisz (17), following the theory of contact between metals and semiconductors (18). The ESR measurements of an acceptor gas, such as oxygen adsorbed on ZnO, revealed the formation of $\text{O}_3^-$, $\text{O}_2^-$, and $\text{O}^-$ on the surface (19-21).

The formation of any of these species on the surface indicates that $\text{O}_2^-$ received an electron from ZnO upon adsorption. In fact, there are few electrons in the conduction band. If these electrons are used up, then further adsorption
of O$_2$ requires electrons from deeper energy levels. The promotion of these electrons needs greater energy, hence the flow of electrons from the surface to the adsorbed species is stopped. As a result, a positive space charge is developed in the semiconductor due to the loss of electrons to the adsorbed oxygen, and a negative charge on the surface O$_2^-$. A field is created in the surface region whose height is increased with each atom adsorbed. Thus, every electron transferred from the conduction band to the adsorbed O$_2$ must surmount a potential barrier. An equilibrium is reached when the potential energy of the electron in the conduction band is equal to that on the adsorbed species. Thus, the number of electrons flowing from and into the conduction band is equal, consequently the adsorption of O$_2$ ceases. Since the concentration of electrons in the conduction band is small, the adsorption stops far before reaching the monolayer coverage. Experimentally it was found that $\theta < 2.5 \times 10^{-4}$ (22).

On the other hand, the adsorption of donor molecules such as hydrogen increases the concentration of electrons in the conduction band and hence increases the conductivity of ZnO (23). Since there is no energy barrier in putting more electrons into the conduction band, it is possible that hydrogen forms a monolayer on ZnO. Engell (16) called the adsorption of H$_2$ a cumulative type.
It must be stated that the weakness of this theory is its failure to include adsorption which involves no charge transfer. It seems that this kind of adsorption is beyond the realm of this theory, and will be considered in the next section.

Electron Theory of The Russian School

The chemisorption of gases on semiconductors has been studied a great deal by Russian scientists, especially Wolkenstein (24-25). Wolkenstein's theory is broader than the double layer theory, in that the chemisorption can be classified as weak or strong. Weak chemisorption involves no charge transfer between the adsorbate and adsorbent. However, in strong chemisorption, the adsorbed molecules may capture electrons or holes from the surface. An "acceptor bond" is formed when an electron is captured by the adsorbed molecules. A "donor bond" is formed if a hole, or a positive charge, is captured by the adsorbed species.

The adsorption of hydrogen on ZnO is an illustrative example of the heuristic value of the Wolkenstein theory. At room temperature hydrogen dissociatively adsorbs on ZnO, thus a charge is captured. However, at liquid nitrogen temperature it is molecularly adsorbed whereby no charge is transferred to, or from the surface (26).
Generally speaking, both theories took into account the concentration of electrons in the conduction band. However, they lacked knowledge of the surface states (27). Furthermore, the mobility of electrons is ignored and the interactions between the ions at the surface and the surface defects are neglected.

One of the purposes of the present investigation is to study the role of the electronic structure in catalytic hydrogenation on ZnO. Thus, it is worthwhile to quote a comprehensive example which permits the correlation of the catalytic activity with the electronic structure. This example is the oxidation of CO on ZnO.

Schwab (28) studied the oxidation of CO on ZnO doped with Li or Ga ions. The addition of Li to ZnO increases the activation energy of the reaction. On the contrary, doping with Ga decreases the activation energy. These findings are in accord with Schwab's view that the adsorption of $O_2$ is the rate determining step. Oxygen is an acceptor molecule, therefore, the larger the concentration of electrons (ZnO doped with Ga), the easier the formation of surface oxygen ions and the smaller the activation energy of the oxidation of CO.

Although Schwab's results are in line with the interpretation deduced by the boundary layer theory, Parravano (29) found the opposite when he studied the oxidation of CO on NiO (p-type) doped with Li or Cr. Li increases rather than
decreases the activation energy. Another observation which contradicts Schwab's results is that the addition of a small amount of Cr ions decreases instead of increases the activation energy. The difference between the two studies could be due to the temperature range at which the reaction was carried out. Schwab studied the reaction in the range of 180-240°C and Parravano at 240-250°C.
III. THE OBJECTIVES OF THIS RESEARCH WORK

In addition to the example cited previously (the oxidation of CO on ZnO), Teichner (30-31) studied the hydrogenation of ethylene on ZnO doped with Li or Ga ions. He found that at a temperature below 140°C, neither the rate nor the activation energy of the hydrogenation reaction varied when Li or Ga is present in the ZnO lattice. However, he recently (32) reported that the addition of Li decreases the rate, while Ga accelerates it in the temperature range 85-125°C. At temperatures above 150°C, both ions accelerate the hydrogenation rate.

Obviously, the correlation between the semiconductivity and the catalytic activity has not been completely established. Hence, more work is required to shed some light on the uncertainties concerning the modification of the electronic structure of ZnO by doping.

The present research is twofold, one is the further investigation of the influence of the electron concentration in the ZnO conduction band on the catalytic hydrogenation, and the mode of ethylene adsorption. The second is the study of the nature of active sites at which ethylene adsorbs. The latter includes the active sites on ZnO and zeolites containing Zn or Cd ions.
The previous work in this laboratory, as well as the work of others, revealed that ethylene adsorbs associatively on ZnO. The proton NMR shift indicates that ethylene donates electrons to the surface (33). According to the boundary layer theory, the lesser the supply of electrons at the ZnO surface, the easier will be the donation of electrons and thus the greater will be the chemical shift of adsorbed ethylene.

In order to check this hypothesis, the adsorption and the chemical shift of ethylene have been measured on pure and doped ZnO. In addition, the catalytic hydrogenation of ethylene over these catalysts has been studied by the NMR technique, in order to examine the effect of the electronic structures on the catalytic activities (Chapter VIII).

Kokes et al. (34) reported that ethylene forms only \( \pi \)-complex species, whereas propene forms \( \pi \)-allyl and \( \pi \)-complexes on ZnO (35). Interestingly, the NMR studies (33) supported the formation of the \( \pi \)-complex species. Although the \( \pi \)-complexes of adsorbed ethylene and propene are similar, these authors (34) suggested that ethylene \( \pi \)-complex stabilizes on the O\(^{2-}\) ion, whereas that of propene stabilizes on Zn\(^{+2}\) ion. Thus, the nature of the adsorption sites for olefins needs more investigation.

In order to study the nature of the active sites at which the \( \pi \)-complex species is stabilized, the chemical shifts of various olefins adsorbed on ZnO are compared to those of the
corresponding ones on silica gel (see Chapter IX).

In addition, successive adsorption of acetylene on ZnO previously covered by ethylene was studied by proton NMR spectroscopy. Carbon-13 NMR was used in investigating the subsequent adsorption of ethylene on ZnO containing adsorbed CO. Such investigation further elucidated the nature of the active sites at which ethylene $\pi$-complex is being stabilized (Chapter X).

The surface and the catalytic properties of Zn- and Cd-zeolite types X and A have been studied less than other cation exchanged zeolites. With this in mind, further studies of these zeolites by NMR spectroscopy may increase our knowledge about the nature of the active sites, and the mode of olefin interaction with these sites. Carbon-13 NMR was used to determine the mode of ethylene adsorption on these zeolites. In addition, the NMR technique was utilized to study the catalytic hydrogenation of ethylene and the isomerization of butene-1 on Zn-, Cd-, Na-zeolite types X and A.

In the following Chapter, a brief account is given of some studies on the surface and the catalytic properties of ZnO and zeolite catalysts insofar as they are relevant to the present work.
IV. STRUCTURE AND SURFACE PROPERTIES OF ZnO

The crystal structure of ZnO belongs to the Wurtzite type. In this crystal, the Zn and O ions are tetrahedrally coordinated and the fractional ionic character of the covalent bond is 0.618 (36).

Kokes et al. (34) considered the Wurtzite structure in interpreting their infrared and adsorption data. They proposed that Zn ions occupy the trigonal holes in the close packed layer of the oxide ions. The radius of the holes is about 0.58\(\text{Å}\), which is big enough to accommodate the Zn ion with radius of about 0.74\(\text{Å}\). This arrangement of ions could be obtained from the cleavage of ZnO crystal to (0001) surfaces. They also believed that the (0001) surface is stable and should not reconstruct. LEED studies supported this view (36-37).

Zinc ions on the (0001) surface relax into the trigonal sites by about 0.3\(\text{Å}\) (38-42). On the (1010) surface, Zn ions relax into the surface by about 0.45\(\text{Å}\) and laterally by about 0.1\(\text{Å}\), whereas the O ions relax by less than 0.1\(\text{ Å}\) (38-42). LEED studies also revealed that the (0001) and (1120) surfaces retain the bulk structure of ZnO crystal (38-42). The surface geometries of (0001), (0001), (1010) and (1120) surfaces are shown in Fig.(2).
Surface geometry of the four low-index surfaces of ZnO. Large circles represent oxide ions, small circles represent zinc ions, shaded circles represent the surface layer and open circles represent the second layer (128).
FIG. 2
Morimoto and Moriskige (43) employed the adsorption of water in deducing a simple model for the surface structure of ZnO. Water is heterolytically fissioned upon adsorption to give OH and H. The OH group is bound to Zn ion, and H to O⁻² ion. Hence, the number of OH groups is equal to that of Zn ions at the surface. The adsorption of water on ZnO preheated in vacuo at 600°C increases the population of OH from 0.32 OH/100Å² to 7.32 OH/100Å². This value could be used as a guide to indicate that the surface is made up of (0001) surfaces with a population of 11 Zn ions per 100Å², and (1010) surfaces with a population 6 Zn ions per 100Å² in equal amounts, since the average population of Zn ions amounts to 8.5 per 100Å².

Heating ZnO at 400°C is necessary to develop catalytic activity. Frequently, heating in an oxygen atmosphere ensures the stoichiometry of the catalyst.

**Hydrogen Adsorption**

The adsorption of hydrogen on ZnO presumably takes place on the same sites involved in the hydrogenation reactions. At or below room temperature the adsorption is simple, whereas at higher temperatures the adsorption becomes complicated. For this reason, the ensuing discussion will be devoted to the adsorption at room temperature.

Although there is a general agreement that both Zn and O ions are involved in the chemisorption of hydrogen, the nature
of the adsorbed species is still debated. Recent infrared studies (44) showed that there are two types of chemisorbed hydrogen at room temperature, namely type I and type II. The former is weak, infrared active, adsorbs fast, reversibly and occupies only 5% of the total BET surface area. The latter is strongly adsorbed, infrared inactive and irreversible.

Type I chemisorbed hydrogen gives characteristic infrared bands at 3490 and 1710 cm\(^{-1}\). These bands are assigned to the stretching vibration of surface OH and ZnH respectively.

The chemisorbed hydrogen (type I) is the active species in ethylene hydrogenation, whereas type II is inactive in this reaction.

Boccuzzi et al. (55) adopted Kokes's model for type I chemisorbed hydrogen. However, they proposed a different picture for type II, in that hydrogen is dissociatively adsorbed, forming bridged O...H...O and Zn--H--Zn structures.

**Ethylene Adsorption and Hydrogenation**

The adsorption of ethylene on ZnO at room temperature is rapid and reversible (34). At low coverage, the heat of adsorption is about 14 kcal/mole vs 3.5 kcal/mole for ethylene heat of vapourization (44). However, it falls as the surface coverage increases and finally reaches a value equal to the heat of adsorption of ethane (5 kcal/mole) above a coverage of about 0.3 cc/gm. Thus, ethylene is weakly chemisorbed at a low
The infrared (44) and the NMR spectra of adsorbed ethylene on ZnO revealed the formation of π-complex species.

Poisoning the surface with water has little effect on the adsorption of ethylene. However, under similar conditions those sites for adsorbed hydrogen type I are totally eliminated (44). Thus, it seems that hydrogen and ethylene adsorb on different sites.

Although it is certain that ethylene forms a π-complex with ZnO surface, there is no confirmed evidence of the nature of the active sites. Kokes (44) suggested that the active sites for ethylene adsorption are the oxide part of the Zn-O ion pair. This is because Zn ion is sequestered between three O ions, thus causing steric hindrance for ethylene to interact with Zn ion. This conclusion is based on the the infrared spectra of co-adsorbed ethylene and deuterium on ZnO. The intensity of the band assigned for Zn-D was insensitive to the adsorption of ethylene, whereas the O-D band lost almost 60% of its intensity upon the adsorption of ethylene.

Kokes's model was disputed recently by Efremov et al. (47), who found that the successive adsorption of ethylene on ZnO previously covered by CO eliminates the band assigned for the Zn-CO complex. This suggests that ethylene may adsorb on the Zn ion.
The hydrogenation of ethylene over ZnO was studied by means of the infrared and kinetic techniques (48). The kinetic derivation showed that the rate of hydrogenation can be given by

\[ \text{Rate} \propto \left( P_{H_2} \right)^{0.5} \left( C_2H_4 \text{ ads.} \right) \]  

The reaction mechanism was investigated by monitoring the surface reaction of ethylene with deuterium. The infrared spectra showed that the intensity of the band assigned for the double bond of chemisorbed ethylene decreased with time and finally disappeared. This declining in intensity was accompanied by a band growing in the C-D region. Therefore, Kokes suggested that $C_2H_4D$ adsorbs on Zn ion because the steric hindrance becomes minimal for the more directional $\sigma$ bond.

The final product of the reaction between $D_2$ and ethylene is $C_2H_4D_2$, whereas over metals a multiplicity of species of the form $C_2H_{6-x}D_x$ are expected. Thus, the formation of $C_2H_4D$ is irreversible step. Obviously, the hydrogenation of ethylene over ZnO is simpler than over metals (44).

Poisoning the surface with water halts the hydrogenation reaction (44). Kokes argued that water reacts with the active sites otherwise available to type I chemisorbed hydrogen.
Adsorption of Propene

Propene forms two surface species, \( \pi \)-complex and \( \pi \)-allyl species (44). The former can be removed by evacuation at room temperature, whereas the latter is strongly adsorbed. Thus, heating at \( 150^\circ C \) is required to remove the \( \pi \)-allylic species from the surface.

Examining the infrared spectra of adsorbed propene on ZnO shows the presence of an C-H vibrational band. This suggests that propene adsorbs dissociatively to form a \( \pi \)-allyl species and a proton. The \( \pi \)-allyl species attaches itself to Zn and the H to the O part of the Zn-O ion pair. This can be represented as

\[
C_3H_6 + ZnO \rightarrow \begin{array}{c}
\text{Zn} \\
\text{O}
\end{array} \quad H
\]

In order to identify which C-H bond is broken during the chemisorption of propene, the adsorption of \( CH_3-CH=CD_2 \) was studied by Kokes et al. (44). The infrared spectra showed an O-H band immediately after the adsorption. The intensity of this band decreased as the time elapsed. This was accompanied by the growing of another band in the O-D region. At equilibrium, the intensity ratio of the OH band to the OD band is \( 3/2 \). Therefore, the surface reaction may be written as
These results suggested that the adsorption of propene occurs by the rupture of the methyl C-H bond to form allylic species.

The infrared spectra of CD$_3$-CH=CH$_2$ and CH$_3$-CH=CD$_2$ are similar after equilibration. This strongly suggests that the π-allyl species is symmetrical and it is likely to be the intermediate in the isomerization of propene. This surface reaction can be written as

\[
CD_3-CH=CH_2 \rightleftharpoons CD_2-CH=CD_2 \rightleftharpoons CH_2D-CH=CD_2
\]

Since the π-allylic species is attached to the Zn ion, Kokes assumed that it has some carbanionic character. Ismailov et al. (49) reported that the π-allyl species is a radical since it has an ESR signal at \(-195^\circ\) C. However, at room temperature, no signal is found. They interpreted the absence of the room temperature signal as a result of fast transition of
the unpaired electrons. Propyl radical and benzene were detected in the gas phase of desorbed propene at 760°C by mass spectroscopy (50). Recently, Nguyen and Sheppard (51) confirmed Kokes's opinion that the \( \pi \)-allyl is an anion, by finding striking similarities between the infrared and Raman frequencies of the \( \pi \)-allyl anion in \( \text{C}_3\text{H}_5\text{MgCl} \) and those formed on ZnO surface.

**Adsorption of Butenes**

Kokes et al. (52) studied the mode of adsorption and the isomerization of butenes on ZnO. The infrared spectra revealed the existence of five surface species, namely, \( \pi \)-complexes of butene-1, butene-2 (cis and trans isomers), syn and anti \( \pi \)-allyl. Only syn species can be produced from the trans isomer, and anti species from the cis isomer. Eutene-1 can produce both syn and anti species.

Lombardo et al. (53) studied the isomerization of butene-1 and butene-2 over ZnO in a temperature range of 0-90°C. A qualitative free energy diagram for the reactions was proposed (see Fig.3). This diagram accommodates all of the five surface species proposed by Kokes. The rate of isomerization is zero order in butene at temperatures below 50°C, however at higher temperatures the rate expression is rather complicated. Tracer studies showed that the conversion of cis to trans isomer occurs without the formation of \( \pi \)-complexed butene-1.
**Figure 3**

Activation energy diagram for the isomerization of n-butenes on ZnO (53). Energies in kJ mol⁻¹. Designations of intermediate states indicate π- and π-allyl complexes identified by infrared spectroscopy.
Furthermore, the intermolecular hydrogen exchange is minimal at room temperature. In general, the infrared and the kinetic data reported in this article are entirely consistent with the work by the late Professor Kokes.

Adsorption of Cycloolefins

Dent and Oyekan (54) have recently published infrared, kinetic, and volumetric studies for some cycloolefins on ZnO. Cyclopentene forms a $\pi$-bonded complex upon adsorption. The infrared spectrum of cyclobutene was similar to that obtained from 1,3 butadiene. This suggests that an opening of the ring occurred immediately after adsorption.

Methylenecyclobutene formed a $\pi$-allylic species upon adsorption. This same species was observed following the adsorption of 1-methylcyclobutene. Thus, the $\pi$-allylic species is believed to be the intermediate for the endo/exo isomerization.

The isomerization of methylenecyclobutane to 1-methylcyclobutene was carried out in a temperature range between 25 and 125°C. The activation energy of this reaction was 14 kcal/mole. However, above 125°C, the reaction proceeded via the formation of a second $\pi$-allylic species following the opening of the ring.
Adsorption of Alkynes

Acetylene is more acidic than ethylene. Acetylene is dissociatively adsorbed on ZnO, forming a proton and $\text{H-C}≡\text{C}^-$. The infrared spectrum showed that the proton is attached to the O ion and $\text{H-C}≡\text{C}^-$ to Zn ion of the Zn-O ion pair (55). Acetylene is strongly adsorbed on ZnO. Heating the sample at 400 °C in an oxygen atmosphere is necessary to remove the adsorbed molecules.

As anticipated, Kokes et al. (55) found that the infrared spectrum of adsorbed methylacetylene is similar to that of adsorbed allene. This suggests that the propargylic species is the intermediate for methylacetylene-allene isomerization. The isomerization can be depicted as

$$\text{CH}_3\text{C=CH}_2 + \text{ZnO} \rightarrow \text{Zn}-\text{CH}_2\text{C}=\text{CH}_2$$

Recent infrared studies by Saussey et al. (56-57) revealed that species like (CH$_3$)$_3$C≡CCH and C$_6$H$_5$-C≡C-H cannot isomerize, however, they form strongly bonded acetylide species on ZnO. Compounds that form propargyl species upon adsorption produce also acetylide species in substantial amounts. This is in contrast to Kokes's findings that the concentration of these species is small. Selective poisoning (57) showed that the sites for propargylic species are those sensitive to acetic acid.
and ammonia. These sites are most likely Lewis acid-base centers such as Zn-O ion pairs. The sites for acetylide species are poisoned only by carbon dioxide.
V. ZEOLITES

Since the discovery of the catalytic activities of zeolites in the 1950's, there have been numerous publications and several books on the catalysis and the surface chemistry of zeolites. Yet, after almost three decades there are many questions that need to be answered. Certainly, the goal of the scientists is to discover new phenomena, but in most cases the new discovery runs ahead of satisfactory interpretation of the previous ones.

Zeolites are used as catalysts for catalytic reactions such as isomerization, hydrogenation, hydrocracking, and hydrodealkylation. In the petrochemical industry alone, 3 billion dollars are saved annually with the use of zeolites as catalysts (58).

Although macroscopic descriptions of zeolite chemistry and catalysis are adequate for many purposes, scientific understanding needs detailed knowledge of the crystal structures and microscopic information regarding the nature of the active sites. For this reason, the following discussion will focus on the crystal structure of zeolites A and X. In addition, a brief account of some spectroscopic studies on zeolites will be presented.
Crystal Structure of Zeolites

The determination of the crystal structure of zeolites faces some difficulties. In the ensuing discussion a few of these problems will be presented. However, details of the crystal structure are given by Smith (59).

Preparing a single crystal wider than 20-50 μm is a difficult process. However, if this crystal is available, then a full set of x-ray intensities could be obtained. On the other hand, if powder is used, most of the x-ray intensities would be lost in the background because of the overlap of the diffraction lines. In addition, the determination of the Na ion location is rather difficult since the atomic weight of Na ion is close to that of water.

Another problem in the determination of zeolite crystal structure is that the distance between different ions occupying similar sites and the oxygen framework may be averaged out. Also, the distance between oxygen and Si or Al ions as obtained from the x-ray diffraction is averaged out because of the random occupancy of Si and Al ions in the framework. Recently, the Si-29 NMR (60) showed that for zeolites with Si:Al ratio close to unity, there is only one kind of Si,Al ordering present in each sample.

Regardless of the difficulties mentioned above and the conflicting x-ray data, it is generally accepted that the
framework of zeolites consists of sodalite units connected to each other in a manner different from one zeolite to another.

If we accept the sodalite unit to be the building block in the framework, then the picture may be clearer if the building units are mentioned as well. These building units are: four-membered rings; six-membered rings; eight-membered rings; twelve-membered rings; and hexagonal prisms and cubes.

Each sodalite unit is comprised of six square rings and eight hexagonal rings. The free diameter of the sodalite cage ($\alpha$-cage) is 6.6Å. However, the diameter of the six-membered ring is only 2.2Å.

Zeolite A

The chemical formula of zeolite A is $\text{Na}_{12} \text{Al}_{12} \text{Si}_{48} \text{O}_{144}$ $\cdot$ $27\text{H}_2\text{O}$. This framework is obtained by connecting the sodalite units by cubes. Hence, another cage is formed which is called the central cage or $\alpha$-cage. This truncated cuboctahedron has twelve 4-membered rings, eight 6-membered rings and six 8-membered rings. Figure (4) shows one face of the truncated octahedron. The diameter of the $\alpha$-cage is about 11Å. Each $\alpha$-cage is entered through six nearly circular apertures formed by six 8-membered rings with a free diameter of 4.2Å. Thus, the access to the sodalite units is through the $\alpha$-cage. For this
Figure 4

Connection of sodalite units in Zeolite A. Vertices represent Si or Al atoms, lines represent -O- connections.
FIG. 4
structural reason, ethylene molecules whose diameter is 4.2 Å (61) can enter only the \( \alpha \)-cage.

There are 12 \( \text{Na} \) ions, therefore there must be twelve \( \text{Na} \) ions. The distribution of these ions is as follows: eight \( \text{Na} \) ions at the center of the six-membered rings, and three \( \text{Na} \) ions near the eight-membered rings. The latter ions determine the sieving properties of the zeolite. The last \( \text{Na} \) ion is located in the \( \alpha \)-cage but its location is not well defined (59).

Sodium ions are readily exchanged with mono or divalent ions. In this study, \( \text{Na} \) ions are replaced by \( \text{Zn} \) ions and \( \text{Cd} \) ions.

Crystal Structure of Zn-Exchanged Zeolite A

Seff et al. (62) studied the crystal structure of partially exchanged Zn-zeolite A. In this crystal, five \( \text{Zn} \) ions replaced ten \( \text{Na} \) ions in the lattice. The abbreviated molecular formula is \( \text{Zn}_5\text{Na}_2\text{A} \), where \( \text{A} \) stands for \( \text{Al}_{12}\text{Si}_{12}\text{O}_{48} \). One \( \text{Zn} \) ion is at the centre of the sodalite unit. This ion is tetrahedrally coordinated to four water molecules. The other four project into the \( \alpha \)-cage where each ion is coordinated with three oxygen ions of the six-membered ring and one water molecule.

Dehydration of Zn-zeolite is always a complicated process. It involves the breaking of the coordination and the
migration of the cations. For example, heating the crystal at 380°C resulted in the relocation of the Zn ion at the center of the sodalite cage, and two more which were located inside the α -cage to positions near the center of the six-membered rings. The other two retained their positions.

The crystal structure of fully Zn-exchanged zeolite A has been recently studied by Seff (63). The location of Zn ions in hydrated crystal is as follows: one ion (Zn1) is at the center of the sodalite unit. This ion is tetrahedrally coordinated to four oxygens (O4) of water molecules. These oxygens, O4, are attached to the oxygen of the six-membered rings (O3) via hydrogen bonds. Four Zn ions (Zn2) are 0.66Å inside the α -cage. Each one is coordinated to only three oxygens (O3) of the six-membered ring and to the oxygen (O5) of one water molecule. The sixth ion (Zn3) is located deep inside the α -cage. This ion is coordinated to two oxygens (O5) and to the oxygen (O8) of two water molecules. The stereoviews of the α -cage and the sodalite unit of Zn·A are shown in Figs (5-6).

Heating the crystal at 600°C leads to a significant rearrangement of the ions. The two Zn ions at Zn1 occupy positions 0.64Å away from the six-membered rings plane inside the sodalite cage. Each of these ions is coordinated with three (O3) and one (O4) deep inside the cage. The remaining four ions at Zn2 lie almost in the plane of the six-membered rings, and each is coordinated in a trigonal planar fashion to three (O3)
Figure 5

Stereoview of the α-cage of hydrated Zn₆A (from ref. 63).

Figure 6

Stereoview of the sodalite unit of hydrated Zn₆A (from ref. 63).

Figure 7

Stereoview of the sodalite unit of Zn₆A dehydrated at 600°C. (from ref. 63)
of the six-membered rings (See Fig.7).

The Crystal Structure of Cd-Zeolite A

The crystal structure of hydrated Cd₆A was determined by Seff (64-65). In this structure all of the Cd ions are coordinated to the oxygens of the six-membered rings. Unlike Zn₆A, heating Cd₆A at 600°C did not drastically rearrange the locations of these ions; but rather they moved closer to the plane of the six-membered rings.

The six Cd ions in Cd₆A, dehydrated at 500°C, are distributed as follows: three Cd ions at Cd1 positions where each ion is coordinated to three O3's. These ions recessed 0.6A inside the sodalite cage. The other three ions are at Cd2, each one is near the six-membered ring in the α-cage and is coordinated to three (O3)'s. Heating the crystal at 600°C changes the number of Cd1 from three to two, hence the number of Cd ions at Cd2 becomes four. (see Fig.8).

Faujasite X

The composition of zeolite X (Linde 13X) is Na₈₆ Al₈₆ Si₁₀₆ O₁₃₄•276H₂O. The framework of Linde 13X is obtained by linking sodalite units with hexagonal prisms. Each sodalite unit is linked to four other units in the tetrahedral configuration by hexagonal prisms attached to four of the eight six-membered rings. The other four six-membered rings are
Figure 8

Stereoview of the sodalite unit Cd₆A (from ref. 64).
unshared as are the six four-membered rings. This peculiar arrangement produces the super cage which has 18 square faces, four six-membered rings and four twelve-membered rings. The twelve-membered rings are very important in determining the sieving propriety of type X zeolite since they are the only entries to the super cage. The diameter of the twelve-membered ring is 8-9Å and the internal diameter of the super cage is about 12Å. The super cage void volume is 7200Å³ compared to 610Å³ of type A α-cage. The values were determined from the saturation volume of adsorbed oxygen at -180°C (66).

The super cage is well defined by eight sodalite units. Each unit can be entered from the super cage through six square faces and four six-membered rings. The others, as mentioned before, are connected to the hexagonal prisms. Thus, the visiting molecules can enter the sodalite unit through the six-membered rings. As with zeolite A, ethylene molecules can not enter the sodalite unit.

The x-ray data of zeolites X is rather complicated and open to various interpretations (59). There is a general agreement that Na ions occupy three different sites, namely, sites I in the hexagonal prisms; sites II in the six-membered rings; sites III are not well defined, but the crystallographers defined these sites as those on the wall of the super cage. There are 16 Na ions at sites I, 32 at sites II, and 38 Na ions at sites III. A projection and section through a sodalite unit are shown
Infrared and Nuclear Magnetic Resonance Studies of Zeolite Surfaces

There have been numerous studies of the surface properties of zeolites. In this section a brief account of the infrared and the NMR studies of some surface properties such as surface acidity and adsorption of olefins is presented.

Structural Hydroxyl Groups and Surface Acidity of Zeolites

Although the surface hydroxyl groups and surface acidity of commercially used zeolite types X and Y have been extensively studied, other zeolites, especially type A, have received little attention.

Zeolite X preheated at 500°C exhibited two hydroxyl bands at 3500 and 3400 cm⁻¹ (67). Since these bands were accompanied by water bending vibration near 1600 cm⁻¹, the OH bands—in the investigators' opinion—may be caused by structural OH groups or physically adsorbed water. Carter et al. (68) found hydroxide bands after heating zeolite X containing the ions Li, Na, Ag, Cd, Ba, Ca, or Sr. The existence of hydroxide bands on zeolites containing monovalent cations is in contrast to the Habgood studies (69), which found no bands after heating similar zeolites at 500°C. To clear up the conflicting experimental results, Habgood (70) used thicker samples for the
Figure 9

Idealized projection and section through a sodalite unit of faujasite. Bottom, this is a section through abodeigí.
infrared measurements. Three bands were observed at 3750 and 3655 cm\(^{-1}\) on NaX. These same bands, however, were observed on NaX washed with distilled water and on samples treated with diluted acids. Thus, it seems that the source of the bands on NaX preheated at 500\(^{\circ}\)C is the deficiency of Na ions because of the partial hydrolysis and/or the existence of impurities in the zeolites.

The concentration of the surface hydroxide groups can be increased by introducing divalent ions or transition metals into the zeolite lattice (71). The origin of the OH groups on zeolites containing these ions is the hydrolytic fission of water viz

\[
M^{+2} + H_2O \rightarrow (M-OH)^+ + H^+
\]

M\(^{+2}\) stands for the transition metal ion. The proton formed is associated with one of the framework oxygens. The extent of water hydrolysis depends on the nature of the cation in the lattice. For example, Zn ion hydrolyzes water more readily than Cd ion.

The use of ammonia and pyridine as indicators suggests that the hydroxide groups on zeolites are acidic in nature and are similar to those on decationized Y zeolites (71). Now, the question is whether the protons of OH groups are mobile or not.
The experimental data, in general, supports the view that they are mobile. For example, protons of the OH groups inside the hexagonal prisms, which are inaccessible for molecules whose diameter is larger than \(2\AA\), can interact with large molecules such as cumene at high temperature (71).

Several attempts have been made to study the mobility of protons by means of infrared spectroscopy (72), whereby the intensity of the OH bands was measured as a function of temperature. The intensity decreased as the temperature increased. However, this observation alone does not give clear cut evidence that protons are mobile, because thermal vibrational changes could be responsible for the intensity change of the bands.

NMR spectroscopy proves itself to be superior to the infrared in measuring the protons' mobility. In the latter technique the time required to observe a resonance is very short. Freude et al. (73) studied the dynamic behavior of protons at the oxygen framework by means of NMR. They found that the mean life time of a proton at oxygen can be measured in terms of hours in the absence of adsorbed molecules such as water, ammonia, or pyridine. However, small amounts of one of these "proton transport vehicles" has a dramatic effect on the mobility of protons. The mean life time of a proton before going to water on CaY zeolite is 60 \(\mu\)s, and before forming pyridinium ion is 16 \(\mu\)s.
Surface Acidity

Zeolites that contain ions from group IA should not be acidic. However, the literature is full of conflicting reports concerning the acidity of these zeolites. For example, it has been reported that NaX has no acidity (74-75), yet in other reports Bronsted acidity (76), or Lewis acidity has been found (77). Apparently, the source of discrepancy between these reports stems from the difference in the zeolite pretreatments and/or these samples may contain different levels of impurities.

The infrared of adsorbed pyridine on zeolite containing ions from group IA shows a band in the range of 1435 to 1450 cm\(^{-1}\) (74-75). This band is weak, easily removed by heating the sample at 200 °C, and sensitive to the cation type. The frequency of this band increases with the decrease in the ionic radius. This indicates that the band in this range results from the interaction of pyridine with the cation not with either Bronsted, or Lewis acid sites.

Exchanging Na ions with transition metal ions introduces acidic sites. Nishizawa et al. (75) studied the influence of Mn, Zn, Co, Ni, and Ti ions on the acidity of zeolites X pretreated at 400 °C. They found no Bronsted acidity on Ni-, Co-, and Ti-X. However, small amounts of protonic acid sites were found on Zn- and Mn-X zeolites. A band at 1450 cm\(^{-1}\) was observed for adsorbed pyridine in all cases, except Tl-X. This
band was attributed to the interaction of pyridine with Lewis acidic sites.

Ward (78) examined the acidity of Mn-, Co-, Cu-, Zn-, Ag-, and Cd-X zeolites in more detail. Bronsted acidity was found on all samples and the acidity increased after hydration. The band in the region $1440-1450 \text{ cm}^{-1}$ is sensitive to the cation type, in that its frequency increases as the field associated with the cation increases. Therefore, this band is assigned to a metal ion-pyridine bond. This contradicts Nishizawa's explanation that the bands resulted from the interaction with Lewis sites.

Ward explained the increase in the Bronsted acidity after hydration as a result of the formation of M-OH. Eberly (77) found no Lewis acidity on transition metal ion-containing Y zeolites.

Adsorption of Olefins on Zeolites

Carter et al. (79) studied the mode of ethylene adsorption on Li-, Na-, K-, Ag-, Ca-, Ba- and Cd-X zeolites. All samples were heated at 450°C in vacuo, then ethylene was admitted and the excess gas was removed by degassing. The infrared spectra of adsorbed ethylene revealed the formation of $\pi$-complexes with the cations in the lattice.

The C=C stretching frequency of ethylene varied with the nature of the exchanged cations. A relationship between the double bond shift and the heat of adsorption is
found. Recently, Huang (80) disputed such correlation because of the lack of consistency. The C=C shift of ethylene on Cu-Y is larger than that on Ag-Y, although ethylene on Cu-Y gives a smaller heat of adsorption.

The line width analysis of adsorbed ethylene on the zeolites mentioned above, indicates the adsorbed species freely rotates on all samples, except Ag-X. The restricted rotation on Ag-X resulted from the back donation of electrons from the ion d orbitals to the vacant π-orbitals of the olefin. This back donation does not exist between the other ions and the adsorbed ethylene.

Eberly (81) studied the adsorption of ethylene on Cd-, Ag-, and decationized Y zeolites at 93°C. Surprisingly, no infrared bands were observed for the adsorbed species. This is in contrast to the present studies where proton NMR signals for adsorbed ethylene were detected at 96°C.

Hall et al. (82) investigated the mode of adsorption of ethylene and propene on acidic zeolites, such as partially decationized Y zeolite. Ethylene adsorbed reversibly while propene was strongly adsorbed. Initially, ethylene adsorbed on Na ions, then hydrogen bonded species were formed. Heating the sample at 150°C is required to start the exchange reaction between deuterated ethylene and zeolite protons. The polymerization reaction started only at temperatures above 240°C.
Over a short period of time, no change was observed in the intensity of the band assigned for adsorbed propene. However, after storing the sample at room temperature for a few days, this band disappeared and a new band was developed. The newly formed band is similar to that found when hexene adsorbed on this zeolite. Thus, propene underwent a polymerization reaction at room temperature.

The heat of formation of hydrogen bonded ethylene on decationized zeolites was determined by Hall et al. (83). It was about 9 kcal per mole. In addition, the activation energy for the exchange reaction between deuterated ethylene and zeolite hydroxyl groups was determined as a function of the pretreatment temperature. This was 16 kcal/mole for zeolite heated at 290°C, and 19 kcal/mole for samples heated at 475°C.

The chemical shifts of adsorbed ethylene and propene on zeolite type Y have been measured by C-13 NMR spectroscopy (84). The shift of =CH- is 4.2 ppm, 0.8 ppm for =CH$_2$, and 0.5 ppm for CH$_3$. The chemical shift of adsorbed ethylene on NaY is 1.7 ppm, and on HY is 2.1 ppm. All the shifts quoted above are downfield relative to the free molecules.

Michel et al. (85) studied the isomerization of butene-1 on CaY by means of C-13 NMR. At low temperatures (17-77°C) isomerization of the double bond occurred. However, at higher temperatures (97-117°C) polymerization proceeded over this zeolite.
The Carbon-13 chemical shifts and the longitudinal relaxation times of adsorbed butenes on NaY and NaX zeolites have been measured by Michel (86). The shifts of C2 of butenes decreased in the following order: isobutene (δ = 10.3 ppm) > butene-1 (δ = 5.7 ppm) > cis and trans butene-2 (δ = 2.2 and 2.4 ppm respectively). These shifts are downfield with respect to gaseous molecules. This suggests that butenes adsorb on the Na ions in a π-complex fashion.

Michel (87) extended his studies to include butene-1 on Ag-X system. The =CH2 exhibited an upfield shift relative to the liquid butene-1. He explained this upfield shift in terms of increasing the electron concentration on the double bond because of the back donation of electrons from the Ag ion.
VI. THEORY

This chapter contains only a simple explanation of the NMR theory. An attempt was made to avoid the rigorous formulation of the theory. However, this should give the reader some basic information regarding the application of the NMR technique in surface chemistry and heterogeneous catalysis. Complete description of the theory can be found in several references, notably, in the books by Abragam (88) and Slichter (89).

The Basic Phenomena of Magnetic Resonance

If a nucleus such as H-1 or C-13 (spin=1/2) is placed in a magnetic field $H$, the magnetic moment $\mu$ interacts with $H_o$ to give two Zeeman energy levels corresponding to the nuclear spin quantum number $m=\pm 1/2$. The energy of these levels is given by

$$E_m = -\gamma h H_m$$

where $h$ is Planck's constant divided by $2\pi$, and $\gamma$ is the magnetogyratic ratio.

The energy difference between the two levels is

$$\Delta E = \hbar \omega = \gamma h H_o \Delta m.$$ The selection rule for the allowed transition is $\Delta m = \pm 1$. This indicates that the only permitted transitions are those between neighbouring levels, then
\[ \Delta E = \hbar \omega = \gamma \hbar H_o \quad [5] \]

or
\[ \omega = \gamma H_o \quad [5-a] \]

The disappearance of \( \hbar \) from equation [5-a] indicates that the resonance \( \omega \) can be described by the classical theory. The interaction between \( \mu \) and \( H_o \) produces a torque \( \mu \times H_o \) in a direction perpendicular to the plane containing \( \mu \) and \( H_o \). This torque is equal to the rate of the angular momentum change with time, or

\[ \frac{d \mu}{dt} = \gamma \mu \times H_o \quad [6] \]

In the above paragraph only one nucleus is considered. However, in a real system there is an assembly of magnetic moments. Hence, the magnetization vector \( M \) which is the vector sum of the \( \mu \)'s will be used instead of \( \mu \) and, thus, equation [6] takes the form

\[ \frac{dM}{dt} = \gamma M \times H_o \quad [7] \]

Equation [7] clearly shows that \( M \) precesses around \( H_o \). A solution to equation [7] can be readily obtained if the

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laboratory coordinates \((x, y, z)\) are transferred to a new coordinate system \((\tilde{x}, \tilde{y}, \tilde{z})\) whereby the latter coordinates rotate around \(H_0\) with the frequency \(\omega\). It has been found that (90)

\[
\left(\frac{dM}{dt}\right)_{\text{lab}} = \left(\frac{dM}{dt}\right)_{\text{rot}} + \omega \times M
\]


\[
\left(\frac{dM}{dt}\right)_{\text{rot}} = \gamma M \left( H_0 + \frac{\omega}{\gamma} \right)
\]

where the term \((H_0 + \frac{\omega}{\gamma})\) is called \(H_{\text{eff}}\), and \(\frac{\omega}{\gamma}\) can be considered as a "fictitious field" resulting from the rotation of the new coordinates. If \(\omega = \omega_0 = -\gamma H_0\), then \(\left(\frac{dM}{dt}\right)_{\text{rot}} = 0\). This means that \(M\) is rotating at an angular velocity \(\omega_0\) with respect to the laboratory axes. \(\omega_0\) is called the Larmor frequency.

If a magnetic field \(H_1\) is applied perpendicular to the field \(H_0\) (\(H_0\) is parallel to the \(z\) axis) and rotates around it with the frequency \(\omega\), then the interaction \(M \times H_{\text{eff}}\) makes \(M\) precess around \(H_{\text{eff}}\), generating a cone (see Fig. 10). The effective field is now equal to \(H_0 + \frac{\omega}{\gamma} + H_1\). By changing the frequency \(\omega\), the vertex angle of the cone changes accordingly. When \(\omega = \omega_0 = -\gamma H_0; H_{\text{eff}} = H_1\). This would certainly force \(M\) to precess around \(H_1\) with an angular frequency \(\omega_1 = -\gamma H_1\).
Motion of magnetization in a magnetic field.

a) Tipping of $M$ through an angle $\theta$.

b) Dephasing of $M$ by spin-spin relaxation mechanism.

c) Reduction of $M_y$ to zero.

d) Reestablishment of $M$ to its equilibrium value, $M_0$. 
In practice, an oscillating field in the $\mathbf{\hat{x}}$ direction is used instead of the field $H_1$. This field consists of two components with amplitude equal to $H_1$. Therefore, it can be given by $H = 2H_1 \cos \omega t$. These components rotate in opposite directions. One rotates in the same sense as the precession of $M$, and therefore interacts with it. The other rotates in the opposite direction, hence it has no effect. In the following discussion a qualitative explanation will be offered.

**Bloch Equations**

In the foregoing paragraphs, I have demonstrated that the magnetization $M$ can precess around $H_0$. Furthermore, we have learned that by applying the magnetic field $H_1$ perpendicular to $H_0$, the magnetization $M$ is forced to precess around $H_{\text{eff}}$ with angular frequency equal to $\gamma H_{\text{eff}}$. Now, assume that the field $H_1$ is turned on long enough to cause $M$ to tip through an angle toward the $\mathbf{\hat{y}}$ axis. The vertex angle $\theta$ of the precession cone is given by (90)

$$\theta = \gamma H_1 t$$  \hspace{1cm} [10]

As can be seen from equation [10], $\theta$ is a function of $t$. If $t$ is chosen so that $\theta = \pi/2$, the magnetization $M$ will tip toward the $\mathbf{\hat{y}}$ axis. After turning $H_1$ off, the magnetization $M$
will be dephased in the $\bar{x}$-$\bar{y}$ plane and eventually decays after a time $T_2$. This is because of the interaction between the spins which constitute the magnetization $M$. Therefore, the time $T_2$ is called spin-spin relaxation time and adequately defined by

$$\frac{\partial M_{xy}}{\partial t} = -\frac{M_{xy}}{T_2} \quad [11]$$

By losing excess energy, the magnetization $M$ tends to go back to its original position parallel to $H_0$. This can be accomplished by transferring energy to the surroundings—the lattice in this case—therefore, maintaining thermal equilibrium between the spins and the lattice. The characteristic time of this process is called spin-lattice relaxation time, $T_1$, which is defined by

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \quad [12]$$

where $M$ is the instantaneous magnetization, and $M_0$ is the magnetization at thermal equilibrium. The relaxation mechanisms are depicted in Figure 10.

Obviously, by the time $M$ approaches its equilibrium value $M_0$, none of its components are left behind in the $\bar{x}$-$\bar{y}$ plane. Thus, $T_2$ will never be longer than $T_1$. In fact, this is true in the case of solids ($T_1 > T_2$), but they are nearly equal in the
case of liquids and gases.

Bloch added the torque resulting from the interaction of $M$ with $H_{\text{eff}}$ (equation [7]) to the relaxation expressions to get

$$\frac{dM_z}{dt} = M_y \omega_1 + \frac{M_0 - M_z}{T_1} \tag{13}$$

$$\frac{dM_x}{dt} = M_y (\omega - \omega_0) - \frac{M_x}{T_2} \tag{14}$$

$$\frac{dM_y}{dt} = -M_z \omega_1 - M_x (\omega - \omega_0) - \frac{M_y}{T_2} \tag{15}$$

These are known as Bloch equations in the rotating frame.

At steady state, the energy absorbed by the spins from the field $H_1$ is effectively countered by the relaxation mechanism where the spins dissipate the heat to the lattice. Therefore, the right hand sides of equations [13-15] are equal to zero and the components of $M$ along $\bar{x}$, $\bar{y}$, and $\bar{z}$ axes can be given by (88)
\[
M_x = \frac{\gamma H_1 T_2^2 (\omega - \omega_o)}{1 + T_2^2 (\omega - \omega_o)^2 + \gamma^2 H_1^2 T_1 T_2} M_o \quad [16]
\]

\[
M_y = \frac{\gamma H_1 T_2}{1 + T_2^2 (\omega - \omega_o)^2 + \gamma^2 H_1^2 T_1 T_2} M_o \quad [17]
\]

\[
M_z = \frac{1 + T_2^2 (\omega - \omega_o)^2}{1 + T_2^2 (\omega - \omega_o)^2 + \gamma^2 H_1^2 T_1 T_2} M_o \quad [18]
\]

At the resonance frequency \( \omega = \omega_o \), the value of the component \( M_x \) is zero and that of \( M_z \) is small. However, at this resonance frequency, the value of \( M_y \) is maximum. On the other hand, if the frequency \( \omega \) is progressively increased, then the sign of \( M_x \) depends on whether \( \omega \) is larger or less than \( \omega_o \). In other words, \( M_x \) changes its sign. The sign of \( M_z \) is always positive, and \( M_y \) maintains the sign of \( \gamma \). This qualitatively explains the discussion presented earlier that the effective component of the oscillating field is the one which rotates in the same direction as the Larmor frequency \( \omega_o \).

The previous discussion clearly demonstrated that \( M_y \) is the only component which contributes to the NMR resonance. Experimentally, the signal or resonance is detected as a voltage
induced in a coil whose axis must be in the y direction. Thus, the amplitude of the voltage produced from the component \( M_y \) is given by

\[
\left| \omega_0 M_y \right| = \frac{\gamma \omega_0 H_1 T_2 M_0}{1 + H_1^2 T_1 T_2} = \frac{\omega_2^2 \chi_0 H_1 T_2}{1 + \gamma H_1 T_1 T_2} \tag{19}
\]

where \( \chi_0 = M_0 / H_0 \). It is called the static magnetic susceptibility, and the term \( \gamma^2 H_1^2 T_1 T_2 \) is called the saturation parameter. The variation of the amplitude with \( H_1 \) is rather interesting. For small values of \( H_1 \), where the saturation parameter is less than one, the amplitude of the induced voltage increases with the increase in \( H_1 \), but at high values of \( H_1 \), equation [19] reduces to

\[
\left| \omega_0 M_y \right| = \frac{\chi_0 H_1^2}{H_1 T_1} \tag{20}
\]

Under these circumstances further increases in \( H_1 \) are accompanied by a reduction of the amplitude. This causes saturation which in turn produces a broad line. This can be explained qualitatively in terms of the spin population difference between the energy levels. Let us assume that \( n_0 \) is the spin population difference in the absence of \( H_1 \), and \( n \) is the population difference after applying the magnetic field \( H_1 \). The population \( n \) is given by
where \( g(v) \) is the line shape function \((g(v))_{\text{max}}=2T_2\). The term \( \gamma H_1^2 T_1 g(v) \) is the saturation factor. If \( H \) is large, \( n \) may become smaller than \( n_0 \). This is because of the possible promotion of spins from the lower to the higher energy level. Since the NMR signal strength is proportional to the population difference, its induced voltage amplitude is reduced with the increase in the magnetic field \( H_1 \). In addition to the reduction in the amplitude, the saturation may cause a distortion of the signal. Maximum reduction occurs at the maximum \( g(v) \). Thus, there will be an apparent increase in the line broadening.

It is convenient if the components \( M_x \) and \( M_y \) are replaced by the magnetic susceptibilities \( \chi' \) and \( \chi'' \). These quantities are defined by the relations

\[
\chi' = \frac{M_x}{2H_1} \tag{21}
\]

and

\[
\chi'' = \frac{M_y}{2H_1} \tag{22}
\]

In the non-saturated magnetic field, the saturation factor can be ignored. Therefore, the magnetic susceptibilities \( \chi' \) and
$\chi'$ can be defined as

$$\chi' = \frac{1}{2} \chi_o \omega_o T_2 \frac{(\omega_o - \omega) T_2}{1 + (\omega_o - \omega)^2 T_2^2}$$  \[23\]

and

$$\chi'' = \frac{1}{2} \chi_o \omega_o T_2 \frac{1}{1 + (\omega_o - \omega)^2 T_2^2}$$  \[24\]

The quantities $\chi'$ and $\chi''$ are called the dispersion and the resonance absorption respectively.

Equation [24] can be expressed in terms of frequency units since $\chi'' = \frac{1}{2} \pi \chi_o \nu_o g(\nu)$, where

$$g(\nu) = \frac{2T_2}{1 + 4\pi^2 (\nu_0 - \nu)^2 T_2^2} = \frac{2 (1/T_2)}{(1/T_2)^2 + 4\pi^2 (\nu_0 - \nu)^2}$$  \[25\]

This equation describes the line shape of the NMR peak. The frequency $\nu$ is equal to $\frac{\omega}{2\pi}$ and $\nu_0$ equals to $\frac{\omega}{2\pi}$. Indeed equation [25] is similar to that used in describing the Lorentz line which is given by

$$g(\nu) = \frac{4 \pi \delta\nu}{(2 \pi \delta\nu)^2 + 4 \pi^2 (\nu_0 - \nu)^2}$$  \[26\]

where $\delta\nu$ is the half width at half peak height. In the latter
equation, \(2\pi \delta v = \delta \omega = 1/T_2\). Thus, a quantitative relation between \(1/T_2\) and the line width of the NMR signal has been established.

**Line Shape**

There are mainly three sources for line broadening which limit the applicability of the NMR technique in studying the mode of interaction of adsorbed species on solid catalysts. These are:

1. dipole-dipole interaction
2. interaction with paramagnetic centers
3. molecular motion of the adsorbed molecules

In the following discussion, an attempt is made to summarize the effect of these sources on the broadening of the NMR line. The reader interested in more information is referred to Abragam (88), Pfeifer (91), and Resing (92, 93).

The dipole-dipole interaction between the nuclei of non-zero spins determines the NMR line shape, since its contribution to the line broadening is usually larger than the contribution of the other sources. The dipolar interaction may be between similar nuclei (homonuclear) or between different nuclei (heteronuclear), and may be either inter- or intramolecular.
If the adsorbed molecule contains two nuclei with magnetic moments \( \mu_1 \) and \( \mu_2 \) (\( \mu_1 \) and \( \mu_2 \) can be similar or different moments), then the interaction between them depends on their magnitudes, the distance between them and their orientation with respect to the applied field \( H_0 \).

The interaction between these moments creates a local magnetic field, \( H_L \). Thus, each magnetic moment is experiencing a field whose components are \( H_0 \) and \( H_L \). The local magnetic field at say \( \mu_1 \) because of \( \mu_2 \) can simply be defined as

\[
H_L = \pm \frac{\mu_1}{r_{12}} \left( 3 \cos^2 \theta - 1 \right)
\]

where \( r_{12} \) is the internuclear distance, and \( \theta \) is the angle between \( r_{12} \) and \( H_0 \). The \( \pm \) sign arises because \( H_L \) can be added to or subtracted from \( H_0 \). The orientation of this local field relative to \( H_0 \) is determined by the spin state of \( \mu_1 \).

Since \( H_L \) can either aid or oppose the magnetic field \( H_0 \), each nucleus may interact with slightly different fields. Thus, it resonates at slightly different frequencies. In a real system there is an assembly of nuclei interacting with each other. Thus, a spread of resonance frequencies results and a significant broadening of the line occurs.

The local field mentioned above has an insignificant effect on the line shape of liquids. This is because the rapid motion
of the molecules makes the angle $\theta$ time dependent and, therefore, the term $(3 \cos^2 \theta - 1)$ is averaged out to zero. This may not be the case for adsorbed molecules since the molecular rotation is much slower.

Homonuclear dipolar broadening is a serious problem in proton NMR of adsorbed molecules. This is because of the high natural abundance of protons and the relatively short distances between protons in the adsorbed species. A multiple pulse technique has been used to reduce the homonuclear interaction between protons. Details of this technique can be found in reference (94). In addition, Carbon-13 NMR (natural abundance is 1%) can effectively reduce the homonuclear dipolar broadening (95).

The second source of line broadening arises from the presence of paramagnetic impurities in the adsorbent. The interaction with the paramagnetic centers is similar to the dipolar interaction except it involves electron dipoles. Since the electron magnetic moment of a paramagnetic ion such as Fe is 1000 times larger than the moment of protons, the interaction with the paramagnetic centers creates a strong local field at the nearby nuclei. As mentioned before, this local field affects the relaxation mechanisms of the adsorbed molecules and causes a spread in the precession frequencies of the nuclei. Therefore, it causes unavoidable broadening of the line.
Most solids that are of interest contain a low concentration of paramagnetic impurities. Hence, only a small number of neighbouring nuclei would interact with these sites, which implies a small contribution of the paramagnetic impurities to the broadening of the line. This may be true if the exchange between the adsorbed molecules on the paramagnetic sites and the remaining sites on the surface is slow (chemisorbed molecules). On the other hand, a fast exchange (physically adsorbed molecules or at high temperature) increases the contribution of the paramagnetic centers to the broadening of the NMR line despite their low concentration.

Even when there is no fast exchange, the paramagnetic impurities may propagate their influence on the broadening of the NMR lines by spin diffusion (88).

Unlike the dipole-dipole interaction between nuclei, the effect of paramagnetic centers on the broadening of the resonance line cannot be eliminated by instrumental means.

The third source of broadening results from the interaction between the nucleus and the surrounding electrons, especially if the molecular motion is slower than $10^4$ Hz (96). The electron rotation around the nucleus placed in a magnetic field, $H_0$, produces an incremental magnetic field opposing $H_0$. This field is proportional to $H_0$, or

$$H = \sigma H_0$$
where $\sigma$ is the proportionality constant and is often called a shielding coefficient. Thus, the field at which the nucleus is resonating can be given by

$$H = H_o (1 - \sigma)$$

Clearly, if $\sigma$ is positive, this resonance occurs at a lower frequency relative to the bare nucleus in a fixed field NMR experiment. This shift of frequency with respect to the bare nucleus, is customarily called the chemical shift. The chemical shift is sensitive to the environment surrounding the nucleus in question. For this reason, the NMR technique is rather valuable in studying the mode of adsorption of adsorbed species on solid surfaces. As mentioned before, the adsorbed species interacts with the solid surface. Therefore, the electron density around the nucleus may change and also the chemical shift. The chemical shift may shed some light on the type of adsorption (chemical vs physical adsorption).

The magnitude of the chemical shift at a nucleus is dependent upon the orientation of the molecule in the magnetic field. Theoretically, the chemical shift can be presented as a symmetric, second rank tensor that is characterized by six independent values. However, experimental measurements of the chemical shifts of powder solids show only three quantities
Figure 11

a) Schematic representation of powder line shape for second rank tensor.

b) Axially symmetric second rank tensor.

c) Typical spectrum of adsorbed species.
FIG. 11
\( \sigma_{xx}, \sigma_{yy}, \) and \( \sigma_{zz}. \) The other three are lost. In liquids, the fast motion of the molecules averages out the three components, hence only one \( \langle \sigma \rangle = \frac{1}{3} \text{Tr}\sigma \) manifests the chemical shift. Figure (11) illustrates the line shape of powder solids.

The motion of the adsorbed molecules is intermediate between the motion in liquids and that in solids. Thus, the principal components of the chemical shift tensor are not well resolved. Accordingly, the line shape would be broader than the one observed if the molecules were in a liquid state, and narrower than the line of the solid. Furthermore, the distinct shoulders of the line characteristics of powdered solids become less defined. This is shown in Fig.(11). However, molecules strongly bound to the surface show NMR lines similar to those of powder solids (97-98).
VII. EXPERIMENTAL

Materials

Zinc Oxide

Zinc oxide was prepared by the pyrolysis of zinc oxalate dihydrate. The oxalate was prepared by mixing equal volumes of 0.5 M zinc nitrate and sodium oxalate solutions. The precipitate was filtered, washed several times with distilled water and air dried for 5-6 hr at 60°C. The oxalate was then processed in various ways. Letters in parentheses in the following description identify the preparations.

The first set of ZnO samples was prepared by pyrolysis of the oxalate at 350°C either in vacuo (A) or in air (B) for 3 hr. The time is sufficient for complete decomposition of the oxalate (99). Another sample (C) was prepared by pyrolysis in vacuo at 400°C for 1 hr, degassing 1 hr at the same temperature, cooling to room temperature in 150 Torr oxygen and pumping for 6 hr.

A second series of samples was prepared by pyrolysis of the oxalate at 400°C under vacuum of a water aspirator. Doped samples were prepared by impregnating this oxide with a measured amount of a solution of lithium or gallium nitrate. The
Impregnated samples were dried over night in air at 100°C and then heated in vacuo at 400°C for 4 hr. These samples are identified by the weight percentage of dopant metal with respect to zinc. Pure ZnO samples (D) in this series were treated in the same way, using distilled water in place of the metal nitrate solution. Analysis by atomic absorption showed a residual sodium impurity of 3.5 ppm in the finished catalysts. In addition to the above samples, a sample (K) of Kadox 25 from the New Jersey Zinc Company was used for comparison. This sample was heated at 400°C for the same length of time and under similar conditions to that of sample (C).

Zinc oxide samples used for the adsorption of olefins were prepared from the oxalate salt by heating in vacuo at 400°C for 3 hr, 170 Torr of oxygen was admitted at the same temperature. After 1 hr, the oxygen was evacuated for 1 hr, then 150 Torr of oxygen admitted. This was followed by cooling the samples to room temperature, then degassing for at least 6 hr before adsorption.

Silica Gel

The silica gel used for the adsorption of olefins was from Baker Chemical Co., Lot no. 1-3405. The samples were degassed for 4 hr at 400°C before use. The surface area was 253 m²/gm.
Adsorbates

1-Methylcyclohexene and 1,2 dimethylcyclohexene were obtained from Chemical Sample Co., and had purities of 99.5% and 99.9% respectively. Cycloheptene, 2,3-dimethylbutene-2 and 2-methylbutene-2 were from Aldrich Chemical Co,. Cyclohexene was obtained from the Baker Chemical Co,. Ethylene, propene, ethane and butenes were Matheson CP grade gases, and were vacuum-distilled before use.

Carbon monoxide and acetylene (90% C-13 enriched) were obtained from Merck Scharp & Dohme Canada Limited in glass breakseal bulbs. Both were used without further purification.

Zeolites

The ion exchange was carried out by mixing 20 gm of zeolites (Linde 4A or 13X) with 500 ml of distilled water containing calculated amounts of $\text{Zn}^{2+} (\text{ZnSO}_4)$ or $\text{Cd}^{2+} (\text{Cd(NO}_3)_2)$ ions. The concentration, the temperature at which the exchange took place and the extent of exchange are tabulated in Table (1). After the above treatment, the product was filtered, then washed several times with cold distilled water until the effluents were free from $\text{SO}_4^{2-}$ or $\text{NO}_3^{-3}$ ions. All samples were dried at $100^\circ C$ in air for at least 12 hr.

The degree of the exchange was determined by simple chemical analysis. The number of Zn ions introduced into the lattice was determined by titrating Zn ions by EDTA solution.
<table>
<thead>
<tr>
<th>Specimen Name</th>
<th>Quantities of Cations (Zn$^{2+}$ or Cd$^{2+}$)</th>
<th>Composition</th>
<th>No. of Residual Na$^+$ ions in Unit Cell</th>
<th>No. of Exchanged Cations per Unit Cell</th>
<th>Temperature at Which the Exchange Took Place</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-X</td>
<td>-</td>
<td>Na$_{86}$(AlO$<em>2$)$</em>{86}$(SiO$<em>2$)$</em>{106}$</td>
<td>86</td>
<td>-</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Zn(I)-X</td>
<td>1X1</td>
<td>Zn$<em>{30}$Na$</em>{26}$(AlO$<em>2$)$</em>{86}$(SiO$<em>2$)$</em>{106}$</td>
<td>26</td>
<td>30</td>
<td>Room temp. -22°C</td>
</tr>
<tr>
<td>Zn(II)-X</td>
<td>2X5</td>
<td>Zn$_{42}$Na$_2$(AlO$<em>2$)$</em>{86}$(SiO$<em>2$)$</em>{106}$</td>
<td>2</td>
<td>42</td>
<td>Refluxing at 90°C</td>
</tr>
<tr>
<td>Cd(I)-X</td>
<td>1X.5</td>
<td>Cd$<em>{24}$Na$</em>{38}$(AlO$<em>2$)$</em>{86}$(SiO$<em>2$)$</em>{106}$</td>
<td>38</td>
<td>24</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Cd(II)-X</td>
<td>1X1</td>
<td>Cd$<em>{37}$Na$</em>{12}$(AlO$<em>2$)$</em>{86}$(SiO$<em>2$)$</em>{106}$</td>
<td>12</td>
<td>37</td>
<td>Room temp.</td>
</tr>
<tr>
<td>NaA</td>
<td>-</td>
<td>Na$_{12}$(AlO$<em>2$)$</em>{12}$(SiO$<em>2$)$</em>{12}$</td>
<td>12</td>
<td>-</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Zn$_4$Na$_4$A</td>
<td>0.2N</td>
<td>Zn$_4$Na$_4$(AlO$<em>2$)$</em>{12}$(SiO$<em>2$)$</em>{12}$</td>
<td>4</td>
<td>4</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Zn$_6$A</td>
<td>0.2N</td>
<td>Zn$_6$(AlO$<em>2$)$</em>{12}$(SiO$<em>2$)$</em>{12}$</td>
<td>-</td>
<td>6</td>
<td>Refluxing at 80°C</td>
</tr>
<tr>
<td>Cd$_4$Na$_4$A</td>
<td>1X0.5</td>
<td>Cd$_4$Na$_4$(AlO$<em>2$)$</em>{12}$(SiO$<em>2$)$</em>{12}$</td>
<td>4</td>
<td>4</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Cd$_6$A</td>
<td>1X1</td>
<td>Cd$_6$(AlO$<em>2$)$</em>{12}$(SiO$<em>2$)$</em>{12}$</td>
<td>-</td>
<td>6</td>
<td>Room temp.</td>
</tr>
<tr>
<td>CaA</td>
<td>1X1</td>
<td>Ca$_4$Na$_4$(AlO$<em>2$)$</em>{12}$(SiO$<em>2$)$</em>{12}$</td>
<td>4</td>
<td>4</td>
<td>Room temp.</td>
</tr>
</tbody>
</table>
Table 1 (cont'd)

For example, $2 \times 5$ indicates that the zeolite sample was treated twice with a solution containing five-fold excess of the cation $\text{Zn}^{+2}$ expressed as equivalent to the $\text{Na}^+$ ions originally present in the lattice. $\text{Zn-X}$ is used in the text to represent $\text{Zn(I)-X}$ and $\text{Zn(II)-X}$, $\text{Cd-X}$ is used also to represent $\text{Cd(I)-X}$ and $\text{Cd(II)-X}$.
before and after the exchange. The decrease in the Zn ion concentration is considered to be the amount of Zn ions incorporated into the lattice.

The number of Cd ions in zeolite was determined gravimetrically using sodium anthranilate solution. The difference between the concentration of the initial solution and the concentration after the exchanging step, gives the concentration of Cd ions in zeolite.

No attempt has been made to determine the number of Na ions in any of the zeolite samples.

**Methods**

**Preparation of Zeolite Samples**

All samples were prepared in vacuo at 400°C for 40-50 hr, unless otherwise stated.

Samples used for hydrogenation of ethylene include the Zn and Cd exchanged zeolite types X and A. Approximately one gm of each sample (fresh) was placed in a 12 mm diameter pyrex tube. The sample was heated as mentioned above, cooled down to room temperature, then brought into contact with ethylene gas till the equilibrium pressure was 10 Torr, followed by hydrogen adsorption. The pressure of hydrogen was increased until the manometer reading was around 300 Torr. The tubes containing the
samples were sealed off and left for at least one day.

Zeolite samples showed catalytic activities in the temperature range 250-400 °C. Such a temperature range cannot be reached by the NMR probe. This is because the maximum temperature obtained by the probe is only 200 °C. Thus, a separate furnace was used to heat the samples.

Each sample was heated rapidly to the temperature at which it exhibited catalytic activity. In most cases several attempts were made to determine the temperature at which the reaction proceeded at a reasonable rate, so that several spectra could be collected during the course of the catalytic reaction. The temperature associated with each sample is shown in Chapter (XI).

The time taken to bring the catalyst up to the desired temperature was not more than one minute. The fluctuation in the temperature was ± 3-4 °C. After heating the sample for a certain time, it was removed, cooled down to room temperature, then inserted in the probe and left for at least 10 minutes. This time was enough for the sample to reach the temperature of the probe (96 °C). None of the samples showed catalytic hydrogenation at 96 °C. This was followed by collecting the proton NMR spectra.

The zeolite samples used for the isomerization of butene-1 were heated at 300 °C for 40-50 hr. These samples include Zn-X; Cd-X; Na-X; Cd-A; and Zn-A. It was found that type X zeolite
isomerized, while type A polymerized butene-1. The
isomerization of the double bond took place over Zn(I)-Y and
Cd-X zeolites in the temperature range 90-120°C, and on Zn(II)-X
at 280°C, whereas on Na-X, the isomerization occurred at 240°C.
On the other hand, the polymerization of butene-1 over Zn and Cd
exchanged A-zeolites occurred immediately at 280°C.

One gm of each sample was put in a 12 mm pyrex tube, heated
as stated above, then cooled down at room temperature. The
sample was exposed to butene-1 till the equilibrium pressure was
approximately 300 Torr. The tube was then sealed off and kept
in liquid nitrogen to halt the isomerization.

These samples were inserted into the probe, the temperature
of which was adjusted, so that the fluctuation in the
temperature was ±0.5°C. The temperature at which each catalyst
is catalytically active varied from one sample to
another. Thus, the isomerization had been carried out at
different temperatures. The C-13 spectra were collected at
suitable intervals for each run.

The Na-X catalyst was heated in a separate furnace, and the
procedure of preparing the sample for the isomerization reaction
was similar to that mentioned for the hydrogenation catalysts.

NMR Measurements of Adsorbed Species on ZnO

The hydrogenation of ethylene on pure and doped Zn0 was
carried out in situ in the NMR probe at 280°C. In each
experiment a fresh sample of 0.7 g was used. This was first exposed to ethylene at a pressure of 40 Torr. The sample with adsorbed ethylene was then placed in the spectrometer, an initial spectrum recorded, and 400 Torr of hydrogen added. The reaction was followed by recording spectra at suitable intervals.

The subsequent adsorption of acetylene on ZnO already covered by ethylene was performed in situ in the NMR probe at 28 °C. ZnO sample was first brought into contact with ethylene gas. The pressure of ethylene was 40 Torr. The sample was then placed in the probe and the initial spectrum was recorded, then 120 Torr of acetylene was co-adsorbed. This was monitored by recording the spectra at suitable intervals.

The successive adsorption of ethylene on ZnO previously covered with CO was also studied in situ in the NMR probe at 28 °C. In this experiment, the C-13 spectrum of adsorbed CO was first recorded, then 120 Torr of ethylene was added. The substitution of CO by ethylene was followed by recording the spectrum of adsorbed CO and ethylene on ZnO.
Nuclear Magnetic Resonance Technique

Apparatus

Proton NMR studies were performed on a Varian model XL-100 spectrometer operating at a magnetic field of 23.5 kilogauss, and an RF frequency of 100 MHz. The field is modulated at a fixed frequency of 40.96 KHz. The temperature of the sample is controlled by a gas flow system, and can be varied from -200 to 180 °C. The temperature of the sample was kept within ± 0.5 °C. It is also equipped with an external F-19 lock for adjusting homogeneity of the magnetic field. The probe unit is a standard Varian model V-4412 with insert for 12 mm sample tubes. A Nicolet 1080 computer is built on-line to the spectrometer for the pulsed-Fourier transform operation. A TT-100 accessory pulse control is utilized for the probe operation, while the data is collected by Nicolet Model 293 pulse timer and a 294 disk accessory.

All the C-13 spectra were measured on the XL-100 spectrometer. In these experiments two types of probes were used. A standard Varian probe model V-4412 for 12 mm sample tubes, and a locally built 22 mm probe following the design of Zens and Grant (100). In all measurements the spectrometer
operated at 25.16 MHz, and proton noise decoupling was used for every spectrum.

The 22 mm probe was very useful in measuring the C-13 spectra of adsorbed olefin on a low surface area ZnO. This is because samples five times larger in weight than those usually used in 12 mm probe were employed. Hence, the experimental run-times were remarkably reduced and the signal to noise improvement was of a factor of five over the Varian 12 mm probe.

The Chemical Shift Measurements

The C-13 and proton chemical shifts were measured by comparing the resonance line of the adsorbed species to a standard sample such as the corresponding gas, neat liquid or tetramethyl silane (TMS). These shifts are inaccurate since there is a difference in the magnetic susceptibilities between the solid sample and the separate standard reference.

The susceptibility correction can be calculated theoretically from the volume susceptibility of the solid. This value depends on the density of the solid. Hence, different degrees of packing may give various susceptibility correction values. Therefore, the calculated corrections are inadequate.

Whitney (101) found that the shifts for adsorbed TMS on ZnO were coverage dependent. At coverages higher than 2 cc/gm, there was no change in the TMS chemical shift. He therefore assumed that the TMS formed liquid like adsorbate on the
surface. Thus, the observed shift resulted from the difference in magnetic susceptibility caused by the ZnO. The proton chemical shift of TMS adsorbed on ZnO can be accurately taken to be the empirical correction for the magnetic susceptibility of ZnO.

The empirical correction for ZnO prepared from oxalate salt was -0.9 ppm, whereas that of Kadox ZnO is -1.0 ppm. Doping ZnO with Ga or Li had an insignificant effect on the susceptibility of the parent oxide. Thus -0.9 ppm was used as an empirical correction for these samples. The negative sign indicates an upfield shift relative to the liquid TMS.

The bulk-susceptibility corrected value of the shift relative to gaseous ethylene was obtained as follows: (1) the empirical correction was measured as stated above. (2) The chemical shift of gaseous ethylene relative to TMS gas was measured. (3) The gas-liquid shift of TMS was measured. Thus, the combination of these values together with the observed chemical shift gives an accurate shift for the adsorbed ethylene on ZnO relative to the gaseous ethylene.

A similar procedure was used to measure the chemical shift of adsorbed acetylene with respect to the free molecules.

The susceptibility corrections for zeolite samples were determined by measuring the proton chemical shifts of adsorbed TMS relative to the neat liquid. These corrections are, -0.5, -0.7, -0.7, -0.6, -0.7, -0.9, -0.8, -0.8, -0.8, and -0.8 ppm for

The errors in the chemical shift measurements depend on the line widths. The error in the empirical correction is about ±0.2 ppm.

**Adsorption Measurements**

The adsorption isotherms of ethylene, ethane and acetylene were measured by using a volumetric apparatus following the design of Emmett (102).

The essential feature of the apparatus is the gas burette which consists of three bulbs connected to each other by a short length of capillary tubing bearing a matching mark. The volume of these bulbs progressively decreases, and the volume of each bulb is accurately determined by mercury displacement. The volume of the gas burette is used as a reference in determining the volume of the dead space and the space above the adsorbent. This can be done by using helium as a working gas. First, the volume of the dead space was determined together with the gas burette by filling the latter with helium gas. The pressure of the gas was measured before and after including the dead space. The application of the ideal gas law gives the volume of the dead space. In order to obtain an accurate volume for the dead space, more values are needed. This can be done by calculating the volume of the dead space from the pressure
reading obtained for each bulb. The volume of the dead space is therefore equal to the average of these values.

The volume of the space above the solid sample was determined as above. The calibration was done twice; once at -195°C and once at room temperature.

The amount adsorbed was measured by admitting the gas to the adsorbent. The pressure of the gas was increased by raising the mercury in the gas burette. The height differences in the manometer were measured with a cathetometer equipped with a vernier and accurate to ±.01mm. Pressure readings were then accurate to ±0.02mm of Hg. After each raise, successive readings of pressure were taken until there was no change in the manometer reading. This was taken as equilibrium pressure.

It should be noted that the specific surface area of ZnO was not measured for each sample, since it is reasonable to assume that there is little change in the area of given samples prepared under similar conditions.
VIII. ADSORPTION AND HYDROGENATION OF ETHYLENE ON ZnO

In 1940, Professor Taylor discovered that zinc oxide is an active hydrogenation catalyst (103). Since that time there have been several research works on the surface and the catalysis of ZnO, notably, the classic work by the late Professor Kokes and his co-workers (21, 26, 34, 35, 44, 46, 48, 52, 54, 55).

Zinc Oxide is a typical n-type semiconductor (13) because it contains excess zinc atoms or ions in interstitial positions within the lattice. These zinc atoms or ions can easily be ionized to give free electrons to the conduction band, and hence increase the conductivity. This can be represented as

\[ \text{Zn}_i^- \rightarrow \text{Zn}^+ + e \]

or

\[ \text{Zn}^+_i \rightarrow \text{Zn}^{+2} + e \]

The subscript \( i \) refers to the interstitial position.

The conductivity of ZnO can therefore be described by the number of electrons in its conduction band. The concentration of the electrons and thus the conductivity of ZnO can be altered by the incorporation of foreign ions into the lattice. For example, doping with monovalent ions decreases the conductivity, whereas doping with trivalent ions increases it. This change in semiconductivity, as a result of doping with mono or trivalent ions, has been known for many years (104).
If Ga ions substitute Zn ions in a 1:1 ratio, then the neutrality of ZnO is sustained by releasing electrons as shown in equation [28].

\[
\text{Ga}_2\text{O}_3 + 2\text{Zn}^{+2} \rightarrow 2(\text{Ga}^{+3})_{\text{Zn}} + 2\text{e} + 2\text{ZnO} + 0.5\text{O}_2 \quad [28]
\]

The \((\text{Ga})_{\text{Zn}}\) refers to Ga ion located in the lattice positions previously occupied by the Zn ions. This ion may trap the liberated electrons to form:

\[
(\text{Ga}^{+3})_{\text{Zn}} + \text{e} \rightarrow (\text{Ga}^{+3})_{\text{Zn}}\cdot\text{e}
\]

On the other hand, doping with Li ions decreases the electron concentration. This can be shown by:

\[
\text{Li}_2\text{O} + 2\text{e} + 2\text{Zn}^{+2} + 0.5\text{O}_2 \rightarrow 2(\text{Li}^{+})_{\text{Zn}} + 2\text{ZnO} \quad [29]
\]

where \((\text{Li})_{\text{Zn}}\) denotes the lithium ion placed in Zn ion lattice sites.

The addition of Ga ions could have an adverse effect on the overall concentration of the electrons in ZnO. The electrons released as a result of doping with Ga ions may disturb the equilibrium, and therefore equation [27] becomes reversible.
Uematsu et al. (105) found optimum conductivity when the concentration of Ga ions was 3 wt%. A further increase in the concentration of Ga decreases the conductivity by about 10%.

Lithium ions diffuse easily, hence they will substitute the Zn ions at a temperature near 300°C (106). However, the replacement of Zn by Ga ions is rather complicated and needs a higher temperature. At 400°C (the temperature at which ZnO is prepared) some gallium may exist as a single oxide or as a double oxide formed by the solid reaction with ZnO, and hence may make the surface heterogeneous.

Preparing ZnO at a higher temperature in order to assure the diffusion of Ga ions into the lattice is undesirable since it causes sintering. A reduction in the surface area would become unavoidable and the use of NMR experiments would be impossible. For this reason, there was no choice but to compromise.

The goal was to study the mode of adsorption and the hydrogenation of ethylene on pure and doped ZnO by NMR spectroscopy. Thus, ZnO with a higher surface area than that of the Kadox sample was more attractive. Decomposition of oxalate salt produces a high surface area ZnC (107). However, it was not self-evident that the samples prepared by pyrolysis of the oxalate salt would have the same adsorption properties as Kadox ZnO.
The first part of this study was the investigation of the effect of the method of preparations on the specific surface area and on the adsorption of ethylene. A comparison was made between the adsorption capacities of ZnO samples and that of Kadox ZnO. The second part was the measurement of the proton chemical shifts of adsorbed ethylene on pure and doped ZnO. In addition, the NMR spectroscopy was utilized to study the hydrogenation of ethylene on these catalysts.

Adsorption Measurements

The BET surface areas for ZnO samples in m²/g are shown in Table (2). The areas were determined by the BET equation [3]. Nitrogen gas was used as the adsorbate with the assumption that the cross sectional area of the molecule is 16.2 Å² (108). All the adsorption measurements were carried out at -195°C using a volumetric apparatus of a conventional design.

The isotherms of ethylene were measured volumetrically on all samples at 21 ± 1°C. These isotherms are shown in Figures (12-14).

As can be seen from Figure (12), all the isotherms except those on ZnO that were prepared at 350°C in vacuo or in air (samples A and B) nearly levelled off at pressures above 40 Torr. This indicates that ethylene is chemisorbed on these samples. However on samples A and B, the isotherms are nearly
Figure 12

Isotherms for ethylene adsorption on pure ZnO: ● Sample A; ○ Sample B; △ Sample C; ▲ Sample K.

Figure 13

Isotherms for ethylene adsorption on pure (D) and Li-doped ZnO: ■ Sample D; ○ 1% Li, ● 2% Li, □ 3% Li.

Figure 14

Isotherms for ethylene adsorption on Ga-doped ZnO: ▲ 0.5% Ga; ○ 1% Ga; ● 2% Ga; □ 3% Ga.
### Table 2. Proton Chemical Shifts of Adsorbed Ethylene on ZnO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (torr)</th>
<th>Coverage (cm³/m²)</th>
<th>Area (m²/g)</th>
<th>Shiftᵃ</th>
<th>Width (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>65</td>
<td>0.002</td>
<td>130</td>
<td>0.0</td>
<td>16</td>
</tr>
<tr>
<td>B</td>
<td>160</td>
<td>0.006</td>
<td>34</td>
<td>0.0</td>
<td>14</td>
</tr>
<tr>
<td>C</td>
<td>30</td>
<td>0.010</td>
<td>53</td>
<td>0.5</td>
<td>76</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>0.016</td>
<td>34</td>
<td>1.0</td>
<td>100</td>
</tr>
<tr>
<td>K</td>
<td>13</td>
<td>0.051</td>
<td>10</td>
<td>0.9</td>
<td>90</td>
</tr>
<tr>
<td>1% Li</td>
<td>15</td>
<td>0.016</td>
<td>32</td>
<td>0.3</td>
<td>40</td>
</tr>
<tr>
<td>2% Li</td>
<td>16</td>
<td>0.017</td>
<td>30</td>
<td>-0.1</td>
<td>30</td>
</tr>
<tr>
<td>3% Li</td>
<td>70</td>
<td>0.011</td>
<td>11</td>
<td>-0.2</td>
<td>24</td>
</tr>
<tr>
<td>.5% Ga</td>
<td>10</td>
<td>0.017</td>
<td>32</td>
<td>0.9</td>
<td>95</td>
</tr>
<tr>
<td>1% Ga</td>
<td>10</td>
<td>0.015</td>
<td>38</td>
<td>1.1</td>
<td>110</td>
</tr>
<tr>
<td>2% Ga</td>
<td>11</td>
<td>0.017</td>
<td>30</td>
<td>1.2</td>
<td>208</td>
</tr>
<tr>
<td>3% Ga</td>
<td>15</td>
<td>0.016</td>
<td>38</td>
<td>1.3</td>
<td>300</td>
</tr>
</tbody>
</table>

ᵃ Shifts are in ppm with respect to gaseous ethylene, corrected as described in the text. Positive shifts are to low field.
linear, hence ethylene is physically adsorbed.

The isotherms shown in Figure (12) do not give information about the nature of the active sites, but the trend of adsorption is in support of the view that heating ZnO at high temperatures is required to produce active sites on the surface. Kokes et al. (44) proposed dehydrated, strained Zn-O pairs as active sites for ethylene adsorption. Narayana et al. (109) on the other hand, suggested a model consisting of isolated Zn ions as adsorption centers. These centers were produced by oxygen removed from the surface by heating ZnO at high temperatures. Clearly, the active sites proposed by these two groups can not be formed until the oxide is heated at a temperature above 350°C.

The adsorption capacities of the ZnO samples prepared by pyrolysis of oxalate salt are much less than that of Kadox ZnO. It is interesting to note that the hydroxylation-dehydroxylation process of ZnO (sample D) increased the number of active sites. Such treatment had insignificant effects on the surface properties of Kadox ZnO. The amount of ethylene adsorbed on sample D is almost half of that adsorbed on Kadox ZnO.

However, a relevant comparison of ZnO prepared from the oxalate salt with Kadox ZnO cannot be made as the ethylene adsorption on Kadox ZnO is inconsistent between oxide lots. It is probable that this oxide varies from one lot to another. For
example, the isotherm presented here is below that measured by Whitney (101), and appreciably above that of Dent and Kokes (48). These differences may be due to the coverage dependence of the heat of adsorption between various lots. All (Whitney, Kokes, and myself) used the standard treatment (see chapter VII), yet the results were as follows: the initial isosteric heat of adsorption of about 14 kcal/mole was similar in all cases. This value is roughly constant at low coverage, nevertheless, the falloff for Kokes's sample occurred at a coverage of about 0.02 cm³/m², for Whitney's sample at about 0.07 cm³/m² and in the present lot at about 0.05 cm³/m². This variation can lead to variations in the adsorption isotherms.

Figures (13) and (14) show the ethylene adsorption isotherms on ZnO doped with Li and Ga ions respectively. Doping with Li ions decreases monotonically the adsorption capacity of the parent ZnO. On the other hand, small amounts of Ga ions increase the adsorption capacity while heavier doping decreases it.

NMR Measurements:

The proton chemical shifts of adsorbed ethylene were measured at 28°C. The shifts of these surface species are shown in Table 2 (page 91). As can be seen, the chemical shifts of adsorbed ethylene on ZnO prepared at 350°C in air or in vacuo are negligible relative to the free molecule. These are the
samples which showed the lowest adsorption capacities. The negligible chemical shifts and the poor adsorption capacities indicate that ethylene is physically adsorbed on these samples. On the other hand, the shift of ethylene adsorbed on sample D is downfield and comparable in value to the shift of adsorbed ethylene on Kadox ZnO and to Whitney's sample at low coverage (101). Thus, sample D has active sites similar in nature to those on Kadox ZnO but fewer in number.

The appearance of the resonance line of adsorbed species at lower field than that of free molecules, suggests that ethylene molecules undergo a chemical interaction with the surface whereby deshielding of the protons occurs. Comparing the shift of adsorbed ethylene to that of the adsorbed ethane (0.1 ppm (101)), suggests that this kind of shift is characteristic of a weakly chemisorbed ethylene in the "\( \pi \)-complex" form of Kokes and Dent.

If one accepts the simple view that ethylene donates its electrons to the surface and thus forms a \( \pi \)-complex, then doping with Li ions may enhance both the adsorption and the formation of \( \pi \)-complexes. This is because the deficiency of electrons as a result of doping with Li ions may modify the surface so that ethylene donates its electrons more effectively. Hence, the proton resonance line of adsorbed ethylene would appear at a lower field. However, what is observed in this study weakens such an argument as doping with
Li ions reduced the shifts of the adsorbed ethylene to a value close to that of gaseous molecules. It seems that the active sites present on the surface of the parent ZnO have been totally eliminated. On the other hand, doping with Ga ions has the opposite effect. It tends to increase slightly the adsorbed ethylene chemical shift. Apparently the incorporation of Ga ions into ZnO lattice modifies the surface sites for the chemisorption of ethylene.

Insufficient evidence exists on whether or not olefins donate electrons into the ZnO conduction band. Bozon-Verduraz et al. (110) reported that the conductivity of non-stoichiometric ZnO slightly increases, whereas that of stoichiometric oxide decreases upon the adsorption of ethylene. These authors found no infrared band for adsorbed ethylene on stoichiometric oxide in a marked contrast to Kokes's findings (34) which suggests a substantial difference in nature between their oxides. Uematsu et al. (111) found an increase in the conductivity when butene adsorbs on ZnO. Thus, the bulk of the research mentioned above suggests that olefins do indeed donate electrons into the surface, at least for pure ZnO.

The line widths of the adsorbed ethylene were measured at half height of the NMR peaks. As can be seen in Table (2), column (6), the change of the line widths is parallel to the change in the chemical shifts. In other words, small shifts are associated with narrow lines and large shifts with broad lines.
Whitney (101) found that the rotation of the adsorbed ethylene is complicated since the molecule can rotate fast around an axis normal to the surface ($c_2$ axis) and flip less frequently about an axis parallel to the surface. Thus, it is acceptable to take the line width as a qualitative measure of how fast the adsorbed molecule is rotating. Narrower lines arise from weakly adsorbed molecules. These are exactly the ones whose chemical shifts are smaller. Thus, supporting the view that they are only physically adsorbed. The widest lines were found for Ga-doped samples where the chemical shifts are also the largest and the chemisorption is presumably the strongest.

**Hydrogenation of Ethylene**

The hydrogenation of ethylene over pure and doped ZnO with Li or Ga ions was performed at 28 °C. A typical kinetic run is shown in Figure (15). As can be seen the peak assigned for the adsorbed ethylene decreases while that of ethane rises as the time elapsed. Although hydrogen certainly adsorbs on ZnO (44), no NMR line is observed in any spectrum collected during the course of the hydrogenation reactions. This presumably is due to the formation of such a strongly adsorbed species that the NMR line is unobservably broad.
Figure 15

NMR spectra during hydrogenation of ethylene on 1% Ga-doped ZnO. Top spectrum before admission of hydrogen, remainder after reaction for the indicated time.
The kinetic data were analyzed by measuring the height and the width at half height for each spectrum. The product of these numbers is proportional to the area of the peak. This was then taken to be proportional to the number of protons giving rise to the peak in question.

The plotting of \( \ln A_t/A_0 \) vs time for each run gives a straight line whose slope is the rate constant of the reaction. \( A_0 \) and \( A_t \) are the area of the adsorbed ethylene peaks at time zero and \( t \) respectively. Thus, the hydrogenation reaction is first order with respect to the adsorbed ethylene. These plots are shown in Figure (16) and the derived rate constants are listed in Table (3).

Kokes (44) found that the kinetics of ethylene hydrogenation to have a complex dependence on the amount adsorbed of ethylene. By assuming that the ethylene isotherm in the presence of hydrogen is the same as that measured for pure ethylene, they were able to deduce that the rate of hydrogenation is first order with respect to the adsorbed ethylene concentration. The results reported here support this view, since the catalytic reaction was monitored directly for the adsorbed phase. Thus, ethylene and hydrogen do not compete for the same sites.

It is interesting to note that doping with Li ions weakens the adsorption sites for ethane as indicated by the absence of the adsorbed ethane line in any kinetic run. However, analyzing
Kinetic plots for the hydrogenation of ethylene. Left: Sample D: ○ 1.1% Li; ● 2% Li; □ 3% Li. Right: ▲ 0.5% Ga; ○ 1% Ga; ● 2% Ga; □ 3% Ga.
Table 3. Rate Constants for Hydrogenation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K \text{ (min}^{-1} \times 100\text{)}$</th>
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<tbody>
<tr>
<td>D</td>
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</tr>
<tr>
<td>.5% Ga</td>
<td>1.30</td>
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<tr>
<td>1% Ga</td>
<td>1.53</td>
</tr>
<tr>
<td>2% Ga</td>
<td>1.32</td>
</tr>
<tr>
<td>3% Ga</td>
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</tr>
<tr>
<td>1% Li</td>
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</tr>
<tr>
<td>2% Li</td>
<td>0.85</td>
</tr>
<tr>
<td>3% Li</td>
<td>0.56</td>
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</table>
the gas phase after the completion of the reaction, revealed the existence of ethane and the absence of any other side reaction products. On Ga-doped ZnO, the line width of adsorbed ethylene increased during the hydrogenation reaction. This indicates that the loosely bound species reacted first with the adsorbed hydrogen, in spite of the overall first order kinetics. The existence of various adsorbed species with different binding strength with the surface, may result from the heterogeneity of the surface as indicated before.

The rate constant of the hydrogenation of ethylene on ZnO doped with Li ions decreases as the concentration of Li ions in the lattice increases. Doping with small amounts of Ga ions increases the rate, whereas a larger amount decreases it. The decrease in the rate at high Ga concentration could be due to poisoning by strongly bound ethylene, as revealed by the NMR measurements.
IX. ADSORPTION OF OLEFINs ON ZnO

The C-13 NMR spectra of adsorbed ethylene, propene, 2-methylpropene, 2-methylbutene-2, 2,3-dimethylbutene-2, cyclopentene, cycloheptene, butene-2 (cis and trans isomers), cyclohexene, 1-methylcyclohexene, and 2,3 dimethylcyclohexene on ZnO and SiO$_2$ were measured at 28$^\circ$C. Figure (17) shows a spectrum typical of those obtained in this study. In general, the lines of nonequivalent carbons are well resolved.

The chemical shift and line width of each peak are listed in Table (4). The widths are measured at the half maximum height for all the adsorbed molecules on both surfaces. Positive shift indicates the carbon which gives rise to the peak in question, resonates at a lower field relative to the corresponding carbon in the free molecules. The shifts are measured relative to the neat liquid of the corresponding olefin, except for ethylene and propene, which are referred to the molecules in the gas phase.

It should be noted the shift of these adsorbed molecules, relative to the liquid phase would appear to be at 1 to 2 ppm lower field if they had been measured relative to the gas. This is because the shift of liquid hydrocarbons is 1-2 ppm lower field than the corresponding gases(112, 113).

Comparing the shift of the olefinic carbons on ZnO, to that
Figure 17

Carbon-13 spectrum of cyclopentene adsorbed on ZnO.
Table 4. Chemical Shifts of Adsorbed Olefins on ZnO and SiO₂

<table>
<thead>
<tr>
<th>Adsorbate</th>
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<th></th>
<th>Silica</th>
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<tbody>
<tr>
<td></td>
<td>shift^a</td>
<td>width^b</td>
<td>shift</td>
<td>width</td>
</tr>
<tr>
<td>ethylene propene</td>
<td></td>
<td></td>
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</tr>
<tr>
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<tr>
<td>C-2</td>
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<td>25</td>
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<td>2-methylbutene-2</td>
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<td>cis-C-1</td>
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<td>C-4</td>
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<td>1-methylcyclohexene</td>
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<tr>
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<td>40</td>
<td>-0.9</td>
<td>25</td>
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</table>

\(^{a}\) shift in ppm; \(^{b}\) width in Hz.
Table 4 (Cont'd)

<table>
<thead>
<tr>
<th>Adsorbate</th>
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<th></th>
<th>Silica</th>
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<tr>
<td></td>
<td>shift&lt;sup&gt;a&lt;/sup&gt;</td>
<td>width&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>60</td>
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<tr>
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<td>unresolved</td>
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<tr>
<td>1,2-dimethylcyclohexene</td>
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<td>45</td>
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<tr>
<td>C-4</td>
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<td>35</td>
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<tr>
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<td>65</td>
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<td>60</td>
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</tbody>
</table>

<sup>a</sup> In ppm with respect to liquid, except ethylene and propylene with respect to gas. Positive shifts to lower field. ±0.2 ppm.  
<sup>b</sup> In Hz, corrected for apodization. ±5 Hz. Blank entries unmeasurable due to insufficient resolution.
on SiO₂, clearly indicates that olefins undergo specific interaction with ZnO surfaces. Such interaction is absent with SiO₂. This is manifested by the larger downfield shift of the adsorbed olefins on ZnO. It is also interesting to note that unsymmetric olefinic carbons experienced greater downfield shift when adsorbed on both surfaces, and the shift increases when the olefinic carbon is more substituted, as indicated from the shifts of CH₃-CH= (5.2 ppm), =CH₂ (0.5 ppm) of propene, and (CH₃)₂C= (7.6 ppm) of adsorbed 2-methylpropene on ZnO. On the other hand, increasing the number of substituted methyl groups around the double bond to three or four, drastically reduces the chemical shifts of the olefinic carbons relative to those found for single or double substitutions. Thus, the bulky methyl groups exert a steric factor which denies the double bond a close approach to ZnO surface.

Caution is necessary in comparing the line widths of the adsorbed molecules on ZnO and SiO₂. The two adsorbents may contain different concentrations of paramagnetic impurities, which may make such comparison meaningless. However, in general, the peak widths of adsorbed olefin on ZnO are broader than the corresponding ones on silica gel. This suggests a stronger interaction with the ZnO surface. As can be seen from Table (4), non-protonated carbons give rise to narrower peaks than the protonated ones. This indicates some contribution of C-H dipolar coupling to the line width, and at least, shows that
the widths of the NMR lines are not completely dominated by the paramagnetic impurities.

The effect of the ring size on the olefinic carbon shifts of cyclopentene, cyclohexene, and cycloheptene is minimal on both surfaces. However, their line widths tend to increase as the ring size increases, which indicates slower motion of the adsorbed cycloalkenes as one goes on from cyclopentene to cycloheptene. It is also interesting to note that, for cyclohexene adsorbed on ZnO, the peak widths of the carbons numbered 3 and 6 are broader than those of carbons 4 and 5. Such distinct differences are not observed on silica gel. This suggests that the shape of adsorbed cyclohexene on ZnO is a distorted chair (114), where the olefinic carbons and the adjacent allylic carbons are in a plane parallel to the surface, hence preferentially held, whereas the others are mobile.

In light of the present results, and the findings that follow in the next chapter, the mode of olefins binding to ZnO and the nature of the adsorption centers proposed by Kokes (34) could be reconsidered.

Kokes et al. (35) identified two surface species by means of infrared spectroscopy when propene adsorbed on ZnO, one is weakly bound and the other is strongly bound to the surface. The weakly bound species results from nondissociative adsorption to form $\pi$-complexes. The shift of the double bond stretching frequency is 30 cm$^{-1}$ relative to the gas phase. Similar species
are formed upon the adsorption of ethylene on ZnO. This species is the intermediate in the hydrogenation reaction. The strongly bound species results from dissociative adsorption to form protons bound to the oxide ion, and \(\pi\)-allyl complex stabilized on Zn ion of the Zn-O pair. This allyl ion is the intermediate in the isomerization reaction, and is characterized by a shift of the double bond stretching frequency of about 100 cm\(^{-1}\).

Kokes (34) proposed that the ethylene \(\pi\)-complex stabilized on the oxide part of Zn-O pair because of steric hinderance, whereas the propene \(\pi\)-complex stabilized on the Zn ion. However, since both complexes are similar, the ethylene \(\pi\)-complex may also be adsorbed on the Zn ion. Thus the nature of the active sites for the adsorption of ethylene and other olefins needs further study. With this in mind, the following discussion and also that in chapter (X) will focus on the mode of adsorption of olefins on ZnO.

The bonding of olefins with transition metal ions whose d orbitals are full or nearly full of electrons is well described by the Dewar model (115). In this model the bond between olefins and transition metal ions is made up of two components: first, is the overlap of the filled \(\pi\)-orbitals of the olefin with the vacant s orbital of the metal, and second, is the overlap of the vacant antibonding \(\pi\)-orbitals of the olefin with the d orbitals of the metal. The latter overlap is affected by the availability of the electrons in the d orbitals which is
determined by the energy of the d orbitals relative to that of π-orbitals. In general, the strength of bonding in these complexes is certainly determined by the ease of the overlapping, as is decided by the steric factors.

The data from the NMR spectra of olefin π-complexes with d^{10} species such as Pt^0 (116, 117), Ag^+ (118, 119), and Hg^{+2} (120) ions support the Dewar model. The proton, and C-13 chemical shifts of olefin-Pt complexes are upfield. In Ag-olefin complexes, the proton shift is downfield, whereas the C-13 shift is upfield. Finally, in Hg-olefin complexes, both proton and C-13 shifts are downfield with respect to the free molecules. These distinct differences in the chemical shifts can be qualitatively explained in terms of a decreasing contribution of electrons from the d orbitals of the metal to the olefin π-orbitals as one proceeds from Pt^0 to Hg^{+2}.

The above examples show the back donation of electrons from the metal d orbitals to the olefin π-orbitals is minimal for the divalent ion Hg^{+2}. By analogy, despite the absence of stable Zn-olefin complexes, one may expect a small contribution of Zn ion d orbitals to Zn-olefin bond, and hence a modest downfield chemical shift for olefin π-complex formation with Zn ions. This is exactly what is observed in the spectra of adsorbed olefins on ZnO, and therefore, strengthens the argument for the π-complex formation on Zn ions.
It is interesting to note that the chemical shifts observed for the adsorbed olefins on ZnO correlate well with the thermodynamic stabilities of Ag-olefin complexes. In most cases, the olefins which give large chemical shifts are those whose complexes with Ag ions are more stable (121). The correlation is even more striking if the average chemical shift of the olefinic carbons on ZnO minus that on SiO₂ is plotted versus the equilibrium constant for the formation of Ag-olefin complexes (Figure 18). A linear relationship is obtained which is statistically significant at the 99.5% confidence level, and the correlation coefficient is 0.95. This correlation, and the downfield chemical shift of the olefinic carbons support the view that the stabilization of the π-complexes takes place on Zn ions.

The chemical shifts of cis and trans butene-2, listed in Table (4), indicate that the surface π-complex of the former isomer is more stable than that of the latter. This behaviour of stability is common for the π-complexes of butene-2 with d¹⁰ transition metals. Muhs and Weiss (121) invoked steric factors to explain the stability of cis and trans isomer complexes with Ag⁺. They adopted the view that, in the cis butene-Ag complex, there is relief of the steric interaction between the two methyl groups. This results from a small degree of twisting of the double bond p orbitals which permits a slight rotation around the π-bond. If this is the case in the cis-butene-Zn
Figure 18

The average chemical shifts of the olefinic carbons on ZnO minus those on SiO$_2$ vs. the equilibrium constant for the formation of Ag-olefin complexes.
$K$ (equilibrium const. for Ag-olefins) vs. $\bar{\overline{\delta}}_{ZnO} - \bar{\overline{\delta}}_{SiO_2}$ (ppm)
complex, then one would expect a downfield shift of the methyl resonance upon complex formation, since the upfield shift of the cis methyl group, relative to that of the trans isomer, is also attributed to a steric interaction (122). This is exactly what is observed (see Table 4). A similar mechanism may be operating in adsorbed 1,2 dimethylcyclohexene, where the methyl groups resonate at a lower field when adsorbed on ZnC. Such a downfield shift is not observed on silica gel.

The infrared (35) and Raman (51) spectroscopy confirm the formation of an allyl anion from propene on the ZnO surface. However, in the present studies, no line attributed to the π-allyl species is observed in any of the adsorbed olefins spectra, even for propene where the concentration of such species is large enough to be observed. The only probable explanation is that, the NMR lines are too broad to be observed by a high resolution spectrometer. In fact, the proton spin-spin relaxation time for low coverage propene is about 200 μs (123). This represents a line of roughly 1.6 KHz in width.

This broad line indicates a restricted rotation of the surface allyl species. In the present studies, it has been suggested that the bond between the olefin and Zn ions is formed by the overlapping of the olefinic π-orbitals and sp orbitals of the ion. If a similar bond is formed between the the π-allyl species and the Zn ion, then there is no obvious reason why it
should not be as mobile as the ethylene $\pi$-complex. Possibly the $\pi$-allyl species is attached to an ensemble of two or more Zn ions. The existence of such an ensemble has been suggested by Boccuzzi et al. (124).

Trans butene-2 catalytically isomerized on ZnO (see Fig. 19). The C-13 spectra of the trans isomer changed with time: the height of the peaks assigned for the olefinic carbons and the methyl groups fell with time, accompanied by the development of the peaks of the cis isomer. This isomerization reaction took place on a time scale of hours at room temperature. It is interesting to note that the equilibrium cis to trans ratio is 0.8, as judged from the relative intensities of the well-resolved methyl peaks. This is appreciably above the gas-phase equilibrium value of 0.3. Chang et al. (52) also suggested that the adsorbed cis/trans ratio in this system is higher than the gas-phase equilibrium value. Greater stability of the adsorbed cis species would, of course, be expected from the difference in shifts, as discussed above.

Within a few days, there was no evidence that methylcyclohexenes underwent a catalytic isomerization over ZnO, as the C-13 NMR showed only the spectra of the original compounds. However, remeasuring the spectrum of the 1-methylcyclohexene sample after storing it for six months at room temperature, showed new peaks at 132.6 and 130.0 ppm with respect to TMS. These are most likely the lines of adsorbed
Carbon-13 spectrum during the isomerization of \textit{trans} butene-2 over ZnO.
4-methylcyclohexene or 3-methylcyclohexene as the shift of the olefinic carbons of 4-methylcyclohexene is 127.1 ppm, and the shift of C_2 of the 3-methylcyclohexene is 126.6 ppm in the liquid state (123). The thermodynamic data (125, 126) indicates that measurable amounts of the three isomers can exist in equilibrium. Thus, the isomerization of 1-methylcyclohexene to 3-methylcyclohexene and 4-methylcyclohexene can be considered.

Remeasuring the C-13 spectrum of 1,2 dimethylcyclohexene after six months, showed new lines at 122.8 and 20.9 ppm relative to TMS. Since there is no C-13 spectrum of this compound's isomers, and the thermodynamic data is absent, it is difficult to know the origin of these lines. However, it is likely that isomerization of 2,3 dimethylcyclohexene proceeded on ZnO.

The formation of an intraring π-allyl species may furnish an isomerization pathway. The slow rate of this reaction when compared with butene isomerization, implies that very few sites are capable of forming these π-allyl species. These π-allyl species have not previously been observed on ZnO, hence more work is required to characterize them. A complete picture of the surface species can be supplied by a combination of spectroscopic and kinetic studies.
X. ADSORPTION OF CARBON MONOXIDE AND ACETYLENE ON ZnO

The purpose of this study is to give considerable insight into the nature of the ethylene mode of adsorption, and to supply further support to the view presented in the previous chapter that the ethylene π-complex species is bound to the Zn ion. This is in direct contrast to Kokes's proposal that ethylene adsorbs on the oxide ion of the Zn-O ion pair. Thus, in order to comprehend the difference between the two views, we ought to use the same oxide used by Kokes (Kadox ZnO).

While this work was in progress, Efremov and Davydov (47) reported a study of the nature of ethylene π-complex on ZnO surface by the infrared spectroscopy, however, minor differences are observed between the two studies.

Adsorption Measurements

The adsorption isotherms of acetylene were measured at 21 ± 1° C. These isotherms are shown in Fig.(20). As can be seen from Fig.(20), the amount of acetylene adsorbed is roughly twice the amount of ethylene as judged from the isotherms of the two gases. Degassing the sample for 12 hr at room temperature, removed approximately 30% of the total acetylene adsorbed on ZnO. The remaining acetylene is strongly bound to the surface,
Figure 20

Isotherms for acetylene and ethylene on ZnO.

- O acetylene
- △ ethylene
- • readsorbed acetylene after the adsorption of acetylene
- ▲ readsorbed ethylene after the adsorption of acetylene
and can only be removed after heating at 400°C in an oxygen atmosphere. As was expected, the amount of readsorbed acetylene is proportional to the equilibrium pressure, which indicates physical adsorption.

Following the exposure of ZnO to acetylene at 200 Torr, the sample was degassed for 12 hr, then ethylene was readsorbed (Fig.20). As can be seen from the linearity of the isotherm, ethylene is physically adsorbed. Heating the sample at oxygen atmosphere at 400°C, restores its original adsorption capacity. Thus, chemisorbed acetylene occupies the sites that would otherwise be available to chemisorbed ethylene.

NMR Measurements

Acetylene is more acidic than olefins. It dissociatively adsorbs on ZnO to give a proton bound to the oxide part, and an acetylide fragment bound to the Zn ion (55). At low coverage, the C-13 spectrum of adsorbed acetylene shows a line at 11.4 ppm downfield relative to TMS. This is most likely the peak of an aliphatic carbon, which indicates the polymerization of acetylene. Kokes et al.(55) observed a similar surface reaction.

The adsorption centers for olefins and alkynes, in Kokes's view, are a limited number of Zn-O ion pairs. Thus, the adsorption of acetylene can be represented by the equations,
and that for ethylene by

\[ \text{C}_2\text{H}_4 + \text{ZnO} \rightarrow \text{Zn} - 0 \]

It is obvious, on the basis of Kokes's results, that the subsequent adsorption of acetylene removes the adsorbed ethylene since acetylene is preferentially adsorbed. Nevertheless, the successive adsorption of acetylene (120 Torr), only removed the chemically adsorbed ethylene, as indicated by the reduction of the shift of adsorbed ethylene to a value close to that of the gaseous molecule, and by the decreasing of the line width (Table 5). A new line is observed at 0.6 ppm downfield relative to gaseous acetylene, which is likely of the physically adsorbed species. This is shown in Fig. (21). Lines of chemisorbed species are absent in these spectra, possibly because the proton line is too wide to observe on a high resolution spectrometer.

While chemisorbed acetylene occupies the sites for chemisorbed ethylene, physically adsorbed ethylene and acetylene seem to occupy independent sites. The shift of adsorbed ethylene on ZnO covered only by strongly bound acetylene is equal in magnitude to that observed when both types of adsorbed acetylene are present (Table 5).
Table 5. The $^{13}$C Chemical Shifts of Adsorbed Ethylene and Carbon Monoxide on ZnO and The Proton Chemical Shifts of Adsorbed Ethylene and Acetylene on ZnO

<table>
<thead>
<tr>
<th>Absorbate</th>
<th>Chemical Shift $\delta$ ppm</th>
<th>$\Delta H$ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-5.4</td>
<td>490</td>
</tr>
<tr>
<td>CO$^{a}$</td>
<td>0.6</td>
<td>270</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>2.1</td>
<td>100</td>
</tr>
</tbody>
</table>

The $^{13}$C Chemical Shifts of Adsorbed Ethylene and Carbon Monoxide on ZnO

The Proton Chemical Shifts of Adsorbed Ethylene and Acetylene on ZnO

<table>
<thead>
<tr>
<th>Absorbate</th>
<th>Chemical Shift $\delta$ ppm</th>
<th>$\Delta H$ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_4$</td>
<td>1.3</td>
<td>50</td>
</tr>
<tr>
<td>C$_2$H$_4$$^{b}$</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>0.6</td>
<td>35</td>
</tr>
</tbody>
</table>

$^{a}$ After the successive adsorption of C$_2$H$_4$.

$^{b}$ After the successive adsorption of C$_2$H$_2$.

Positive $\delta$ indicates lower field.

$\Delta H$ is corrected for apodization.

The shifts are measured with respect to the free molecules.
Figure 21

(a) Carbon-13 spectra of adsorbed CO and ethylene on ZnO.

(b) Proton NMR spectra of adsorbed ethylene and acetylene on ZnO.
Up to this point, because of the complexity of acetylene reaction, it is difficult to deduce the nature of the active sites for ethylene adsorption. Therefore, further study needs to be done in order to elucidate on which ion the stabilization of ethylene π-complex takes place. The candidate is certainly CO, because of its simplicity, and also its adsorption on ZnO has been extensively studied (124, 126-129).

The infrared studies of CO adsorbed on ZnO suggest that polarized C≡O is formed on the surface (124, 127-129) because the stretching frequency increases substantially upon adsorption. Thus, CO can adsorb via oxygen at the anion site (O⁻) or, via carbon at the cation site (Zn²⁺). The first hypothesis is ruled out because the adsorption of a base such as pyridine (124), or ammonia (129), known to adsorb only on Zn ion, completely replaces CC. Thus, the surface complex is probably a species of the type Zn...C≡O (47, 124, 127-129).

It is not clear if electrons are transferred from or to the adsorbed CO. Magarjunan et al. (128) found a decrease in ZnO conductivity upon the adsorption of CO. This indicates a withdrawal of electrons from the surface to CO. On the other hand, Gay et al. (129) reported some donation of electrons from CO to ZnO. However, it is generally accepted that CO is weakly adsorbed and that the adsorbed molecules are polarized with a negative and positive charge on the carbon and the oxygen respectively.
The negatively charged carbon of adsorbed CO would be expected to resonate at a higher field because of the electron shielding, and this is exactly what is observed: the C-13 shift of adsorbed CO is upfield relative to the free molecules (see Table 5).

If Kokes's view that ethylene adsorbs on the oxygen ion is correct, then the subsequent adsorption of ethylene on ZnO covered with CO (3 \( \mu \text{m} / \text{m}^2 \)), presumably adsorbed on Zn ion, would not eliminate the peak assigned for OC-Zn complex. In fact, the successive adsorption of ethylene (120 Torr) displaced a major portion of the chemisorbed CO and left the physically adsorbed species, as indicated by the decrease in the line width and the reduction in the shift to a value near that of gaseous CO (see Fig. 21).

In view of this study, it is likely that ethylene adsorbs on Zn ion. This supports the arguments presented earlier.

Clearly, the general qualitative aspect of these results, and those of Efremov and Davydov (47) are the same. Ethylene adsorbs on Zn ion. Efremov reported that ethylene completely removed CO, but our studies show ethylene removes only the chemisorbed CO. The difference between the two works may result from using different ZnO samples. We used Kadox ZnO, while Efremov used ZnO prepared from the oxalate salt.
XI. ADSORPTION OF OLEFINS ON ZEOLITE TYPES X AND A

The adsorption isotherms of ethylene and ethane on zeolites were measured at 21±1°C. The general feature of the ethylene isotherms is that they all are non-linear, and the adsorption reaches near saturation at a pressure of about 120 Torr.

The adsorption of ethylene is reversible, except at a pressure below 15 Torr, where the desorption points lie above the adsorption points (hysteresis). This indicates that the chemisorption is weak, and that some ethylene is physically adsorbed. To investigate this assumption, the adsorption of ethane (E.P=-104°C) is compared to that of ethylene (E.P=-89°C). As can be seen in Figures (22-23), all the ethane isotherms are nearly linear, and the amount of ethane adsorbed is in all cases less than the amount of ethylene adsorbed on the same catalyst. Thus, ethylene is weakly chemisorbed on zeolites. This assumption is further investigated by NMR spectroscopy.

Adsorption On Zeolite X

The adsorption isotherms of ethylene and ethane on Na-, Cd-, and Zn-X are shown in Figure (22). As can be seen from Figure (22), exchanging 58% of Na by Cd ions has an insignificant effect on the adsorption capacity of the parent
zeolite. However, a further exchange (86%), decreases the capacity by almost 28%. On the other hand, the amount of ethylene adsorbed decreases as the concentration of Zn ions increases in the lattice. The capacity of Zn(I)-X is 80% and that of Zn(II)-X is almost 40% as large. This trend of adsorption capacity apparently depends on the nature, number, and location of the ions in the lattice.

There are three sites at which ions are likely to be located: site (I) at the center of the hexagonal prism; site (II) at the center of the six-membered ring between the sodalite units and the supercage; and site (III) at the wall of the supercage. Sodium ions are distributed over these sites as follows: 16 at site (I), 32 at site (II), and 38 at site (III) (130).

The distribution of Cd ions over these sites is not known as there are no x-ray diffraction structure studies reported in the literature. It might be assumed with great probability that, in the case of zeolite type X, the divalent cations (Cd$^{+2}$) replace Na ions at site (I) first, then exchange with Na ions at sites (II) and (III) (130-134).

The preferable site for Zn ions is determined by two factors. Firstly, the Zn ion is small, and hence prefers the formation of a tetrahedral structure. Secondly, the heat of hydration of Zn is high, and therefore the site should be
Figure 22

Isotherms for ethylene and ethane on zeolites X (see Table 1 for the identification of these zeolites).

- ▲ Na-X
- □ Cd(I)-X
- ● Cd(II)-X
- ○ Zn(I)-X
- ■ Zn(II)-X
accessible to water. For these two reasons, Zn ions prefer sites (II) and (III) over sites (I) (135). The distribution of the cations over these sites is shown in Table 6.

Cadmium or Zinc ions at sites (II) and (III) are accessible for ethylene molecules, whereas those at sites (I) are not. This is because ions at sites (I) are in the hexagonal prisms whose entrances (2.2Å in diameter) are too narrow for ethylene with a diameter of 4.2Å (60) to penetrate deep inside. Hence, ethylene cannot interact with these ions. However, it is known that ions at sites (I) may relocate themselves at a nearby site in the supercage upon the adsorption of a strong ligand such as ethylenediamine (136). The relocation of Zn or Cd ions is ruled out because of the absence of distinct infrared bands for different types of adsorbed species (79, 136).

The adsorption of ethylene is likely to occur first on Cd or Zn ions, then further adsorption presumably takes place on Na ions. In other words, the number of accessible ions may determine the extent of adsorption. If this is so, then why does Cd(I)-X, with only 46 ions in the supercage, adsorb ethylene in a similar amount to that of Na-X with 70 ions in the supercage? To answer this question, and others, the population of ethylene molecules in the supercage of each zeolite is determined from the isotherm, assuming that a saturation occurs at a pressure around 120 Torr. These values are listed in Table (7). As can be seen, the number of ethylene molecules in the
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>% of Exchange</th>
<th>No. of Cations of Na&lt;sup&gt;+&lt;/sup&gt; in the Unit Cell</th>
<th>Assumed Number of Na&lt;sup&gt;+&lt;/sup&gt; and the Exchanged Ions in the Unit Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>S&lt;sub&gt;I&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>NaX</td>
<td>0</td>
<td>86</td>
<td>16</td>
</tr>
<tr>
<td>Cd(I)-X</td>
<td>59</td>
<td>62</td>
<td>-</td>
</tr>
<tr>
<td>Cd(II)-X</td>
<td>86</td>
<td>49</td>
<td>-</td>
</tr>
<tr>
<td>Zn(I)-X</td>
<td>70</td>
<td>56</td>
<td>16</td>
</tr>
<tr>
<td>Zn(II)-X</td>
<td>98</td>
<td>44</td>
<td>2</td>
</tr>
</tbody>
</table>
Table 7. The Number of Ethylene Molecules Adsorbed in the Supercages of Zeolites X

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>No. of Ethylene Molecules</th>
<th>No. of Cations at Sites II and III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-X</td>
<td>43</td>
<td>70</td>
</tr>
<tr>
<td>Cd(I)-X</td>
<td>43</td>
<td>46</td>
</tr>
<tr>
<td>Cd(II)-X</td>
<td>32</td>
<td>33</td>
</tr>
<tr>
<td>Zn(I)-X</td>
<td>34</td>
<td>40</td>
</tr>
<tr>
<td>Zn(II)-X</td>
<td>15</td>
<td>42</td>
</tr>
</tbody>
</table>
supercage of Cd(I)-X, amounted to 43. This number is remarkably close to that of Cd and Na ions in the supercage (46 ions). However, only 43 ethylene molecules adsorb on Na-X at 120 Torr. In order to check the validity of this number, the maximum adsorption capacity of the supercage is calculated with the assumption that ethylene is present in a liquid phase. This calculation shows the supercage can only accommodate 50 molecules. Clearly, the condition prevailing during the measurement of the present isotherm, is by no means close to that required to liquefy ethylene. Hence, a smaller number is expected. Although Na ions at sites (II) and (III) are accessible for adsorption, only 60% of these ions interact with ethylene because of the limitation imposed by the supercage void volume. Good agreement between the number of ethylene molecules and that of the cations in Cd(II)-X is obtained.

As can be seen from Table (7), ethylene adsorption on Zn(I)-X supports the view presented above, as there are 34 ethylene molecules vs 40 ions at sites (II) and (III). On the other hand, there are only 15 molecules held on Zn(II)-X. The poor adsorption capacity of Zn(II)-X may result from the migration of some of the Zn ions at sites II to the vacant sites I after the dehydration process. The X-ray diffraction powder patterns of the dehydrated Na-X and Zn(II)-X indicate that the zeolites undergo no major structural change upon the exchange of Na by Zn ions.
The adsorption of ethane on zeolites X is less specific. The amount of ethane adsorbed on Na-X and Cd-X is almost the same, whereas exchanging Na with Zn ions decreases the capacities in a manner similar to that observed for \( \text{C}_2\text{H}_4 \).

Adsorption Of Ethylene and Ethane On Zeolite A

Figure (23) shows the adsorption isotherms of ethylene and ethane respectively. As can be seen from Figure (23), partial exchanging of Na with Zn ions increases, whereas full exchanging decreases the capacity of the parent zeolite. Unlike Zn, the introduction of four or six Cd ions into the lattice, equally increases the amount adsorbed of ethylene relative to that by Na-A.

The x-ray diffraction studies (59) suggest the existence of eight Na ions at the center of six-membered rings (sites (I)), three ions near the center of eight-membered rings (sites (II)), and only one ion on sites (III) at the wall of the central cage. Sites (II) are located near the aperture to the central cage. Thus, the sieving properties of zeolite A are largely determined by the number and kind of ions occupying these sites.

Zinc ions can easily replace Na ions in the lattice. There are definitely four Zn ions at sites (I) (62, 63), but the location of the fifth and the sixth is still debated. Takaishi et al.(137) studied the adsorption of some polar and non-polar molecules on zeolites containing different concentrations of Zn.
Figure 23

Isotherms for ethylene and ethane on zeolite A (see Table 1).

▲ Na-A
○ Cd₄Na₄A
● Cd₆ A
□ Zn₄Na₄A
■ Zn₆A
ions. They suggested that the fifth and sixth ions may occupy sites (II). Nitta et al. (138), reported that the theoretical calculations of the interaction of Zn ions with each site confirm the location of only the sixth ion at sites (II). Seff (63) on the other hand, suggested that all the six ions are located at sites (I).

Comparing the adsorption isotherms of ethylene on Zn$_4$Na$_4$A and Na-A, easily confirms the view that all Zn and Na ions in the former zeolite are at sites (I). Replacing four Zn by eight Na ions, leaves sites (II) and (III) empty. Thus, the rigid ethylene molecules can penetrate easily into the central cage. Another factor which increases the amount of uptake is that the void volume of Zn$_4$Na$_4$A central cage is larger than that of Na-A. This is because Zn$_4$Na$_4$A contains four ions less than Na-A. In addition, the space occupied by the four Zn ions in the central cage of Zn$_4$Na$_4$A is smaller than if it were occupied by four Na ions.

Fully exchanged Zn-zeolite is a poor adsorber. This can not be attributed to the locations of Zn ions, because if all Zn ions are at sites (I) (63), then one may expect larger capacity than Zn$_4$Na$_4$A for the same reason mentioned in the previous paragraph. Furthermore, if sites (II) are occupied by one ion (138) or even by two (Takaishi (137)) Zn ions, Zn$_6$A presumably adsorbs more ethylene than Na-A or Zn$_4$Na$_4$A. This poor capacity can not be attributed to a loss of crystallinity, since powder
x-ray measurements indicated no change in the crystal structure of dehydrated Zn6A. Therefore, the reason for this poor capacity is not obvious at the present time.

By comparing the ethylene isotherms on Cd4Na4A and Zn4Na4A, it is possible to see the effect of the ion size and in turn the central cage void volume on the adsorption capacities of these zeolites. Each one of these zeolites contains four Na and four divalent ions (Zn or Cd), but because Zn is smaller than Cd ion, the void volume of Zn4Na4A is larger, and thus its adsorption capacity is larger.

Cd4Na4A and Cd6A show similar capacities. Apparently, the replacement of four Na by two Cd ions of similar ionic size, causes a small change in the central cage void volume and so its capacity.

Interestingly, the amount of adsorbed ethane on zeolites A decreases in the following order:

Zn4Na4A > Cd4Na4A = Cd6A > Na6A > Zn6A

This trend of adsorption is similar to that observed for ethylene on these zeolites. Thus, supporting the foregoing discussion that the central cage void volume is the prime factor in determining the adsorption capacities of at least the first four zeolites.
Carbon-13 Chemical Shift Measurements

The C-13 chemical shifts, coverages, and line widths at half-height of the NMR lines of adsorbed ethylene and ethane on zeolite types X and A are listed in Tables (8, 10). The shifts of butene-1 on Na-X, and Cd-X are shown in Table (8).

The shifts of the olefinic carbons on zeolites are downfield relative to the free molecules. This indicates that the adsorption of olefins occur via the formation of π-complexes with Zn or Cd ions. This mode of adsorption implies the overlapping of the olefin π-orbitals with the sp orbitals of these cations (Dewar's Model).

The modest downfield shifts of adsorbed ethylene on Zn-exchanged zeolite types A and X, may offer further support for the view presented in the previous chapters that the stabilization of the π-complexes occurs at the Zn ions in ZnO.

Olefins on Zeolite X

Comparing the chemical shifts of ethylene to that of ethane, suggests that ethylene is weakly chemisorbed on these zeolites (Table 8).

Divalent ions such as Zn and Cd are associated with higher electrostatic potential. The electrostatic potential created at the cation site polarizes the olefin π-orbitals, which then interact strongly with the cation (139). The potential on the ions is qualitatively measured by its charge/radius ratio.
Table 8. Chemical Shifts of Adsorbed Ethylene and Ethane on Zeolite X

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>C₂H₄</th>
<th>C₂H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>δ ppm</td>
<td>ΔH</td>
</tr>
<tr>
<td>Zn(II)-X</td>
<td></td>
<td>1.7</td>
<td>.110</td>
</tr>
<tr>
<td>Zn(II)-X</td>
<td></td>
<td>1.7</td>
<td>190</td>
</tr>
<tr>
<td>Cd(I)-X</td>
<td></td>
<td>2.1</td>
<td>40</td>
</tr>
<tr>
<td>Cd(II)-X</td>
<td></td>
<td>4.1</td>
<td>180</td>
</tr>
<tr>
<td>Na-X</td>
<td></td>
<td>1.7</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 8a. The Chemical Shifts of the Olefinic Carbons of Adsorbed Butene-1 on Zeolite X

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Coverage</th>
<th>=CH₂</th>
<th>-CH=</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm/gm</td>
<td>δ ppm</td>
<td>ΔH</td>
</tr>
<tr>
<td>Cd(I)-X</td>
<td>1.5</td>
<td>10.7</td>
<td>210</td>
</tr>
<tr>
<td>Cd(II)-X</td>
<td>1.5</td>
<td>14.1</td>
<td>250</td>
</tr>
<tr>
<td>Ag-X†</td>
<td>0.9</td>
<td>-11.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Na-X</td>
<td>1.3</td>
<td>6.0</td>
<td>50</td>
</tr>
</tbody>
</table>

† From Reference 86.

* The coverage expressed in mm/gm

Postive δ indicates shift to lower field.

ΔH is corrected for apodization.

Shifts are measured with respect to gaseous butene-1.
Thus, for ions bearing the same charge, the smaller the radius, the greater is the electrostatic potential (Table 9).

As can be seen from Table (8), the shifts are not in accord with the polarizing power of the cations. The chemical shift of adsorbed ethylene on Na-X is similar in magnitude to that observed for ethylene on Zn-X. This is in contrast to the polarizing power dependence of adsorbed CO on Zn-Y (140). The heat of adsorption of CO on Zn-Y is 17 Kcal/mole vs 5.8 Kcal/mole for CO on Na-Y. Then one may ask, why is this so? This discrepancy could lie in the difference of the mode of interaction.

Ethylene molecules laterally approach the cation and simultaneously experience three opposing forces. First, the overlapping of their π-orbitals with the cation sp orbitals. This force determines the stability of the π-complex. Secondly, there is a repulsion between the π-electrons and the negatively charged oxygen in the lattice framework. Thirdly, there is shielding of the cation by the neighbouring bulky oxygen ions. The last two forces oppose and thus weaken the interaction between the olefin and the cation. For small ions such as Zn, the shielding and the repulsion forces hinder the approach of ethylene, and therefore reduce the ethylene-Zn interaction. As a result, the chemical shift of the olefinic carbons becomes small. This is exactly what is observed
Table 9. Physical Parameters of the Exchanged Ions

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic Radius Å</th>
<th>Electrostatic Potential $\times 10^2$ (esu/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.95</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn</td>
<td>0.74</td>
<td>12.0</td>
</tr>
<tr>
<td>Cd</td>
<td>0.97</td>
<td>9.9</td>
</tr>
<tr>
<td>Ca</td>
<td>0.99</td>
<td>9.7</td>
</tr>
</tbody>
</table>
(see Table 8). On the other hand, CO may be attached to the Zn ions in end-on configuration, hence the repulsion and also the shielding by the oxide framework becomes less effective. Evidence for the shielding effect of small ions has been reported by Yates (79) and Kiselev (141).

On the other hand, large cations such as Cd protrude further from the neighbouring oxygen ions, thus minimizing their shielding effect. As a result, ethylene can interact strongly with Cd ions, hence increasing its chemical shift. As can be seen in Table (8), the shift of adsorbed ethylene on Cd(II)-X is larger in magnitude than on Zn-X zeolites.

The chemical shift of ethylene on Cd(I)-X is only downfield by 2.1 ppm relative to the free molecules. This is not a surprising result, because this zeolite contains 38 Na and only 8 Cd ions at sites (II) and (III), thus the \( \text{C}_2\text{H}_4\text{-Na} \) shift is the predominant one.

The line width of the adsorbed species, qualitatively reflects its rotational correlation time. Strongly adsorbed molecules have larger shifts, and presumably broader lines. However, weakly adsorbed ones have smaller chemical shifts, and narrower lines. The line widths reported in Table (8), clearly show that the lines of adsorbed ethylene on Zn-X are broader than those on Na-X and Cd(I)-X, though they all have similar shifts.
There are few factors which contribute to the broadening of the line. These factors may operate individually or in concert: (a) the presence of more than one unresolved line, (b) the presence of paramagnetic impurities, and (c) dipolar coupling.

The infrared spectra of adsorbed ethylene on Zn-Y (80), show only one surface species. Thus, the first factor can be ruled out. It is certain that commercial zeolite contains some paramagnetic impurities, but since all samples were prepared from the same batch, then the contribution of the paramagnetic centers to the line broadening must be the same in all systems. Finally, Yates and Muha (142) measured the proton NMR spectra of adsorbed ethylene on Li-, Na-, K-, Ag-, Ba-, and Cd-X before and after converting the surface OH groups to OD groups. They found no change in either the chemical shifts or the line widths of the adsorbed ethylene. Thus, they ruled out the possibility that the hydroxyl groups may contribute to the broadening of the ethylene line by dipolar coupling or exchange mechanism. Thus we may be forced to invoke the hypothesis that the rotation of ethylene is slowed down by some sort of interaction with the OH groups at nearby sites or with the oxide framework. These hydroxyl groups are known to be on these zeolites even after heating at a temperature above 400°C (78).

As can be seen from Table (8), butene-1 forms π-complex species upon the adsorption on Cd-X. The terminal carbon =CH₂ exhibits a downfield shift relative to the free molecules. This
shift increased as the concentration of Cd ions increased in the lattice. Obviously, Cd(II)-X is a good adsorbent for both ethylene and butene-1.

If one examines the chemical shift data of $\equiv\text{CH}_2$ carbon of adsorbed butene-1 on Cd and Ag ions, a distinct trend of behaviour can be observed. For Cd ions, the shift of this carbon is downfield, whereas for Ag (86) it is upfield with respect to the resonance line of the free molecules. This can be interpreted in terms of Dewar's model presented in Chapter (IX), as due to back-donation of silver d orbitals to the olefin orbital (86). Such d orbital contribution is minimal in the case of olefin-Cd complexes.

The chemical shift measurements of butene-1 on Zn-X were less accurate because of the isomerization reaction.

Ethylene On Zeolite A

The shifts of adsorbed ethylene and ethane along with their coverages, and their line widths are shown in Table (10). As can be seen from Table (10), ethylene adsorbs on the cations in a metal-olefin $\pi$-complex fashion, and the chemical shift is sensitive to the cation type in the lattice.

The data reported in Table (10), suggests that the shift of adsorbed ethylene increases with the increase in the cation polarizing power, in marked contrast to the trend of adsorption found on zeolites X. In the latter system, the shift
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>C₂H₆</th>
<th>ΔH</th>
<th>Δmolec./M⁺²</th>
<th>0 mm/g</th>
<th>0 ppm</th>
<th>ΔH</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn₄Na₄A</td>
<td>5.9</td>
<td>0.5</td>
<td>-0.9</td>
<td>1.2</td>
<td>90</td>
<td>0.9</td>
<td>30</td>
</tr>
<tr>
<td>Zn₆A</td>
<td>6.2</td>
<td>0.5</td>
<td>-0.5</td>
<td>1.2</td>
<td>100</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>Cd₄Na₄A</td>
<td>4.8</td>
<td>0.5</td>
<td>-0.5</td>
<td>1.1</td>
<td>125</td>
<td>1.1</td>
<td>35</td>
</tr>
<tr>
<td>Cd₆A</td>
<td>2.9</td>
<td>0.2</td>
<td>-0.2</td>
<td>0.9</td>
<td>135</td>
<td>0.9</td>
<td>10</td>
</tr>
<tr>
<td>Ca₄Na₄A</td>
<td>4.2</td>
<td>0.2</td>
<td>-0.2</td>
<td>1.0</td>
<td>120</td>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>Na₁₂A</td>
<td>1.0*</td>
<td>0.2</td>
<td>0.2</td>
<td>1.0*</td>
<td>260</td>
<td>0.2</td>
<td>180</td>
</tr>
</tbody>
</table>

*Expressed in mm/gm. Positive shifts to lower field. The line widths are corrected for apodization. The shifts are measured relative to the free molecules.
Table 10. Chemical Shifts of Adsorbed Ethylene and Ethane on Zeolite A

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>C₂H₄</th>
<th>C₂H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ ppm</td>
<td>ΑH</td>
</tr>
<tr>
<td>Zn₄Na₄A</td>
<td>6.2</td>
<td>90</td>
</tr>
<tr>
<td>Zn₆A</td>
<td>5.9</td>
<td>100</td>
</tr>
<tr>
<td>Cd₄Na₄A</td>
<td>4.2</td>
<td>125</td>
</tr>
<tr>
<td>Cd₆A</td>
<td>4.8</td>
<td>135</td>
</tr>
<tr>
<td>Ca₄Na₄A</td>
<td>4.2</td>
<td>120</td>
</tr>
<tr>
<td>Na₁₂A</td>
<td>2.9</td>
<td>260</td>
</tr>
</tbody>
</table>

* Expressed in mm/gm.
Positive shifts to lower field.
The line widths are corrected for apodization.
The shifts are measured relative to the free molecules.
on Zn is similar to that on Na ions despite the difference in their electrostatic potentials. This is because of the shielding of the Zn ions by its neighbouring oxygens, which is enhanced by the repulsion between the ethylene $\pi$-electrons and the oxygens. Then, why is not a similar degree of screening observed in the case of Zn in zeolite A? Although the crystal structure of Zn-X zeolite has not been well studied, and the exact location of Zn ions is not known, the crystal structure of Zn-A and Zn locations in the lattice are known(63). In hydrated Zn-zeolites A, four Zn ions are $0.66\text{Å}$ away from the plane of the six-membered rings inside the central cage (63). After heating the sample at $400^\circ\text{C}$, this distance may be reduced, but these ions could still be extended into the cage, hence minimizing the degree of shielding. Another factor which may reduce the shielding of Zn ions by neighbouring oxygens is that these ions are pulled out of their original positions upon the adsorption of ethylene, as in the case of ethylene on Fe$^{+2}$-A (143). Thus, the $\pi$-electron-cation interaction becomes the predominating force, and the correlation between the shift and the polarizing power of the ion is possible. Forster and Seele\-mann (144) found that the C=C stretching frequency is influenced by the Zn ion polarizing power in ZnA zeolite.

If the above argument is valid, then the shift of ethylene on Ca in CaA should be equal in magnitude to that on CdA, because both ions are associated with similar electrostatic
potentials. Table (10) shows that this is correct.

It is interesting to note that, the central cage void volume contributes to the broadening of the NMR line. The broadest line is that of the adsorbed ethylene on Na-A, though its shift is the smallest, and the narrowest line is that on Zn4Na4A, despite it shows the largest chemical shift (see Table 10). In the latter system, there is a relatively large space for the adsorbed ethylene to rotate. However, in Na-A central cage, the adsorbed molecules are short distances apart, hence a restricted rotation results from the possible interactions between themselves.

Isomerization Of Butene-1

The isomerization of butene-1 on Zn- and Cd-X zeolites was studied in the temperature range of 28-130°C, and on Na-X at 240°C. The C-13 NMR spectra during a typical kinetic run are shown in Figure (24). The common features of these spectra are that, the peaks assigned for the olefinic carbons of butene-1 fall, while only one peak rises with time. The latter is that of the olefinic carbons of cis and trans isomers. In addition, the -CH2- and -CH3 lines of the adsorbed butene-1 also fall as the time elapsed. A new line is developed between these lines, which is assigned for the CH3 group of trans isomer. Initially, the line for cis methyl group is superimposed on the -CH3 line.
Figure 24

Carbon-13 spectra during the isomerization of butene-1 over Zn(I)-X. The sample was preheated at 400°C in vacuo.
of butene-1. However, at equilibrium, the only lines shown in these spectra are those for methyl carbons of trans and cis isomers.

The present views for the isomerization of butene-1 suggest that for base catalyzed reactions, butene-1 loses a proton, and thus forms an allylic species. This surface reaction is followed by the readdition of hydrogen from the surface to form isomeric olefins. This is called carbanion ion mechanism (144). This mechanism is operating in butene-1 isomerization over ZnO (52). In general, for a base catalyzed reaction, the cis isomer is the predominant product (145). On the other hand, for acid catalyzed reaction, the isomerization proceeds via the formation of carbonium ions. These are formed by protons transferred from acidic sites to one of the olefinic carbons. The carbonium ions undergo further surface reaction by losing a proton, thus regenerating the acid sites again and forming cis and trans isomers. Over acidic catalysts, the trans/cis ratio is always greater than one (146).

The C-13 spectra of the isomerization of butene-1 over zeolites do not show surface intermediates. However, at equilibrium, trans to cis ratios in all systems predict the formation of carbonium ions (Table 11). The trans/cis ratios are determined from the relative intensities of the well resolved -CH₃ lines of the two isomers. Increasing the pretreatment temperature of Zn-X catalysts from 300 °C to 400 °C,
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pretreatment Temperature (°C)</th>
<th>Temperature at Which the Reaction Occurs (°C)</th>
<th>Initial Rate × 100 min⁻¹</th>
<th>trans/cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(I)-X</td>
<td>300</td>
<td>95</td>
<td>0.057</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>110</td>
<td>0.018</td>
<td>0.6</td>
</tr>
<tr>
<td>Zn(II)-X</td>
<td>400</td>
<td>28</td>
<td>0.016</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>28</td>
<td>too fast to measure</td>
<td></td>
</tr>
<tr>
<td>Cd(I)-X</td>
<td>300</td>
<td>125</td>
<td>0.016</td>
<td>1.3</td>
</tr>
<tr>
<td>Cd(II)-X</td>
<td>300</td>
<td>96</td>
<td>0.075</td>
<td>1.5</td>
</tr>
<tr>
<td>Na-X</td>
<td>300</td>
<td>240</td>
<td>0.033</td>
<td>1.0</td>
</tr>
</tbody>
</table>
favors the carbanion ion mechanism as judged from the trans/cis ratio. The isomerization of butene-1 over Cd-X zeolites preheated at 400°C was difficult to measure because the reaction was slow, hence higher temperatures than 180°C were required. At higher temperatures polymerization occurred.

The disappearance rate of adsorbed butene-1 can give a reliable measure of the catalytic activity of zeolite samples. This was done kinetically by measuring the height and the width at half height of the line assigned for the -CH₂-carbons for each spectrum. The product of these numbers is proportional to the area of the peak. This product was then taken to be proportional to the concentration of the C-13 nuclei giving rise to the line in question. Plotting the area of the -CH₂-peaks vs time for each run, initially gives a straight line whose slope is the initial rate for the isomerization of butene-1 to butene-2. This linear relationship indicates that the isomerization reaction is first order with respect to the adsorbed butene-1 on Na-, Zn-, Cd-X. Cross et al. (147) found first order kinetics for the isomerization of butene-1 over transition metals containing X zeolites.

The comparison between the catalytic activities of Zn-X and Cd-X zeolites should not be made directly from the rates shown in Table 11. This is because the isomerization of butene-1 was measured at different temperatures depending on the catalytic activity of each sample. In addition, it was impossible to
obtain several spectra for the isomerization of butene-1 over Zn(II)-X preheated at 300 °C, because the reaction was completed after a short time (30 mins).

However, examining the data given in Table 11 may suggest that the Zn(II)-X zeolite is a good catalyst for the isomerization of butene-1. Over Zn(II)-X zeolite, the isomerization takes place at 28 °C, while that over Cd-X proceeds at higher temperatures (96-125 °C). This implies that the acidity of the catalyst must play an important role in the catalytic isomerization. Ward (78) reported that equal concentrations of Bronsted acidic centers are on Cd- and Zn-X zeolites, but the latter contains stronger sites. On both samples, it is likely that the active centers for carbanion and carbonium ions are respectively, the $M^{+2}$, and the protonic centers on the surface (78). $M^{+2}$ stands for the Zn or Cd ions. Furthermore, the catalytic activities for the isomerization reaction increase with the concentration of the exchanged ions in the lattice for both Zn-X and Cd-X zeolites. The increase of the activity with the increase of Zn ion concentration has been reported by Otsuka (149), and Cross (148).

Butene-1 polymerizes over Zn- and Cd-exchanged zeolites at room temperature. The C-13 spectra for butene-1 on these zeolites were poor because of the overlapping lines of the reaction products.
The products of the polymerization reaction were collected. Butene-1 was adsorbed on 5 gm of the catalyst in a Pyrex tube. The tube was sealed off, and left for at least 4 hr at room temperature. Then, the products were collected in a separate tube which was connected to the one containing the sample. The collection was carried out by immersing the tube in a liquid nitrogen Dewar, followed by heating the catalyst slowly up to 200 °C to desorb the products (cracking of some of the products may occur). Finally, the attached tube was then sealed off. The mass spectroscopic analysis of the desorbed products showed butene-2 as a major product, and a small amount of C₈ olefinic compounds which may include, octene-2, octene-1, 2-methylheptene-1 and 5-methylheptene-3. These products suggest two paths for this reaction. First, is the formation of carbonium ions which leads to the formation of butene-2. Second, is the reaction between the carbonium ions and butene-1 either in the gas phase or adsorbed on the surface to form the olefinic compounds mentioned above, and possibly higher molecular weight compounds. The latter may be trapped inside the zeolite cage.
Hydrogenation of Ethylene Over Zn- and Cd-zeolite Types X and A

The hydrogenation of olefins over zeolites containing metals has been extensively studied (149-156). Their catalytic activities are greatly affected by the method of preparation, pretreatments, and the reduction temperatures. Furthermore, it was found that the activity of Pd-zeolite was modified by increasing the acidity of the support (156). This was achieved by exchanging Na ions first with divalent ions, then Pd ions were introduced into the lattice. These results were interpreted in terms of the interaction of the support with Pd which in turn modified the electronic configuration of the metal.

The hydrogenation of olefins over cation exchanged zeolites has received far less attention than zeolites containing metals. Herein, we report that Zn- and Cd-zeolites are active hydrogenation catalysts. The hydrogenation of ethylene is a convenient, simple model for this classic catalytic reaction. Furthermore, since the NMR technique was utilized in the present studies, it is necessary to use simple, symmetric and weakly bound molecules to the surface. Certainly, ethylene meets all of these requirements.

Figures (25-32) show the proton spectra of ethylene hydrogenation over Zn(I)-X, Zn(II)-X, Cd(I)-X, Cd(II)-X, Zn$_4$Na$_4$A, Zn$_6$A, Cd$_4$Na$_4$A, and Cd$_6$A. The Na-X and Na-A were inactive at temperatures below 450°C. As can be seen from NMR
The proton NMR spectra during hydrogenation of ethylene over zeolite X and A.

25. Zn(I)-X
26. Zn(II)-X
27. Cd(I)-X
28. Cd(II)-X
29. Zn$_4$Na$_4$A
30. Zn$_6$A
31. Cd$_4$Na$_4$A
32. Cd$_6$A
spectra, the peaks of adsorbed ethylene decrease, while those of ethane increase with time. In addition, there is no line for adsorbed hydrogen in any spectrum.

The main purpose of this work was to study the hydrogenation reaction kinetically in order to understand the effect of the cation type and the cation concentrations on the catalytic activity of these zeolites. However, since these zeolites are catalytically active at high temperatures, there is always the possibility of a side reaction, such as the polymerization of ethylene. The products of such reaction might not be seen in the proton spectra because of their broad lines. Therefore, the following discussion is certainly qualitative in nature.

By examining the temperature at which each catalyst is active, it is possible to say that the activity increases with the increase in the concentration of Zn or Cd ions in the lattice. This trend of activity is in contrast to that observed when propene is hydrogenated over Y- and Cr-zeolites. In this reaction, the activities decreased as the exchange of Na by Cr or Y ions exceeds certain limits (157).

The mechanism of hydrogenation on zeolites is not known. Topchieva (157) used the concept of donor-acceptor complexes in explaining the kinetic data of olefin hydrogenation over Cr- and Y-zeolites. Clearly, more research is necessary to reach an adequate mechanistic formula for the hydrogenation of
olefins over cation exchanged zeolites.
XII. CONCLUSIONS

The general conclusions which can be drawn from the present investigation are:

(1) There is no simple correlation between the catalytic hydrogenation and the electron concentration in ZnO conduction band. Doping with Li ions decreases the catalytic hydrogenation of ethylene. Whereas, doping with small amounts of Ga ions increases the catalytic activity, while heavy doping decreases it.

(2) We checked the hypothesis of the boundary layer theory. It states that decreasing the electron concentration in the conduction band, may enhance the adsorption since ethylene donates electrons to the surface upon adsorption. The chemical shifts, and the adsorption measurements indicate that the incorporation of Li ions into ZnO lattice (which decreases the number of electrons in the conduction band) eliminates the active sites for ethylene adsorption, whereas doping with Ga ions increases the adsorption capacity of the oxide and the chemical shift value of the adsorbed ethylene. It seems that the electrons in the conduction bands are necessary for the weak chemisorption of ethylene.

(3) The adsorption of ethylene takes place on the Zn
ions. This contradicts Kokes's view that the stabilization of ethylene π-complex occurs on the oxide part of Zn-O pair. The conclusion that ethylene adsorbs on the Zn ion is drawn from the correlation between the chemical shifts of the adsorbed olefins on ZnO and the thermodynamic stabilities of the corresponding olefin-Ag complexes.

Further support to the above postulate was obtained from the successive adsorption of ethylene on ZnO previously covered with CO. CO adsorbs on ZnO surface in a OC-Zn fashion. Thus, if the above assumption is correct, ethylene would displace CO since both molecules are competing for the same site. This was exactly the case; the successive adsorption of ethylene displaced a major portion of the chemisorbed CO.

(4) Ethylene adsorbs on the cations (Na, Zn or Cd) present in the zeolite types A and X. The adsorbed species resonate at a lower field relative to the free molecules, which indicates that ethylene forms π-complexes with these ions.

(5) The chemical shift of adsorbed ethylene on zeolite A containing Zn, Cd or Na ions is in accordance with the polarizing power of these ions: the shift of ethylene on Zn-A is the largest, and that on Na-A is the lowest. However, such correlation does not exist in the case of ethylene adsorbed on Zn-, Na-, and Cd-X zeolites. The shift of adsorbed ethylene on Zn-X is equal in magnitude to that on Na-X, however, on Cd-X, ethylene underwent a specific interaction with the Cd ions. The
small shift of adsorbed ethylene on Zn-X is interpreted as a result of shielding by the neighbouring oxygen, which prohibits the close approach of ethylene to a small ion such as Zn.

(6) The adsorption capacity of zeolite X containing Zn or Cd ions is determined by the number of ions at sites accessible to the ethylene molecules (sites II and III). However, the amount of ethylene adsorbed on zeolites A, is largely decided by the void volume of the central cage. Fully exchanged Zn-zeolite types A and X showed poor adsorption capacities.

(7) The catalytic isomerization of butene-1 on zeolite X is determined by the type and the concentration of the ions in the supercage. Fully exchanged Zn-X is a good catalyst for the isomerization of butene-1. Apparently, Zn-zeolites are better catalysts than Cd-zeolites as indicated by the rate constants of the isomerization reaction. The trans/cis ratios indicate that the reaction proceeded over these catalysts via the formation of carbonium ions.

(8) Zn- and Cd-zeolite types A and X are hydrogenating catalysts. Although we were not able to calculate the rate constants for the ethylene hydrogenation reaction over these catalysts, because of the polymerization of some of the adsorbed species. It is possible to say that, at least for zeolite X, the activity increases as the concentration of Zn or Cd ions increases in the lattice.
It is hoped that the work presented in this thesis would increase our knowledge about the mode of adsorption of olefins on ZnO and zeolites, and will help to stimulate further research in that direction.
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