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CATALYTIC ALUMINA: ITS DUAL-SITE NATURE IN ISOMERIZATION AND DEUTERIUM EXCHANGE REACTIONS OF UNSATURATED HYDROCARBONS

by

Michael P. Rosynek

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN CHEMISTRY

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I. INTRODUCTION

The underlying purposes of any investigation of heterogeneous catalytic phenomena are the elucidation of the structural and chemical nature of the surface sites on the catalyst that promote the process being studied, and a determination of the importance of various transport effects on the system. The correlation of this information with observed kinetic and mechanistic data on the reaction or adsorption process in question then allows intelligent predictions to be made about the behavior of related catalytic systems. The present investigation was undertaken to obtain more information about the sites on catalytic alumina that are active for certain reactions of unsaturated hydrocarbons.

Historically, one of the first uses of catalytic alumina was for the dehydration of alcohols to corresponding mono-olefins having the same carbon skeleton as the original alcohol [71, 72, 150]. This retention of skeletal configuration was the feature of these reactions that made alumina unique among the various acidic dehydration catalysts in use at that time. Subsequently, alumina was used as an active catalyst for various other hydrocarbon conversions, viz., polymerization [37, 38] and hydrogenation [65, 153] of olefins and, at sufficiently high temperatures, cracking of olefins to smaller mono- and di-olefins [56]. In addition, alumina is an effective catalyst for promoting the exchange of certain olefinic [64, 85] and aromatic [98, 129] hydrogen atoms with gaseous deuterium, and for the double-bond isomerization of light olefins.
with retention of skeletal configuration [24, 54, 95, 115]. These latter two processes are of particular interest for the present study and will be discussed in detail later.

Prior to this discussion, however, it is instructive to examine at some length the structural and crystallographic information that is available about alumina, since a thorough knowledge of the bulk and surface structure of any material is a prerequisite to a proper understanding of its catalytic properties.

A. Crystallography of alumina

The aluminum oxide-aluminum hydroxide system has been extensively studied during the last fifty years [19, 22, 43, 44, 77, 97], and considerable data have been accumulated on lattice constants [23, 80, 136, 159], phase transitions [1, 18, 19, 43, 44, 52, 70, 79, 102, 119, 121, 149, 156, 157, 160], dehydration schemes [29, 102, 108, 111, 120], and lattice structures [58, 136, 145, 146, 147]. At least eight crystallographically distinct aluminas have been described [88, 119, 124], not all of which are universally accepted. The appearance of a recent review [91] has finally allowed a relatively complete description to be presented of this rather complicated system. Much of the following descriptive material is based on this review.

1. Aluminum hydroxides and oxidehydroxides

A discussion of the crystallography of the aluminas must begin by considering the various hydroxides and oxidehydroxides from which the aluminas are obtained by dehydration. Three
trihydroxides of aluminum are recognized, viz., gibbsite, bayerite, and nordstrandite, all having the nominal composition Al(OH)₃ or Al₂O₃·3H₂O. In addition, two oxidehydroxides exist, boehmite (two forms) and diaspor, having the composition AlO(OH) or Al₂O₃·H₂O. Each of these six materials has a distinct crystallographic structure and dehydration scheme by which the various aluminas are formed.

a. Gibbsite. Gibbsite is the most common of the aluminum trihydroxides and is the principal constituent of North and South American bauxite. It is best prepared in the laboratory by slow addition of carbon dioxide to an aqueous solution of sodium aluminate at 20°C, to a final pH of greater than 12 [48, 49, 103]. Both synthetic and naturally occurring gibbsite always contain 0.2-0.3% Na₂O. The structure of gibbsite is based on a double-layer AB of cubic close-packed hydroxyl groups, with two-thirds of the octahedral holes occupied by aluminum atoms [100]. The lattice is somewhat deformed due to the alternation of filled and vacant octahedrons, the occupied ones being smaller and the vacant ones larger [88]. The stacking of the double-layers may be represented by ABBAABBA, etc. The layers are held together by hydrogen bonds between the hydroxyl groups, and the resulting distance between two adjacent A or B layers is 2.81 Å, compared with 2.03 Å between A and B [88]. The structure is shown schematically in Figure 1.

The thermal dehydration of gibbsite can follow two separate pathways, depending on whether the process is carried out in air or under vacuum, as shown below:
FIGURE 1. Gibbsite Structure
The classification and structures of the various aluminas formed by these dehydrations will be discussed later.

b. Bayerite. Bayerite does not occur naturally, but it can be prepared in the laboratory by the hydrolysis of aqueous aluminum ethylate solutions at a temperature of less than 70°C [139] or by the oxidation of amalgamated aluminum with water at 25°C [130]. Various other methods have been used, but none of these produce a pure product [91]. In contrast to gibbsite, bayerite can be prepared with no substantial alkali content. The structure of bayerite is somewhat uncertain at present because no single crystals are available for accurate X-ray studies. It is very likely similar to gibbsite with double-layers of hydroxyl groups stacked as ABABAB, etc., and with two-thirds of the octahedral interstices occupied by aluminum atoms. The layers are held together by hydrogen bonds between the hydroxyls, with a distance between adjacent A or B layers of 2.64 Å, and between A and B layers of 2.07 Å [91].

The dehydration of bayerite is somewhat similar to that of gibbsite, and is also influenced by carrying out the process
in air or under vacuum:

\[
\begin{align*}
\text{BAYERITE} & \xrightarrow{230^\circ \text{air}} \eta-\text{Al}_2\text{O}_3 & \xrightarrow{850^\circ} \theta-\text{Al}_2\text{O}_3 & \xrightarrow{1200^\circ} \alpha-\text{Al}_2\text{O}_3 \\
 & \xrightarrow{180^\circ} \text{BOEHMITE} & \xrightarrow{450^\circ} \gamma-\text{Al}_2\text{O}_3
\end{align*}
\]

\[
\begin{align*}
\text{BAYERITE} & \xrightarrow{200^\circ \text{vac}} \rho-\text{Al}_2\text{O}_3 & \xrightarrow{750^\circ} \gamma- \text{or} \eta-\text{Al}_2\text{O}_3 & \xrightarrow{1200^\circ} \alpha-\text{Al}_2\text{O}_3 \\
 & \xrightarrow{180^\circ} \text{BOEHMITE}
\end{align*}
\]

c. Nordstrandite. The recently-discovered nordstrandite occurs naturally in Serawa and Guam. It is prepared synthetically by the aging of gelatinous hydroxide in the presence of chelating agents such as ethylenediamine, ethylene glycol, or EDTA under conditions which in the absence of these agents would produce bayerite [20, 57]. The structure of nordstrandite also consists of double-layers of hydroxyls, with aluminum atoms filling two-thirds of the octahedral interstices. The stacking has been described [2, 88] as ABABBABA, etc., which is a combination of the stackings in gibbsite and bayerite. Other X-ray data [126], however, indicate a triclinic unit cell containing only the gibbsite stacking. The dehydration of nordstrandite is identical to that of bayerite shown above.

d. Diaspore. Diaspore occurs naturally in some types of clay and bauxite. It can be prepared by the hydrothermal conversion of active \(\alpha-\text{Al}_2\text{O}_3\) at 375-450°C and 60-100 atm of water pressure [138], or by the conversion of any of the other oxides or hydroxides of aluminum at 275-425°C and a
water pressure of 140 atm, with a seeding of diaspore present [40, 86, 104]. The structure of diaspore is a cubic close-packed lattice of oxygen atoms and hydroxyl groups with aluminum atoms in certain of the octahedral holes. It is built up essentially of infinite strips of the brucite type, linked together by sharing of oxygen atoms at the corners of AlO$_6$ octahedra [155].

An easily visualized representation of the diaspore structure has been given by van Oosterhout [144]. It consists of a series of chains of the form shown in Figure 2a. A side view of such a chain appears as in Figure 2b. Two of these chains can be arranged anti-parallel to each other as in Figure 2c, a schematic representation of which is given in Figure 2d. The double-chain units are then arranged as in Figure 2e to give the diaspore structure.

Diaspore is unique among all the trihydroxides and oxidehydroxides in going directly to corundum upon dehydration:

\[
\text{Diaspore} \xrightarrow{450^\circ \text{air}} \alpha\text{-Al}_2\text{O}_3
\]

e. Boehmite. Boehmite exists in two forms, viz., well-crystallized boehmite and gelatinous or pseudo-boehmite. The latter is the main constituent of European bauxites and is prepared by the neutralization of aqueous solutions of aluminum salts, allowing the precipitate to age somewhat in contact with the mother liquor [81, 151, 152]. Well-crystallized boehmite is the end product of the aging of aluminum hydroxide gel at 80°C and a pH of greater than 12
FIGURE 2. Diaspore Structure
[103]. In contact with alkaline solutions, gelatinous boehmite slowly converts into the well-crystallized form via bayerite and gibbsite, an unexplained phenomenon considering the similarity between the two forms of boehmite [91]. The structure of well-crystallized boehmite is related to that of diaspore. Aluminum atoms are surrounded by distorted groups of oxygen atoms, with these octahedra linked to form a complex layer structure [155]. Using the representation illustrated above for diaspore, the structure of well-crystallized boehmite is shown schematically in Figure 3. The structure of pseudo-boehmite is similar to that of the well-crystallized form, except that excess water is bound between the layers with strong hydrogen bridges, causing an irregular extension of the lattice and imperfect stacking of the layers [88, 89].

The dehydration of boehmite is similar for both forms, except for differences in certain phase transition temperatures:

\[
\begin{align*}
\text{BOEHMITE (well-crystallized)} & \xrightarrow{450^\circ \text{air}} \gamma-\text{Al}_2\text{O}_3 \xrightarrow{600^\circ} \delta-\text{Al}_2\text{O}_3 \\
 & \quad \downarrow 1050^\circ \\
 & \quad \alpha-\text{Al}_2\text{O}_3 \xleftarrow{1200^\circ} \theta-\text{Al}_2\text{O}_3 \\
\text{BOEHMITE (gelatinous)} & \xrightarrow{300^\circ \text{air}} \gamma-\text{Al}_2\text{O}_3 \xrightarrow{900^\circ} \delta-\text{Al}_2\text{O}_3 \xrightarrow{1000^\circ} \\
 & \quad \downarrow 1200^\circ \\
 & \quad \alpha-\text{Al}_2\text{O}_3 \xleftarrow{1200^\circ} \theta-\text{Al}_2\text{O}_3
\end{align*}
\]

2. Classification of aluminas

A number of systems have been proposed to classify the
FIGURE 3. Well-crystallized Boehmite Structure
various aluminas into practical groupings. The most useful of these appears to be that of Ginsberg et al. [50], later modified by Lippens [88], which is based on the temperature at which the aluminas are obtained from the various hydroxides by dehydration. This system divides the aluminas into two principal groups:

- **γ-Group**: \( \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O} \), where \(0 < n < 0.6\)
  Obtained by dehydrating at \(< 600 ^\circ\text{C}\)

- **δ-Group**: \( \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O} \), where \(n=0\)
  Obtained by dehydrating at temperatures of 900-1000 ^\circ\text{C}.

The γ-group includes \(\rho^-, \chi^-, \eta^-\), and \(\gamma-\text{Al}_2\text{O}_3\), while the δ-group consists of \(\kappa^-\), \(\theta^-\), and \(\delta-\text{Al}_2\text{O}_3\). \(\alpha-\text{Al}_2\text{O}_3\) is placed in a class by itself, being totally anhydrous material obtained at temperatures of 1200 ^\circ\text{C} or higher (except from diaspore).

With rare exceptions, the term "catalytic alumina" refers to members of the γ-group, and particularly to \(\eta^-\) and \(\gamma-\text{Al}_2\text{O}_3\) and mixtures of these two. Examination of the various dehydration schemes shown above reveals that, while it is difficult to prepare \(\eta^-\text{Al}_2\text{O}_3\) free of \(\gamma-\text{Al}_2\text{O}_3\), the latter can be prepared in relatively pure form by dehydrating either of the boehmites at a temperature not exceeding 550 ^\circ\text{C}. However, since the catalytic properties of \(\eta^-\) and \(\gamma-\text{Al}_2\text{O}_3\) are virtually identical, a suitable catalyst can also be obtained by the vacuum dehydration of bayerite at a temperature of less than 700 ^\circ\text{C}. Both of these methods are used to prepare commercial alumina catalysts [149]. All subsequent references to "active alumina" or "catalytic alumina" in the
present work will imply \( \eta^- \) or \( \gamma^-\text{Al}_2\text{O}_3 \) or mixtures of the two.

3. Structures of aluminas

a. \( \gamma^-\text{Alumina} \). The lattice of \( \gamma^-\text{Al}_2\text{O}_3 \) is closely related to that of spinel (\( \text{MgAl}_2\text{O}_4 \)), but is strongly disordered [143]. A tetragonal deformation exists that increases with increasing water content [156]. The unit cell is formed by a cubic close-packing of 32 oxygen atoms, with the resulting 24 cation interstices (16 octahedral, 8 tetrahedral) being filled by 21 1/3 aluminum atoms and 2 2/3 vacancies. Some workers [73, 148] believe that the octahedral holes are completely filled and the 2 2/3 vacancies are entirely tetrahedral, while others [125] have found just the reverse situation.

b. \( \eta^-\text{Alumina} \). The structure of \( \eta^-\text{Al}_2\text{O}_3 \) is very similar to that of \( \gamma^-\text{Al}_2\text{O}_3 \), and, in fact, the two were once thought to be identical materials [119]. The principal difference between them is the type of lattice disorder, due to pseudo-morphosis relations between the oxides and hydroxides [90]. \( \eta^-\text{Al}_2\text{O}_3 \) is often regarded as a cubic spinel, but tetragonal deformation, similar to that in \( \gamma^-\text{Al}_2\text{O}_3 \), undoubtedly exists [88, 156]. The disorder in both \( \gamma^- \) and \( \eta^-\text{Al}_2\text{O}_3 \) is determined mainly by the disorder of the aluminum atoms, particularly those in tetrahedral positions [91].

c. \( \chi^-\text{Alumina} \). The lattice of \( \chi^-\text{Al}_2\text{O}_3 \) is hexagonal, with \( a = 5.56 \text{ Å} \) and \( c = 13.44 \text{ Å} \) [124]. The structure is nearly cubic, but with a definite trigonal deformation. A one-dimensional disorder exists in the stacking of the oxygen layers perpendicular to the c-axis, similar to \( \eta^-\text{Al}_2\text{O}_3 \) but
much stronger.

d. δ-Alumina. Some controversy exists [91] about the X-ray patterns of δ-Al₂O₃, probably due to differences in methods of preparation. Electron diffraction patterns of δ-Al₂O₃ obtained from boehmite single crystals show a long c-axis of 23.5 Å [91]. The lattice is probably a superstructure of three Al₂O₃-spinel cells containing an integral number of aluminum atoms. The vacant positions are ordered on a four-fold screw axis parallel to the c-axis [88, 122, 137].

e. θ-Alumina. θ-Al₂O₃ is monoclinic and isomorphous with β-Ge₂O₃ [124]. The lattice parameters are a = 11.24 Å, b = 5.72 Å, c = 11.74 Å, and β = 103°20'. The oxygen lattice is still nearly cubic close-packed, with aluminum atoms mostly in tetrahedral positions.

f. κ-Alumina. The hexagonal structure of κ-Al₂O₃ is similar to that of χ-Al₂O₃, with a = 9.71 Å and c = 17.86 Å [124]. Close-packed oxygen layers parallel to the cleavage plane of gibbsite are persistent through both χ- and κ-Al₂O₃ and probably also in α-Al₂O₃ obtained at higher temperatures.

g. ρ-Alumina. ρ-Al₂O₃ is a transient species that converts to η- or γ-Al₂O₃ during the vacuum dehydration of the three aluminum trihydroxides, and consequently no structural information has yet been obtained for this modification.

h. α-Alumina. α-Al₂O₃ is the eventual end product of the thermal dehydrations of all the oxides, trihydroxides, and oxidehydroxides of aluminum. It is totally anhydrous with virtually no deformation, and has a well-ordered cubic
close-packed lattice of oxygen atoms, with aluminum occupying two-thirds of the octahedral interstices [91].

The persistence of the basic cubic close-packed oxygen lattice during dehydration of all of the aluminas indicates that cation displacement in the lattice is the most important mechanism for the formation of the different forms of alumina. It is interesting to note that in going from the hydroxide stage to the corundum (α-Al₂O₃) stage, both of which have aluminum atoms only in octahedral holes, stages are passed in which aluminum exists in tetrahedral positions, due principally to the lattice disorder generated by the dehydration process [91].

B. Surface properties of active alumina

Having discussed the bulk structures of the various aluminas, an examination will now be made of the characteristics of the surface of active (γ- and η-) alumina, since it is these surface properties that are of primary significance for catalytic purposes. The most important features of the surface of partially dehydrated (active) alumina are the existence of isolated hydroxyl groups and the inherent acidity of the surface. Each of these topics will be discussed in the following sections, as well as information presently available regarding the nature of the surface sites on aluminas that are active for certain hydrocarbon conversions.

1. Surface structure

a. Hydroxyl groups. The existence of at least a portion of the residual water of partially dehydrated alumina in the form of surface hydroxyl groups is a well-established
characteristic of this catalyst [14, 16, 33, 45, 47, 61, 84, 111, 127, 142]. The condensation of these hydroxyl groups upon dehydration is one of the factors that introduces the strain and disorder that exist on the surface of catalytic alumina [17, 29, 108, 110, 111].

Peri [111] has made an extensive study of the nature and environment of the hydroxyl groups remaining on the surface of alumina after partial dehydration. Assuming the initial surface to consist only of the (100) face of γ-Al₂O₃ with a monolayer of hydroxyl groups, he used a computer program to simulate random condensation of adjacent pairs of -OH groups, with the restriction that local order on the surface be preserved, i.e., formation of adjacent vacancies or adjacent O⁻ ions was not allowed. This condition allowed the removal of 67% of the surface hydroxyls. Elimination of the local order restriction allowed the removal of 90.4% of the original -OH monolayer, such that no adjacent hydroxyls remained. At this degree of dehydration, visual inspection of the computer representation of the surface revealed that the 9.6% of hydroxyls that remained were of five types, having zero, one, two, three, or four nearest O⁻ ion neighbors. Peri verified this result by observing five distinct O-H stretching bands in the infrared region on γ-Al₂O₃ samples dried at 650°C [108, 110]. He assigned the observed IR bands to the five types of -OH obtained from the computer model as follows:
<table>
<thead>
<tr>
<th>IR Band</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Nearest $O^{=}$ Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3700</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>3733</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>3744</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>3780</td>
<td>3</td>
</tr>
<tr>
<td>A</td>
<td>3800</td>
<td>4</td>
</tr>
</tbody>
</table>

Although Peri's basic assumption in obtaining the computerized surface model, viz., the preferred exposure of only the (100) face on $\gamma$-Al$_2$O$_3$, is somewhat unrealistic, his results are at least qualitatively useful since other workers [127] have also reported evidence for more than one kind of hydroxyl group on the surface of catalytic alumina.

Studies of the lability of hydrogen atoms of the surface -OH groups by replacement with other atoms, particularly gaseous deuterium, indicate that this exchange is almost negligibly slow at 25°C [46, 55, 84, 98]. At 500°C, however, exchange with D$_2$ proceeds with a half-time of less than one minute [55, 84, 127]. These studies have shown that the concentration of -OH groups on the surface of alumina dried at 500-600°C is approximately $2-4 \times 10^{14}$ OH per cm$^2$ of surface.

b. Acidity. The inherent acidity of a partially dehydrated alumina surface is another well-documented feature of this material [53, 82, 94, 95, 99, 132, 140, 150]. The principal point of investigation in this regard has been the nature of the surface acidity, i.e., Brönsted acidity resulting from the surface hydroxyls or other potential proton sources, or Lewis acidity due to some type of electron-deficient
surface structure. Although the -OH groups on the surface may be considered to have varying degrees of partially acidic nature due to their O⁻ environment [111], the majority of work in this area [55, 105, 107, 115], involving titration with organic bases, has confirmed that the acidity of alumina measured at low temperatures (<100°C) is of the Lewis-type, occurring at a concentration of approximately 4–7 x 10¹³ acid sites per cm² of surface [115, 133].

The origin of this Lewis acidity may be partially explained on the basis of the surface structures resulting from partial dehydration. The condensation of adjacent -OH groups on the alumina surface during dehydration causes the removal of certain of the oxygen atoms from the surface layer, resulting in an increasing exposure of aluminum atoms in the underlying interstices with increasing extent of drying. The severe electron-withdrawing effect of the surrounding oxygen atoms imparts an electron deficient nature to the exposed aluminum atoms that results in the observed Lewis acidity. Certain investigators [107, 115] have reported the existence of two different types of Lewis sites on alumina. This observation may be due to the difference in acid strengths of Lewis sites that occur in relatively strain-free regions of the surface and those that occur at more highly strained points, such as domain boundaries [84].

In this regard, the acidity of catalytic alumina is in sharp contrast to that of the related silica-alumina catalysts. While the measurable acidity of alumina at 25°C is almost entirely of the Lewis-type, silica-alumina exhibits
both Lewis acidity and Brönsted acidity [107], and in many cases it is only the latter that is of measurable significance [105]. This comparison will be returned to in a later section when the mechanism of olefin isomerization, a reaction promoted by both types of catalyst, is discussed.

2. Active sites on alumina

The primary reason for studying the surface properties of alumina has been to determine the chemical natures of the sites on the catalyst that promote the various reactions and adsorption processes for which alumina is active. One of the most effective methods of accomplishing this purpose is by the use of various test reactions, i.e., relatively simple reactions whose kinetics and mechanisms may be studied in considerable detail. By investigating such factors as kinetic isotope effects, the variation of certain reaction parameters, and the effect of various poisons on the reaction, considerable information can be obtained about the sites on the catalyst that promote the particular reaction being studied. On alumina, the most widely studied test reactions of this sort have been the double-bond isomerization of various light (five carbon atoms or less) olefins, and the exchange of certain olefinic and aromatic hydrogen atoms, as well as H₂ itself, with gaseous deuterium. A brief summary will now be given of the cogent results obtained from these investigations.

a. Deuterium exchange reactions. The simplest exchange process involving D₂ is the H₂-D₂ equilibration to form HD. This reaction has been extensively studied on alumina [64,
65, 66, 116, 142, 153] and occurs at temperatures as low as 
-124°C [153]. The process is effectively poisoned by the ad-
dition of small amounts of water [65, 116, 153] or by cool-
ing the catalyst in an atmosphere of hydrogen from a pre-
treatment temperature of 650°C to the reaction temperature 
of -100°C [66]. Selective poisoning techniques (to be de-
scribed in detail later) using carbon dioxide have given an 
active site density at 0°C of $1.6 \times 10^{13}$ sites/cm$^2$ for a 
catalyst pretreated at 525°C [142]. Pines and Ravoire [116] 
have proposed that Lewis acid sites (exposed underlying alu-
minum atoms) on the surface are responsible for promoting 
the reaction. They believe that $H_2$ and $D_2$ are adsorbed het-
erolytically on the catalyst, with the $H^+$ and $D^+$ attaching 
to $O^{5-}$ to form $-OH$ and $-OD$, and the $H^-$ and $D^-$ attaching to 
an $Al^{5+}$ to form Al-H and Al-D. Desorption then leads to $H_2$, 
$D_2$, or HD. Water acts as a poison by causing the formation 
of hydroxyl groups and blocking the exposed aluminum atoms, 
thus preventing adsorption of $H^-$ and $D^-$. This mechanism is 
probably consistent with the postulate of Hindin and Weller 
[66] that strain sites on the surface caused by dehydration 
are the active sites, since the formation of such surface 
strain is accompanied by the exposure of underlying aluminum 
atoms and an increase in Lewis acidity, as discussed pre-
viously (p. 17).

Alumina has also been used to catalyze the exchange of 
benzenic hydrogen atoms with gaseous $D_2$ [34, 98, 129] and 
for the $C_6H_6-C_6D_6$ [129] and $CH_4-CD_4$ [84] equilibration reac-
tions. In the main, these processes apparently have much in
common with the $\text{H}_2$-$\text{D}_2$ reaction. They are poisoned by the addition of water [98], and selective poisoning with carbon dioxide has given an active site concentration of $0.8 \times 10^{13}$ sites/cm$^2$ for the $\text{C}_6\text{H}_6$-$\text{C}_6\text{D}_6$ and $\text{C}_6\text{H}_6$-$\text{D}_2$ reactions [129] and $0.5 \times 10^{13}$ sites/cm$^2$ for the $\text{CH}_4$-$\text{CD}_4$ equilibration [84], both measured at $25^\circ\text{C}$. The similarity of these site densities to that described above for the $\text{H}_2$-$\text{D}_2$ equilibration and the similar susceptibilities to poisoning are evidence that all these exchange-type reactions are promoted by the same surface sites on alumina. The mechanism of Pines and Ravoire [116] for the $\text{H}_2$-$\text{D}_2$ equilibration may, in modified form, apply equally well to the $\text{C}_6\text{H}_6$-$\text{D}_2$, $\text{C}_6\text{H}_6$-$\text{C}_6\text{D}_6$, and $\text{CH}_4$-$\text{CD}_4$ processes, with the active sites consisting of exposed aluminum atoms having Lewis acid nature.

The exchange of olefinic hydrogen atoms with gaseous $\text{D}_2$ has also been studied over alumina [64, 85], but these reactions are complicated by the simultaneous double-bond isomerization of the olefins. One of the more unusual features of these olefin exchange reactions on alumina is that deuteration occurs at $25^\circ\text{C}$ with no significant saturation [85]. In a study of a series of cyclic and non-cyclic olefins, Hightower and Hall [63, 64] observed that the only hydrogen atoms that undergo exchange with $\text{D}_2$ at $25^\circ\text{C}$ are those in a vinyl position and those that can acquire a vinyl position via isomerization. They proposed [63] that the acid-base sites of Peri's surface model of alumina [111] are probably strained Al-O-Al linkages that may be involved in the exchange of the vinyl hydrogen atoms by causing dissociative
adsorption of the olefin:

\[
\begin{align*}
\text{Al-O-Al} + \begin{array}{c}
\text{C} \\ \\
\text{H} \\ \\
\text{H}
\end{array} & \rightarrow \begin{array}{c}
\text{C-H} \\ \\
\text{H} \\
\text{H}
\end{array} + \begin{array}{c}
\text{Al} \\ \\
\text{Al}
\end{array}
\end{align*}
\]

or

\[
\begin{align*}
\text{Al-O-Al} + \begin{array}{c}
\text{C} \\ \\
\text{H} \\
\text{H}
\end{array} & \rightarrow \begin{array}{c}
\text{C-H} \\
\text{O}
\end{array} + \begin{array}{c}
\text{Al} \\
\text{Al}
\end{array}
\end{align*}
\]

with the second possibility above considered to be the more likely. Desorption is then accompanied by acquisition of either a neighboring hydrogen atom from the surface or a deuterium atom from the gas phase in a Rideal-type mechanism.

For exchange reactions of various cyclic olefins, Hightower and Hall [64] obtained an exchange site density of \(1.4 \times 10^{13}\) sites/cm\(^2\), again suggesting the inherent similarity of all these \(D_2\) exchange reactions on alumina.

b. Olefin isomerization reactions. The other main type of test reaction that has been used in studies of the alumina surface is the double-bond isomerization of various light olefins [24, 54, 56, 64, 95, 115]. Although these isomerization reactions have been even more extensively studied than the various deuterium exchange processes described above, very little is known about the surface sites that promote them. One of the reasons for this sparsity of information is that no effective poison for these reactions has been found that would give some clue as to the chemical nature of the site density by selective poisoning techniques, as done for the exchange reactions.
The most widely used olefin isomerization has been of the system of n-butenes \([24, 28, 53, 96, 105, 112, 131, 140]\). In an extensive study of this system, Hall and co-workers \([45, 46, 59, 60, 61, 62, 63]\) have found that interconversion of the three n-butenes occurs by a triangular scheme of first-order reactions of the following type:

![Chemical Reaction Diagram]

and that all of the indicated pathways are significant, i.e., none of the six rate constants are negligible. A large primary isotope effect was observed \([61]\) for the isomerization when perdeuterated butene was used as the reactant, indicating that C-H bond rupture occurs in the transition state during both double-bond and cis-trans interconversion.

Details of the isomerization mechanism on alumina are still somewhat uncertain. Originally, it was proposed \([54]\) that a carbonium ion mechanism was responsible for olefin isomerization on these catalysts, and that the transition state separating the carbonium ion and olefin was non-olefinic in nature.

\[
\begin{align*}
&\text{C-C-C-C} \\
&\text{(trans)} \quad \xrightarrow{\text{C-C-C-C}} \quad \text{C-C-C-C} \\
&\text{C=C=C} \\
&\text{cis} \\
\end{align*}
\]

Loss of a proton from the carbonium ion was thought to occur
via a $\pi$-complex:

Subsequent studies [45, 46, 60], however, have made it clear that the active sites for the isomerization process are not protonic in nature at 25°C, and that a classical sec-butyl carbonium ion is not involved [61]. The most common alternate postulate has been that certain of the Lewis acid sites on the catalyst are responsible for promoting the reaction [46, 47, 105, 108, 140], although Hightower and Hall [61] are probably correct in their assessment that the process is considerably more complex than was originally thought and that different sites and transition states operate on the surface during the overall isomerization process.

An interesting comparison may be made between the isomerization of the n-butenes on alumina and on the related, but considerably different, silica-alumina catalysts [21, 74, 75, 87, 93, 109]. As noted previously (p. 17), silica-alumina has considerable Brönsted surface acidity at 25°C in the form of labile -OH groups, and, as might be predicted, interconversion of the n-butenes on this catalyst occurs largely via a carbonium ion intermediate [60, 61], in contrast to the situation on plain alumina. In addition, the
formation of a carbonaceous residue has been observed on the surface of silica-alumina during the initial stages of the reaction [59, 61, 74, 75, 76], a phenomenon never observed with plain alumina [28, 59, 61]. This residue consists principally of polymeric butene [74, 75, 76], and the number of butene molecules in the residue is close to the number hydroxyls on silica-alumina \(1.4 \times 10^{14}/\text{cm}^2\) [59]. This is consistent with the difference in acidities of the -OH groups on the two catalysts, since olefinic polymerization reactions characteristically occur via a carbonium ion mechanism. The Brönsted acidity of the silica-alumina hydroxyls promotes such a mechanism, while the absence of significant protonic acidity on plain alumina prevents such polymerization at 25°C.

c. Various adsorption studies. Additional information about the surface sites on active alumina has been obtained from studies of the adsorption of various materials onto the catalyst. The adsorption of benzene [35, 83, 114, 141] and the n-butenes [108, 112, 114] on alumina have been studied by several investigators, and the results are consistent with those obtained from the various exchange and/or isomerization reactions of these materials discussed previously. Infrared studies [108, 112, 114] of adsorbed benzene and n-butenes indicate that both materials are strongly adsorbed on the so-called "α-sites" or "ion-pair sites" (O⁻ ion with adjacent exposed aluminum atom) or Peri's surface model [111] of partially dehydrated alumina. Peri [114] has obtained a value of approximately \(5 \times 10^{12}/\text{cm}^2\) for the density
of these sites by titration of adsorbed carbon dioxide with 1-butene. Such adsorption would at least be necessary if these sites are responsible for the $D_2$ exchange reactions of olefins and benzene, as discussed above.

The adsorption of ammonia on alumina has also been studied [7, 36, 39, 42, 47, 56, 67, 101, 115, 127, 133], and it appears likely that the adsorption sites at low temperatures (<100°C) are not protonic in nature, since the adsorption is independent of the surface hydroxyls [47, 56]. Infrared studies [36, 112] of adsorbed ammonia at low temperatures have shown that the resulting surface species are chiefly molecular $NH_3$, $NH_2^-$, and $NH^\equiv$. The protonized species $NH_4^+$ was not present at <100°C. These results are also consistent with the observed lack of Brönsted acidity on alumina at these low temperatures. It is significant, however, that the adsorption of ammonia at temperatures in excess of 400°C can lower the rate of olefin isomerization at 25°C [42, 101, 112, 115], although adsorption at <100°C has virtually no effect on the reaction [112]. Peri has found [112] that when alumina containing ammonia adsorbed at 50°C is heated to 400°C, molecular ammonia either desorbs as such or reacts with $O^\equiv$ to form $NH_2^-$ and $OH^\equiv$, and that the sites on which this process occurs are essential for butene isomerization.

Exposure of active alumina to water vapor is generally believed to result in the formation of excess hydroxyl groups [26, 29, 33, 135, 141] and an increase in Brönsted acidity on the surface [67, 101]. This increase in protonic
acidity indicates that the -OH groups formed by water adsorption are evidently different in some way from those remaining on the surface after partial dehydration, since the latter do not exhibit Brönsted acidity at 25°C. No formal speculation about this environmental difference has been made, but from the previous discussion of the alumina surface it might be postulated that at least a portion of the excess -OH groups formed occur on exposed aluminum atoms, since the electron-deficient environment at these sites would enhance the lability of the hydroxyl protons.

The high-temperature adsorption of hydrogen on alumina has been investigated by Weller and Montagna [154] who observed a slow, reversible uptake of H₂ at 450-555°C, corresponding to the reaction:

\[
\text{Al}_2\text{O}_3 \text{ (surf)} + \text{H}_2 \text{ (g)} \rightarrow 2 \text{AlO} \text{ (surf)} + \text{H}_2\text{O} \text{ (g)}
\]

Total uptake over a period of two days corresponded to a surface coverage of less than 1% if considered as chemisorption, or to the production of Al₂O₂.₉₉₈ if considered as a reduction leading to the formation of non-stoichiometric alumina. Significantly, such high-temperature hydrogen adsorption effectively poisons the H₂-D₂ equilibration at -124°C [153]. A simple correlation between the high-temperature H₂ adsorption sites and the sites catalyzing the exchange process cannot be made, however, due to the relative ease of hydrogen diffusion on the alumina surface [84].

The adsorption of carbon dioxide on alumina is of particular significance for the present study since this
substance was extensively employed as a poison for the various D₂ exchange reactions to be described later. Peri [114] has observed that CO₂, like benzene and the n-butenes, is strongly adsorbed by the "α-sites" of alumina. Hall and Larson [84] found evidence for the existence of more than one kind of adsorbed carbon dioxide on alumina, with the more strongly adsorbed types acting as a poison for the CH₄-CD₄ equilibration reaction. This finding may be consistent with the results of Saunders and Hightower [129] who observed that alumina is capable of adsorbing almost twice as much CO₂ as is required to completely poison the C₆H₆-D₂ exchange reaction at 25°C.

Parkyns [106] has made a careful infrared study of the adsorption of carbon dioxide on alumina and observed three principal types of absorption bands for the surface species. The intensities of bands at 2346, 1850, and 1180 cm⁻¹ were dependent upon the pressure of CO₂ admitted to the sample, the 2346 cm⁻¹ band being predominant at lower pressures (<5 torr) and the 1850 and 1180 cm⁻¹ bands obtaining at higher pressures (>8 torr). The second main type of absorption was time-dependent, with bands at 3605, 1640, 1480, and 1233 cm⁻¹ becoming gradually stronger on standing, and a band at 1820 cm⁻¹ becoming progressively weaker with time. The third band-type was observed at 1780 cm⁻¹ and was neither time- nor pressure-dependent, nor was it removed by heating to 100°C. These infrared absorption bands have also been reported by Little and Amberg [92] for CO₂ on alumina, although the time- and pressure-dependencies were not investigated.
Parkyns postulated the following assignments for the observed bands:

**Pressure-dependent**

2346 - Physically adsorbed CO$_2$

1850, 1180 - Asymmetric and symmetric C-O stretching vibrations of structure I below, rather than the bidentate structure II:

![Structure I](image)

![Structure II](image)

**Time-dependent**

3605 - Stretching frequency for the O-H bond of a monomeric HCO$_3$ group

1640 - Asymmetric stretching of HCO$_3$

1480 - Symmetric stretching of HCO$_3$

1233 - Bending frequency of C-O-H linkage

1820 - May be due to a weakly-held form of CO$_2$ adsorbed directly onto aluminum-cation sites and having the linear structure III below:

![Structure III](image)
Band at 1780 cm\(^{-1}\)

Believed to be due to a linear structure of the form IV or V:

Structures IV and V are similar to the one proposed for the 1820 cm\(^{-1}\) band, and, in fact, the difference between the two bands may lie only in the energy of the sites on which the adsorptions occur. Those associated with the 1780 cm\(^{-1}\) band are especially exposed aluminum atoms, and those associated with the 1820 cm\(^{-1}\) band are more completely coordinated aluminum atoms prior to CO\(_2\) adsorption.

Using these band assignments, Parkyns has proposed the following mechanism to explain the adsorption of carbon dioxide on alumina at 25°C:

The last step to form the CHO\(_3\) group occurs by a hydroxyl
shift from aluminum to carbon, not by a shift of the hydroxyl proton to an oxygen atom in CO₂, since no ¹⁸O-H stretching in the HCO₃ was observed when C¹⁸O₂ was used as the adsorbate. CO₂⁻ and CO₃⁻, both of which have characteristic infrared absorption bands, were not observed during the adsorption.

3. Dual-site nature of alumina

One of the more interesting phenomena that has been observed in certain investigations of the alumina surface is the possible existence of more than one type of catalytically active site. In their study of the simultaneous isomerization and D₂ exchange of olefins, particularly the n-butenes, Hightower and Hall [60, 61, 63, 64] observed that the relatively large amount of exchange that occurred during the isomerization might indicate that the two reactions are entirely unrelated on alumina. Yates and Lucchesi [158] found that ethylene and acetylene adsorb on alumina independently of each other. Acetylene adsorbed at 25°C retains its triple-bond character and undergoes hydrogen exchange with the surface hydroxyls. Ethylene, on the other hand, adsorbs by losing its double-bond nature and self-hydrogenating to a C₂H₅ species. No exchange of hydrogen atoms, however, occurred between adsorbed ethylene and adsorbed acetylene, and the adsorption of either was virtually unaffected by the presence of the other on the surface.

The other principal evidence for the dual-site nature of alumina catalysts has come from the temperature-programmed desorption (TPD) work of Amenomiya and Cvetanovic [3, 5, 6,
9, 10, 11, 32]. In studies of the interaction of olefins with alumina they observed that adsorption occurs on two different kinds of sites, having different heats of adsorption. Upon exposure to an active alumina surface, the olefins first saturated the high-energy sites and then adsorbed on the low-energy sites, with any excess remaining in the gas phase. In the presence of gaseous H₂, adsorbed ethylene underwent hydrogenation to ethane at 25°C only on the low-energy sites and polymerization to n-butenes only on the high-energy sites, with virtually no interaction between the two. In all cases, a certain degree of site heterogeneity was observed for both types of sites, i.e., a range of adsorption energies, rather than a unique heat of adsorption.

4. Halided alumina catalysts

In recent years, an interest has developed in alumina catalysts that have been prepared in the presence of halide ions or that have been exposed to various of the hydrogen halides, particularly HF [14, 15, 45, 47, 118] and, to a lesser extent, HCl [101, 113, 134]. Of particular interest [13, 14, 17, 25, 31, 69] has been the nature of the acidity of these halided aluminas, compared with that of the pure alumina from which they are derived. It has been assumed by various investigators [14, 45, 47] that upon exposure of alumina to HF, for example, the fluorine atoms become incorporated onto the alumina surface by simply replacing various of the surface -OH groups, which combine with the residual hydrogen atoms to form water. However, the
observed [13, 15, 17, 69] increase in protonic (Brönsted) acidity of alumina after fluoridation and a concomitant decrease in Lewis acidity [17] suggest that this postulate may be an oversimplification. It appears likely that the fluorine atoms of HF become attached to exposed aluminum atoms (Lewis sites) and the hydrogen atoms to surface oxygens, as proposed by Hughes et al. [77]:

\[
\begin{align*}
&\text{O} \\
&\mid \\
&\text{[Al Al or Al } \overset{\text{O}}{\text{Al}} \overset{\text{O}}{\text{Al}}] \rightleftharpoons \text{OH}^+ \overset{\text{+HF}}{\text{\hspace{1cm}}} \overset{\text{F}}{\text{F}} \overset{\text{+HF}}{\text{\hspace{1cm}}} \overset{\text{F}}{\text{F}} \overset{\text{H}_2\text{O}}{\text{Al Al Al}} \\
&\text{Al} &\text{Al} &\text{Al} \\
\end{align*}
\]

This mechanism explains both the observed decrease in Lewis acidity and the increase in Brönsted acidity, since the -OH groups formed by this process should have considerably more protonic acidity than the usual hydroxyls of active alumina due to the close proximity of the strongly electron-withdrawing fluorine atoms. Some evidence has been reported [13, 14], however, that the Brönsted acidity of fluorided alumina may not be due to -OH groups.

Fluorided alumina catalysts having approximately 0-6% F have been used for several of the reactions that are catalyzed by plain alumina, including benzene adsorption [27] and n-butene isomerization [41, 45, 59, 117, 118]. However, unlike the results on plain alumina, considerable polymeric residue is formed on fluorided alumina during n-butene isomerization, and the reaction occurs with considerable skeletal rearrangement to iso-butene [117, 118], a process that typically takes place via a carbonium ion intermediate. In addition, fluorided alumina is active for various other
reactions that characteristically occur on catalysts having significant protonic acidity and for which plain alumina is inactive at low temperatures. These include paraffin cracking [47, 68], olefin polymerization [68], and cumene (isopropylbenzene) cracking [13, 14, 15, 30, 31]. Extensive study of the latter process has shown that the reaction rate increases with increasing protonic acidity of the surface and that this acidity is a direct function of the fluorine content up to a certain limiting value (=6% F) at which point the catalyst is almost indistinguishable from alumina-supported AlF₃ [47].

It is apparent that fluorided alumina has much in common with the silica-alumina catalysts discussed previously, due principally to the existence of considerable protonic acidity on the surface. It is significant, however, that although silica-alumina also forms a polymeric surface residue during n-butene isomerization, it does not promote significant skeletal rearrangement at low temperatures as fluorided alumina does suggesting that the protonic acidity of the latter may arise from more than one source.

C. Present Investigation

The present study was undertaken to investigate further the nature of the sites on catalytic alumina that are active for certain isomerization and deuterium exchange reactions of unsaturated hydrocarbons. Using the C₆H₆-D₂ test reaction, previous studies of the active site density for D₂ exchange reactions of cyclic olefins [64] and benzene [129] on a specially prepared and very pure alumina were extended to a
commercial alumina catalyst and two fluorided aluminas. In addition to the previously-used carbon dioxide poison, the effect of various other poisons, particularly ammonia and carbon monoxide at varying temperatures of adsorption, was studied, as well as the effect of reaction temperature on the measured site densities.

The other principal aspect of the present work was an examination of the previously-suspected [60, 61, 63] dual-site nature of alumina catalysts for the simultaneous isomerization and deuterium exchange of 1-butene. Various poisons, especially carbon dioxide, were used to determine their effect on one or both of the reactions. The TPD studies of Amenomiya and Cvetanovic [5, 6, 9] that suggested a dual-site nature of alumina for the hydrogenation/polymerization of ethylene were extended to include 1-butene and benzene and mixtures of these with deuterium. The effect of carbon dioxide poisoning of the catalyst on the TPD results was investigated, and a cursory infrared study of the interaction of 1-butene and benzene with CO₂ on alumina was also made.
II. EXPERIMENTAL

A. Catalysts

Two alumina catalysts were used for the present study. The first (A-1) was a 0.100 g sample of a product prepared from the neutral hydrolysis of redistilled aluminum isopropoxide by the MK Research and Development Co., Pittsburgh, Pa. [62]. It had a specific surface area of 158 m\(^2\)/g and a total metallic impurity content of less than 50 ppm. X-ray examination of the catalyst during the final stages of preparation indicated that it was probably a mixture of gamma and eta alumina. The second catalyst (A-2) was a 0.250 g sample of a commercial gamma alumina prepared by the American Cyanamid Co. Its specific surface area was 175 m\(^2\)/g and was used in the form of irregular 20/40 mesh particles.

The two fluoridated aluminas used in the present work were prepared by Shell Development Co., Deer Park, Tex., by addition of appropriate amounts of ammonium bifluoride solution to the A-2 alumina followed by calcination at 500°C. The two catalysts had fluorine contents of 1.6 wt% (FA-1) and 3.2 wt% (FA-2), and surface areas of 168 and 160 m\(^2\)/g, respectively. The 0.250 g charges of both preparations were also used in the form of irregular 20/40 mesh particles.

All catalyst samples were pretreated prior to each use by slow heating to 520°C, treatment with oxygen for two hours, and subsequent evacuation to 10\(^{-6}\) torr at the same temperature. This pretreatment procedure will be described in more detail later.
B. Reagents and chemicals

1. Reactants

Benzene was Matheson, Coleman, and Bell spectroquality, having a purity of 99+ mole%. It was outgassed thoroughly before use by cooling to -195°C with liquid nitrogen, evacuation for 30 min to $10^{-6}$ torr, and warming to 25°C with no applied vacuum. This freeze-pump-thaw cycle was repeated four times for each outgassing operation. Perdeuterobenzene ($\text{C}_6\text{D}_6$) was obtained from Mallinkrodt Chemical Co. and had an isotopic purity of 99.5%; it was also outgassed before use. The three $n$-butenes were Phillips Research Grade having purities of 99.92 mole% ($1$-butene), 99.6 mole% ($\text{trans}-2$-butene), and 99.9 mole% ($\text{cis}-2$-butene). Each was distilled from -78 to -195°C and thoroughly outgassed prior to being used. Deuterium was prepared electrolytically with a Milton Roy Co. deuterium generator, using deuterium oxide (Merck, Sharpe, and Dohme) that had an isotopic purity of 99.7%. The $\text{D}_2$ was purified by passage through a -195°C trap before use.

2. Poisons

Pyridine was Baker and Adamson Reagent grade with a purity of 99.5 mole%. Prior to use, it was outgassed thoroughly and stored over Linde 5A molecular sieve drying agent. Carbon disulfide was Matheson, Coleman, and Bell spectroquality and had a purity of 99+ mole%; it was treated with four outgassing cycles before being used. All gaseous materials used as poisons were obtained from the Matheson Co. Carbon dioxide (bone-dry, 99.8%), ammonia (anhydrous, 99.99%), hydrogen chloride (technical, 99.0%), nitrogen dioxide (99.5%), nitric oxide
(technical, 98.5%), and sulfur dioxide (anhydrous, 99.98%) were all outgassed before use. Carbon monoxide (C.P., 99.5%) was passed through a trap at -195°C prior to being used.

3. Others

Helium carrier gas was Matheson high purity grade (99.995%) and was purified on stream by passage through a Matheson Model 450 molecular sieve gas purifier fitted with a Type A cartridge suitable for removal of oil, water, and particulate matter down to 12 microns. Hydrogen (Matheson prepurified, 99.95%) and oxygen (Iweco, 99.9%) were purified by passage through a trap at -195°C before use.

C. Apparatus

1. Recirculation system

All reactions and adsorptions were carried out using the Pyrex recirculation system shown schematically in Figure 4, and described in detail previously by Saunders [128]. Connection of this system was made via stopcocks $S_1$ and $S_{26}$ to a conventional high vacuum manifold employing a rotary fore-pump and mercury diffusion pump. Pressure measurements were made with a McLeod gauge, and the pressure due to non-condensables could be routinely reduced to $10^{-6}$ torr or less. The five-liter bulbs $B_1$-$B_4$ with their associated closed-end manometers $M_1$-$M_4$ were used for storage of oxygen, deuterium, carbon dioxide, and 1-butene. Other reactants and poisons were admitted from sample vessels via the standard taper $J_3$. The glass bead-filled trap $T_1$ was cooled with liquid nitrogen to -195°C when necessary to purify oxygen, hydrogen,
FIGURE 4. Recirculation System
deuterium, and carbon monoxide. The U-shaped trap $T_2$ was similarly cooled with liquid nitrogen to condense carbon dioxide and other desorbates during pretreatments of the catalyst samples prior to each experiment.

The reactor $R$ containing the catalyst charge $A$ was thermostatted with a tubular well furnace connected to a Leeds and Northrup Electromax temperature controller. Reaction or pretreatment temperature could be maintained to within ± 0.5°C. A distilled water-ice bath was used for experiments made at 0°C. Reactant pressures were measured to ± 0.1 torr with either of the two mercury manometers $M_5$ or $M_7$; the former was used for pressures under 200 torr, and the latter for higher values. Pressures less than 20 torr were measured with the silicone oil manometer $M_6$ to ± 0.02 torr; the stopcock $S_{18}$ permitted selection of either $M_5$ or $M_6$.

Circulation of gas mixtures within the system was accomplished by the pump $P$ which consisted of a Pyrex tube containing a close-fitting glass piston and two one-way glass ball valves. A length of glass-enclosed iron rod was sealed within the piston, and a wire-wound toroid surrounded the upper half of the pump. A motor-driven cam wheel continually opened and closed a microswitch, causing a pulsed current to be applied to the toroid and resulting in a vertical pulsation of the piston at a rate of two cycles/sec. Two rheostats allowed adjustment of piston amplitude, and circulation was in a counter-clockwise direction, as indicated by the arrows in Figure 4.
Total volume of the circulation loop with the reactor in position was 339 cc, of which approximately 85% was contained in the spherical mixing volume V. Manipulation of stopcocks \( S_{11} \) and \( S_{12} \) caused a circulating gas mixture to pass a fine capillary L which led directly to the ion-chamber of a mass spectrometer (to be described later), permitting continuous monitoring of hydrocarbon deuterium content within the system. Reactant loss from the circulation loop through the capillary bleed was approximately 0.3%/hr at an inboard pressure of one atmosphere.

A salient feature of the recirculation system was the T-shaped section of tubing enclosed within stopcocks \( S_{13} \), \( S_{14} \), and \( S_{15} \), located just upstream from the reactor. Using manometer \( M_5 \) or \( M_6 \), a known pressure of gaseous material could be admitted to this "doser" and added to the reaction mixture when desired by a 180° rotation of stopcocks \( S_{13} \) and \( S_{14} \). Before being sealed into the system, the doser was calibrated with mercury and had a volume of 2.23 cc. Assuming ideal gas behavior, the amount of gaseous material within the doser at any time was thus \( 7.23 \times 10^{16} \) molecules per torr of pressure.

2. GLC system

The three n-butene mixtures in reacting mixtures were separated and analyzed by gas-liquid chromatography (GLC) using the system shown in Figure 5. The helium carrier gas inlet pressure was reduced to 16 psig by the dual-outlet regulator \( Z \), and the Whitey 1VS4 1/4 inch valves \( V_1 \), \( V_2 \), and \( V_3 \) allowed on-off control of the various gas streams. All connections
FIGURE 5. Gas-Liquid Chromatography Sampling System
were made with 1/4 inch or 1/8 inch O.D. copper tubing and brass Swagelok fittings. The reference stream was maintained at a constant flow rate of 10 ml/min by the Nupro Series "M" fine metering valve NVT1, while the regulator inlet pressure gave a sample stream flow rate of 150 ml/min, both flow rates being measured with a soap-film flowmeter. The detector was a Gow-Mac No. 9258 thermal conductivity unit employing rhenium-tungsten filaments in No. 9225 mounts and was contained within an insulated 10 inch cubical oven constructed of 1/2 inch thick Transite. The detector temperature was maintained at 110° ± 1°C for all analyses. Detector output was monitored with a Hewlett-Packard No. 7100B strip chart recorder equipped with a disc integrator. The separatory column was a 27 ft x 3/8 inch O.D. copper spiral packed with 25% propylene carbonate on 60/80 mesh Chromasorb W (both from Varian Aerograph, Walnut Creek, Cal.). The column was thermostatted at 0°C for all analyses by immersion in a Dewar vessel containing an ice-water bath.

In operation, S28 was closed, and S27 was rotated to allow an aliquot of the reacting mixture from the mixing volume in Figure 4 to expand into the previously-evacuated 9 cc sample loop G. Further rotation of S27 and S28 caused the carrier stream to favor passage through G rather than through the capillary restriction C and carried the sample to the column for separation. The separated isomers were collected through J5, when desired, in glass-bead-filled traps at -195°C (99% trapping efficiency) for subsequent mass spectral analyses of deuterium contents. Using the conditions
described in the preceding paragraph, base-line resolution of the three isomers was attained, with retention times of 10.3, 12.3, and 14.2 minutes for 1-butene, trans-2-butene, and cis-2-butene, respectively. The relative sensitivities of the three components were determined by filling the sample loop G to identical pressures of each isomer in separate analyses and measuring the resulting peak areas. These sensitivities were 1.000 (1-butene), 0.953 (trans-2-butene), and 0.931 (cis-2-butene), with 1-butene giving the smallest peak area for a given amount of sample. In all subsequent analyses the integrated peak area of each isomer was multiplied by the appropriate sensitivity factor before calculating the gas mixture composition.

3. TPD system

The temperature-programmed desorption (TPD) experiments were performed using a modification of the technique developed by Cvetanovic and Amenomiya (4, 7, 12, 32). The recirculation and GLC systems were adapted for these experiments as shown in Figure 6. The bottom half of the reactor R was covered with a layer of asbestos paper, wound evenly with 30 Ω of 36 gauge nichrome heating wire, and finally covered with six layers of 1/16 inch thick asbestos tape. The heating wire was connected to a Hewlett-Packard Model 350 temperature-programmer TP, and an iron-constantan thermocouple situated in a well in the catalyst bed served as both a sensor and a pyrometric temperature readout. After proper temperature-matching of the thermocouple and readout indicator, the controller could be set to increase the catalyst temperature at any of ten linear program rates between 0.5 and 30.0 °C/min.
Helium carrier gas was admitted via stopcock $S_{10}$, and, after flowing through the reactor, was directed by $S_{24}$ to the thermal conductivity cell TC (the same cell as that in the GLC system). The detector output was monitored by one pen of a Hewlett-Packard No. 7100B two-pen recorder, the other pen being connected to a second iron-constantan thermocouple situated in the reactor. Previously-adsorbed material that desorbed from the catalyst into the carrier gas stream during the temperature increase appeared as peaks on the recorder output, similar to a GLC trace, the abscissa of such a trace representing temperature rather than time. The temperature range over which each desorption occurred could be read directly from the second recorder pen after suitable calibration. Desorbed material was collected for subsequent GLC and/or mass spectral analyses in -195°C traps at $J_5$, as described above for the GLC system. All TPD experiments performed in the present study employed a temperature program rate of 30.0 °C/min and a carrier gas flow rate of 90 ml/min, as controlled by the needle valve $NV_2$ (similar to $NV_1$ in Figure 5). The reference flow rate was 10 ml/min. The procedure used for a typical TPD experiment will be described in a later section.

4. Mass spectrometer

The mass spectrometer used for all analyses was a modified Consolidated Electrodynamics Corp. No. 21-104 operated at low ionizing voltage (5-8 ev). Amplifier output was monitored on a Leeds and Northrup strip chart recorder. Suitable corrections were made for carbon-13 and, in the case of the
n-butenes, fragmentation contributions before using parent-peak heights to make quantitative calculations of deuterium levels. A detailed description of the mathematical treatment given the mass spectral data will be considered later.

5. IR equipment

All infrared spectra were recorded with a Perkin-Elmer Model 21 instrument operated in double-beam mode with air as the reference. Scans were made at the slowest practical speed (8 min/micron) with maximum recorder gain and a programmed slit setting. The latter adjustment resulted in slit widths of 20 microns at 5000 cm\(^{-1}\) and 120 microns at 1000 cm\(^{-1}\), the frequency range of interest for all spectra. Other instrument controls were set to give the highest resolution and signal-to-noise ratio attainable with the expanded transmittance scales required for the spectra.

The infrared cell used is depicted in Figure 7 and was connected via the 10/20 standard tapers to J\(_1\) and J\(_2\) in Figure 4 for admission of adsorbates and pretreatment of the sample. The upper portion of the cell down to the 40/50 joint was of Pyrex glass; the lower portion was fabricated from a 10 inch length of one inch I.C. square quartz tubing. 1/8 inch thick polished sodium chloride windows were sealed with epoxy cement over one inch high oval holes cut in opposite faces of the tube 1/2 inch from the sealed bottom. A four-inch section of the tube 3-7 inches above the windows was covered with asbestos paper, wound evenly with 80\@ of 36 gauge nichrome heating wire, and then covered with six layers of 1/16 inch thick asbestos tape. The heating wire was
FIGURE 7. Infrared Cell
connected to the previously-described Hewlett-Packard temperature-programmer which was also operable in an isothermal mode. The iron-constantan thermocouple sensor was located in a thermowell, the bottom tip of which was situated just above the midpoint of the heated region.

The alumina sample was in the form of a circular wafer having a nominal density of 25 mg/cm$^2$. It was prepared by evenly distributing 0.071 g of finely-ground (<500 mesh) A-2 alumina over the face of a 3/4 inch I.D. hardened steel die, followed by hydraulic pressing at 45,000 psi. The pellet was subsequently trimmed to suitable size (a 0.060 g sample was used for all spectra) and positioned vertically in a 7/8 inch cubical holder constructed from short lengths of 1/8 inch Pyrex rods. The holder was connected by a length of fine, flexible nichrome wire to the crank assembly in the upper portion of the cell. The latter assembly was used to raise the sample into the heated region for 520°C oxygen pretreatment prior to each run, and then lower it into the path of the IR beam. The procedure used for adsorption of various materials onto the sample prior to IR scans will be described below.

D. Experimental procedures

1. Catalyst pretreatment

Prior to each use, all catalyst samples were pretreated by evacuating the circulatory system in Figure 4 for one hour with the reactor in position and thermostatted at 520°C. Stopcocks $S_1$, $S_9$, and $S_{27}$ were then closed, and manometer $M_5$
was used to admit 150 torr of oxygen from bulb \( B_1 \) into the system. \( S_{15} \) was closed; trap \( T_2 \) was cooled to -195°C by immersion in a Dewar vessel containing liquid nitrogen, and the circulation pump was switched on. Circulation of oxygen was continued for two hours during which time carbon dioxide and other desorbates from the catalyst condensed in \( T_2 \). \( S_{21} \) and \( S_{22} \) were then rotated 180° to bypass the reactor; \( T_2 \) was warmed rapidly to 25°C with a heat gun, and the system was evacuated for 10 minutes. \( S_{21} \) and \( S_{22} \) were returned to their original positions to evacuate the reactor overnight (20 hours) to a final pressure of \( 10^{-6} \) torr. Just prior to a run, the 250°C furnace was lowered, and the reactor was cooled to the desired temperature.

2. Benzene/deuterium exchange reactions

The sample vessel containing the outgassed benzene was attached to \( J_3 \), and all connecting tubing was evacuated to \( 10^{-6} \) torr. With \( S_{21} \) and \( S_{22} \) rotated to bypass the reactor, \( S_9 \), \( S_{16} \), and \( S_{27} \) were closed, and monometer \( M_5 \) or \( M_6 \) was used to monitor the admission of the desired pressure of gaseous benzene (typically 10.0 torr) into the circulatory loop. \( S_{15} \) was then closed, and \( T_2 \) was cooled to -195°C to condense the benzene into the trap, while \( S_{16} \) was opened to evacuate the connecting tubing. After closing \( S_1 \) and opening \( S_{15} \), manometer \( M_5 \) was used to admit the required pressure of deuterium (normally 100.0 torr) from bulb \( B_2 \) into the system. \( S_{13} \) and \( S_{14} \) were then rotated 180° to bypass the "doser" \( D; \) the pump was switched on, and \( T_2 \) was rapidly warmed to 25°C with a heat gun. After homogenization of the gas mixture by
circulation for 15 minutes, $S_{11}$ and $S_{12}$ were rotated $180^\circ$ to divert circulation past the mass spectrometer capillary leak $L$, and the reactor was thermostatted to the desired reaction temperature. After scanning masses 78 and 79 two or three times to establish the carbon-13:carbon-12 ratio, the reaction was initiated by rotating $S_{21}$ and $S_{22}$ $180^\circ$ at time $t=0$ to cause the circulating gas mixture to pass through the catalyst bed. The exchange rate was established by scanning the mass range 78 to 85 five or six times at 4-5 minute intervals.

During this time, the "doser" was filled to a measured pressure with gaseous poison either from bulb $B_3$ (carbon dioxide) or from a sample vessel attached to $J_3$ (other poisons). At the desired reaction time (typically about 30 minutes), $S_{13}$ and $S_{14}$ were simultaneously rotated $180^\circ$ to divert circulation through the doser and carry the poison to the catalyst. The exchange rate after poison addition was measured by again scanning the mass range 78 to 85 at 4-5 minute intervals. At the conclusion of each experiment, the entire system was evacuated 10 minutes before returning $S_{11}$ and $S_{12}$ to their original positions.

3. l-Butene isomerization/exchange reactions

The procedure used for these experiments was very similar to that described above for the benzene exchange runs, except that the mass spectrometer capillary leak was not used. Typical reactant pressures were 100.0 torr of l-Butene and 400.0 torr of deuterium, manometer $M_7$ being used to measure the latter pressure. Prior to poison addition, four
samples were normally taken at 40 minute intervals by expansion into the evacuated sample loop G in Figure 5, and four more samples were taken at similar intervals after poison addition. In each case, the three n-butenes were separated by GLC as described previously, and each was collected separately in a liquid nitrogen-cooled trap for subsequent mass spectral analysis after removal of excess helium carrier gas by a one minute evacuation at -195°C. The butenes were admitted to the mass spectrometer via an independent inlet system, and the mass range 54 to 65 was scanned for each isomer to establish its deuterium content (Masses 54 and 55 are P-2 and P-1 peaks, respectively).

In some experiments, the catalyst was prepoisoned prior to admitting the reactants by filling the doser to the desired pressure with gaseous poison, and then opening $S_{14}$ and $S_{21}$ to expose the catalyst to the poison for 10 minutes at the eventual reaction temperature. After a five minute evacuation, the reactants were admitted and the reaction run as usual.

4. TPD experiments

After pretreatment in the usual manner, the catalyst was hydrogenated or deuterated, as desired, by circulation of 150 torr of $H_2$ or $D_2$, respectively, for 60 minutes at 500°C. Mass spectral monitoring of one such deuteration indicated that H-D equilibrium between catalyst and gas phase was attained within 10 minutes at 500°C. The reactor was then thermostatted at 25°C; $S_{13}$, $S_{14}$, and $S_{22}$ were closed, and the doser was filled to the desired pressure with
1-butene, benzene, or a mixture of one of these with gaseous 
D₂. (In some experiments the catalyst was prepoisoned with 
carbon dioxide, as described above). S₁₅ was closed, and S₁₄ 
was opened to expose the catalyst to the gas mixture in the 
doser. After the desired exposure time, the helium carrier 
gas flow was started by opening S₁₀, S₁₃, S₂₂, and S₂₄, and 
the residual gas phase in the reactor was collected for five 
minutes in a -195°C trap attached to J₅. The programmed 
temperature-increase was started, and the reactor tempera-
ture and various desorptions were monitored with the two-pen 
recorder. Each desorption process appeared as a peak on the 
recorder trace, and the effluent corresponding to each peak 
was collected in a separate -195°C trap at J₅. Temperature-
programming was normally continued to approximately 520°C.

The helium in each collection trap was removed by evac-
uation at -195°C for one minute, and the material remaining 
in the trap was transferred by expansion into the sample loop 
G in Figure 5 for GLC analysis. The separated butene iso-
mers were again collected in -195°C traps for subsequent mass 
spectral analysis of deuterium content. In the case of TPD 
experiments involving benzene as the adsorbate, no GLC sepa-
ration was required.

5. Infrared experiments

The IR cell (Figure 7) was attached to the recirculation 
system (Figure 4) at J₁ and J₂ and evacuated for one hour at 
25°C. The alumina pellet was then given the usual 520°C 
oxxygen pretreatment for two hours by raising the sample 
holder into the heated region of the cell. The pretreatment
was followed by evacuation at 520°C for one hour. After sub-
sequent cooling to 25°C, S_{31} and S_{32} were closed; the cell 
was removed from the system and secured by a ringstand 
mounted on the infrared instrument. The sample holder was 
lowered to center the infrared beam on the alumina pellet, 
and the spectrum was scanned using the instrument settings 
described previously (p. 46).

After completing the scan of the plain sample, the cell 
was reattached to the recirculation system, and, following a 
30 minute evacuation, the calibrated doser was filled to 
the desired pressure with the material to be adsorbed. With 
S_{13} and S_{15} closed, S_{14}', S_{21}', and S_{32} were opened to expose 
the sample to the adsorbate for the required length of time 
(normally five minutes); a five minute evacuation followed 
to remove gas phase material. S_{32} was again closed; the cell 
was removed from the system, and another spectrum was 
scanned, as before. Exposure of the sample to additional 
adsorbates during the same run followed the same procedure, 
and each spectrum was recorded on a separate sheet to avoid 
confusing similar absorption bands among the various spectra.

E. Mathematical treatment of data

1. Deuterium exchange reactions

Raw mass spectral data from the deuterium exchange reac-
tions of benzene and 1-butene were analyzed by the method of 
Kemball [78], as discussed previously by Saunders [128]. 
After correcting for fragmentation and isotopic carbon-13 
contributions, the parent-peak heights of the various
deuterated species in a particular sample was used to calculate an extent of reaction variable $\phi$, where

$$\phi = d_0 \cdot 0 + d_1 \cdot 1 + d_2 \cdot 2 + \ldots = \sum_{i}^{n} i d_i$$  \hspace{1cm} (1)$$

Here, $d_i$ is the fraction of the total hydrocarbon containing $i$ deuterium atoms, and $n$ is the total number of hydrogen atoms per molecule of hydrocarbon (eight for the butenes, six for benzene). When calculated in this manner, the value of $\phi$ represents the average number of deuterium atoms per molecule of hydrocarbon. The symbol $\phi$, with appropriate subscripts, will have this definition throughout the present work.

Due to the complicating interconversion of the three n-butenes, deuterium exchange analysis of the 1-butene/D$_2$ system could only be used to determine the effects of various added poisons on the steady increases of $\phi$ for each isomer with increasing time of reaction. Immediately after poison addition, a plot of $\phi$ vs. time for each isomer exhibited a sharp break. The extent of the break depended upon the type and amount of poison added. Examples of such plots will be seen in a later section.

In the case of the relatively simple benzene/D$_2$ system, however, the analysis can be carried considerably further [78] to furnish quantitative deuterium exchange rate information. Since all hydrogen atoms in the benzene molecule are equivalent and equally susceptible to exchange, the course of the reaction (ignoring isotope effects of the various deuterated species) is given by the first-order
equation:

\[
\frac{d\phi}{dt} = k_\phi (1 - \frac{\phi}{\phi_\infty})
\]  

(2)

where \( k_\phi \) is a rate constant equivalent to the number of deuterium atoms entering 100 molecules of hydrocarbon in unit time during the initial states of the reaction. \( \phi_\infty \) is the value of \( \phi \) at equilibrium, and reflects the ratio of D-atoms to total hydrogenic (H + D) atoms in the system. It may be calculated from a simple statistical approach as

\[
\phi_\infty = \frac{2P_D}{2P_D + 6P_B} \cdot 6
\]  

(3)

where \( P_D \) and \( P_B \) are the initial partial pressures of \( D_2 \) and benzene introduced into the system.

Integration of equation (2) gives

\[
-ln(\phi_\infty - \phi) = (k_\phi/\phi_\infty)-ln(\phi_\infty - \phi_0)
\]  

(4)

\( \phi_0 \) being the value of \( \phi \) at time \( t=0 \), and since all benzene exchange experiments in the present study were made using pure \( C_6H_6 \) as reactant, \( \phi_0 = 0 \) for all experiments. Hence, a plot of \(-ln(\phi_\infty - \phi)\) vs. time should give a straight line with intercept \(-ln(\phi_\infty)\) and slope \( k_\phi/\phi_\infty \) if the rate of deuterium exchange is first-order in benzene pressure and uninhibited by products.

A second rate constant, \( k_0 \), representing the initial rate of disappearance of the undeuterated species \( C_6H_6 \), is obtained from the empirical first-order equation

\[
-ln(X_0 - X_\infty) = \frac{k_0}{100 - X_\infty} t - \ln(100 - X_\infty)
\]  

(5)
where $X_O$ is the percentage of $C_6H_6$ present at time $t$, and 100 and $X_o$ are the initial and final percentages of this species. The ratio of the two rate constants

$$M = k_\phi / k_o$$

has been termed the "reaction multiplicity" and represents the mean number of hydrogen atoms that are replaced by deuterium atoms in each molecule of hydrocarbon per residence on the catalyst during the initial stages of the reaction. On alumina, the exchange of benzeneic hydrogen atoms with deuterium at low temperatures (less than 100°C) occurs with a reaction multiplicity of unity, i.e., a separate adsorption-desorption process occurs for the exchange of each successive hydrogen atom in a molecule of benzene with gaseous $D_2$.

Addition of an active poison to the benzene/$D_2$ reaction causes a deactivation of a certain fraction of active sites on the catalyst, and the first-order rate constant $k_\phi$ decreases to a new value $k_{\phi,P}$, the ratio $k_{\phi,P}/k_\phi$ representing the fraction of catalytic activity remaining. If it is assumed that each molecule of poison deactivates one active site, a plot of $k_{\phi,P}/k_\phi$ vs. the number of molecules of poison added can be extrapolated to $k_{\phi,P}/k_\phi = 0$ to determine the active site density of the catalyst in terms of sites per unit area (since the total surface area of the sample is known).

Activation energies for the benzene/$D_2$ exchange process on the various catalysts were determined by carrying out the reaction at several different temperatures on each catalyst.
and then applying the usual Arrhenius relation:

\[ k_\phi = A \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} (7)

or

\[ \ln k_\phi = -\frac{E_a}{RT} + \ln A \]  \hspace{1cm} (8)

The slopes of \( \ln k_\phi \) vs. \( 1/T \) were used to calculate the various activation energies, \( E_a \).

2. 1-Butene isomerization reactions

As discussed previously [123], the extent of 1-butene isomerization reactions may be described by the first-order equation:

\[ \ln \frac{X_e}{X_e - X} = Skt \]  \hspace{1cm} (9)

where \( X \) and \( X_e \) are the fractional conversions of 1-butene to 2-butenes at time \( t \) and at equilibrium, respectively (At 25°C \( X_e = 0.969 \) [51]). \( S \) is the total catalyst surface area in \( m^2 \). Although equation (9) is strictly valid only for two components involved in first-order, reversible reactions, it is a reasonable approximation of the three-component system of \( n \)-butenes if the two 2-butenes are taken together and treated as a single product. Plots of the LHS of equation (9) vs. time should be linear during the initial stages of the reaction (less than 50% conversion), and the rate constants, \( k \), obtained from the slopes may be considered valid measures of the "isomerization activity" of the catalyst for comparison purposes.
III. RESULTS

A. Benzene-D$_2$ exchange on A-1 alumina

Preliminary experiments were carried out to determine the effect of various poisons, other than carbon dioxide, on the benzene-D$_2$ exchange reaction at 50°C on 0.100 g of A-1 alumina. These results are summarized in Table I. As seen, both ammonia and hydrogen chloride had a negligible effect on the exchange rate, while pyridine, on the other hand, had a definite, though non-linear, poisoning effect on the reaction. Smaller amounts of pyridine (<0.5 x 10$^{13}$ molecules/cm$^2$) had less effect per molecules than larger doses (>0.8 x 10$^{13}$ molecules/cm$^2$), as illustrated in Figure 8 where these data are shown in graphical form. The results for pyridine were somewhat erratic, however, since in one experiment (not shown in Table I) a dose of 0.4 x 10$^{13}$ molecules/cm$^2$ completely poisoned the reaction.

B. Benzene-D$_2$ exchange on A-2 alumina — Carbon dioxide poison

Carbon dioxide poisoning studies of the benzene-D$_2$ exchange reaction on A-2 alumina were undertaken in an attempt to correlate the results with those obtained previously [128, 129] in similar experiments using A-1 alumina. Data from a typical run (expt. 80) are illustrated in Figure 9, and the results of all experiments are shown in Table II. The linearity of the points in Figure 9 confirms that the reaction closely follows the first-order kinetics given by equation (4). Prepoisoning of the catalyst in expt. 87 (and in all later runs that involved preadsorption of a poison) was
TABLE I

Benzene/D₂ Exchange on A-1 Alumina *

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Reaction Temp(°C)</th>
<th>Poison</th>
<th>Molecules/cm² (x 10⁻¹³)</th>
<th>kₚ (min⁻¹) (x 10²)</th>
<th>kₚ₂ (min⁻¹) (x 10²)</th>
<th>kₚₚ/kₚ</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>51</td>
<td>None</td>
<td>-</td>
<td>8.10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>53</td>
<td>Pyridine</td>
<td>0.14</td>
<td>8.91</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>53</td>
<td>&quot;</td>
<td>0.46</td>
<td>7.16</td>
<td>8.45</td>
<td>.948</td>
</tr>
<tr>
<td>15</td>
<td>50</td>
<td>&quot;</td>
<td>0.87</td>
<td>7.01</td>
<td>6.28</td>
<td>.876</td>
</tr>
<tr>
<td>11</td>
<td>55</td>
<td>&quot;</td>
<td>1.09</td>
<td>7.48</td>
<td>3.82</td>
<td>.544</td>
</tr>
<tr>
<td>12</td>
<td>53</td>
<td>NH₃</td>
<td>1.09</td>
<td>8.40</td>
<td>1.80</td>
<td>.240</td>
</tr>
<tr>
<td>13</td>
<td>53</td>
<td>HCl</td>
<td>1.09</td>
<td>8.17</td>
<td>8.40</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.10</td>
<td></td>
<td>.990</td>
</tr>
</tbody>
</table>

* All experiments were run using 0.100 g of catalyst and a 10:100 torr mixture of benzene: deuterium reactants.
FIGURE 8. Benzene/D₂ Exchange on 0.100 g of A-1 Alumina at 50°C - Pyridine Poison
FIGURE 9. Benzene/D$_2$ Exchange on 0.250 g of A-2 Alumina at 23°C - CO$_2$ Poison
<table>
<thead>
<tr>
<th>Expt.</th>
<th>Reaction Temp(°C)</th>
<th>Molecules CO₂/cm² (x 10⁻¹³)</th>
<th>kₚ(min⁻¹) (x 10²)</th>
<th>kₚ,p(min⁻¹) (x 10²)</th>
<th>kₚ,p/kₚ</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>23</td>
<td>-</td>
<td>10.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>77</td>
<td>23</td>
<td>-</td>
<td>10.82</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>164</td>
<td>22</td>
<td>-</td>
<td>9.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>79</td>
<td>24</td>
<td>.165</td>
<td>12.07</td>
<td>10.32</td>
<td>.855</td>
</tr>
<tr>
<td>82</td>
<td>22</td>
<td>.330</td>
<td>10.95</td>
<td>7.55</td>
<td>.690</td>
</tr>
<tr>
<td>81</td>
<td>23</td>
<td>.495</td>
<td>10.44</td>
<td>5.91</td>
<td>.566</td>
</tr>
<tr>
<td>80</td>
<td>23</td>
<td>.660</td>
<td>10.29</td>
<td>4.20</td>
<td>.407</td>
</tr>
<tr>
<td>127</td>
<td>23</td>
<td>.660</td>
<td>11.08</td>
<td>4.76</td>
<td>.430</td>
</tr>
<tr>
<td>175**</td>
<td>21</td>
<td>.660</td>
<td>4.57</td>
<td>1.92</td>
<td>.420</td>
</tr>
<tr>
<td>83</td>
<td>22</td>
<td>.825</td>
<td>8.90</td>
<td>2.47</td>
<td>.276</td>
</tr>
<tr>
<td>128</td>
<td>21</td>
<td>.825</td>
<td>11.45</td>
<td>3.44</td>
<td>.300</td>
</tr>
<tr>
<td>84</td>
<td>22</td>
<td>.990</td>
<td>9.97</td>
<td>1.78</td>
<td>.179</td>
</tr>
<tr>
<td>85</td>
<td>22</td>
<td>1.155</td>
<td>9.64</td>
<td>1.17</td>
<td>.121</td>
</tr>
<tr>
<td>86</td>
<td>22</td>
<td>1.320</td>
<td>8.45</td>
<td>0.25</td>
<td>.029</td>
</tr>
<tr>
<td>78</td>
<td>25</td>
<td>1.650</td>
<td>11.81</td>
<td>0.00</td>
<td>.000</td>
</tr>
<tr>
<td>87</td>
<td>22</td>
<td>1.650 (Preads.)</td>
<td>-</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>186+</td>
<td>22</td>
<td>.660</td>
<td>5.02</td>
<td>1.96</td>
<td>.390</td>
</tr>
</tbody>
</table>

* All experiments were run using 0.250 g of catalyst and a 10:100 torr mixture of benzene:deuterium reactants, except as noted below.

** Benzene:D₂ = 20:200 torr.

+ Reactant mixture was C₆D₆:H₂ = 10:100 torr.
accomplished by filling the calibrated doser to the required pressure with carbon dioxide, exposing the catalyst to the poison for ten minutes at 22°C, and then evacuating the reactor for five minutes to remove gas phase material. The benzene and deuterium reactants were then admitted and the reaction run as usual.

The data in Table II were plotted (Figure 10) to determine the surface density of the exchange sites. Experiment 175, using twice the usual pressures of reactants, and experiment 186, using perdeuterobenzene/H₂ reactants, although occurring at lower absolute rates than the other runs, gave rate constant ratios that were very close to that of a similar (expt. 80) made under the usual conditions. Extrapolation of the linear portion of the curve in Figure 10 to kₚ,p/kₚ = 0 gave an exchange site density of approximately 1.1 x 10⁻¹³ sites per cm², assuming that each molecule of carbon dioxide poisons only one active site. (That this assumption is probably valid can be seen by noting that a site density of 10⁻¹³/cm² corresponds to an average distance between sites of more than 30 Å). This site density is in close agreement with that reported previously (1.0 x 10⁻¹³ sites/cm²) by Saunders [128, 129] for A-1 alumina at 20°C, indicating the inherent similarity of the two catalysts.

From these experiments, the term "lethal dose," used in later discussions in connection with both carbon dioxide and other poisons, was chosen to be an amount 20% in excess of the amount of carbon dioxide required to just poison the benzene-D₂ exchange at 25°C. A "lethal dose" of any material
Extrapolated Site Density = $1.13 \times 10^{13}/\text{cm}^2$

FIGURE 10. Deuterium Exchange Site Density of A-2 Alumina by CO$_2$ Poisoning at 25°C
was thus $1.65 \times 10^{13}$ molecules per cm$^2$.

To check the temperature-dependence, if any, of the CO$_2$ poisoning process, several of the experiments in Table II were repeated at 0°, 60°, and 100°C, runs at the latter temperature being made with 0.100 g of catalyst. These results are summarized in Table III and plotted for 0° and 100° in Figure 11. It is seen that the extrapolated site density at 0° ($1.6 \times 10^{13}$/cm$^2$) is higher, and that at 100° ($0.35 \times 10^{13}$/cm$^2$) is lower than the value of $1.1 \times 10^{13}$/cm$^2$ obtained at 25°. A possible explanation of this phenomenon will be considered in a later section.

The average exchange rates before poisoning at each of the four temperatures (0°, 25°, 60°, and 100°) were used to determine the activation energy of the reaction from the Arrhenius plot shown in Figure 12. The value obtained from this plot (4.7 kcal/mole) is also in good agreement with the result (4.3 kcal/mole) obtained by Saunders [128] for the reaction on A-1 alumina.

C. Benzene-D$_2$ exchange on A-2 alumina - Ammonia poison

Poisoning of the benzene-D$_2$ exchange reaction was extended to investigate the effect of preadsorbed ammonia on the process. The results of these experiments are contained in Table IV. As expected from the previous results on A-1 alumina (expt. 12, Table I), a "lethal dose" of ammonia, preadsorbed at 20°C was an ineffective poison for the reaction. With increasing temperature of adsorption, however, the poisoning effect of ammonia increased until, at an adsorption
### TABLE III

**Benzene/D$_2$ Exchange on A-2 Alumina at Various Temperatures - CO$_2$ Poisoning**

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Reaction Temp(°C)</th>
<th>Molecules CO$_2$/cm$^2$ (x 10$^{-13}$)</th>
<th>$k_A$(min$^{-1}$) (x 10$^2$)</th>
<th>$k_{\phi,p}$(min$^{-1}$) (x 10$^2$)</th>
<th>$k_{\phi,p}/k_{\phi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>144</td>
<td>0</td>
<td>.165</td>
<td>4.66</td>
<td>4.02</td>
<td>.871</td>
</tr>
<tr>
<td>140</td>
<td>0</td>
<td>.330</td>
<td>5.08</td>
<td>4.02</td>
<td>.791</td>
</tr>
<tr>
<td>139</td>
<td>0</td>
<td>.660</td>
<td>4.85</td>
<td>2.66</td>
<td>.550</td>
</tr>
<tr>
<td>141</td>
<td>0</td>
<td>.990</td>
<td>4.98</td>
<td>1.94</td>
<td>.390</td>
</tr>
<tr>
<td>142</td>
<td>0</td>
<td>1.320</td>
<td>5.20</td>
<td>1.09</td>
<td>.210</td>
</tr>
<tr>
<td>143</td>
<td>0</td>
<td>1.650</td>
<td>5.02</td>
<td>0.31</td>
<td>.061</td>
</tr>
<tr>
<td>147</td>
<td>60</td>
<td>.330</td>
<td>23.35</td>
<td>16.22</td>
<td>.695</td>
</tr>
<tr>
<td>145</td>
<td>60</td>
<td>.660</td>
<td>24.09</td>
<td>8.88</td>
<td>.368</td>
</tr>
<tr>
<td>146</td>
<td>60</td>
<td>1.320</td>
<td>22.91</td>
<td>5.50</td>
<td>.024</td>
</tr>
<tr>
<td>135</td>
<td>103</td>
<td>.083</td>
<td>24.97</td>
<td>18.32</td>
<td>.734</td>
</tr>
<tr>
<td>134</td>
<td>104</td>
<td>.165</td>
<td>24.78</td>
<td>12.77</td>
<td>.515</td>
</tr>
<tr>
<td>136</td>
<td>104</td>
<td>.248</td>
<td>23.91</td>
<td>9.74</td>
<td>.407</td>
</tr>
<tr>
<td>133</td>
<td>104</td>
<td>.412</td>
<td>22.61</td>
<td>4.52</td>
<td>.200</td>
</tr>
<tr>
<td>137</td>
<td>104</td>
<td>.577</td>
<td>23.00</td>
<td>2.23</td>
<td>.097</td>
</tr>
<tr>
<td>138</td>
<td>103</td>
<td>.825</td>
<td>20.08</td>
<td>0.12</td>
<td>.006</td>
</tr>
<tr>
<td>129**</td>
<td>104</td>
<td>.650</td>
<td>64.84</td>
<td>3.63</td>
<td>.056</td>
</tr>
</tbody>
</table>

* Experiments at 0° and 60°C were run using 0.250 g of catalyst; those at 100°C were run using 0.100 g of catalyst, except expt. 129.
All experiments employed a 10:100 torr mixture of benzene:deuterium reactants.

** Experiment using 0.250 g of catalyst
FIGURE 11. Deuterium Exchange Site Densities of A-2 Alumina by CO₂ Poisoning at 0°C and 100°C
Slope = $-2370 \, \text{O.k}\cdot l = -E_a/R$

$E_a = 4.70 \, \text{kcal/mole}$

**FIGURE 12.** Arrhenius Plot for Benzene/D$_2$ Exchange Reaction on A-2 Alumina
<table>
<thead>
<tr>
<th>Reaction Temp (°C)</th>
<th>molecules NH₃/cm² (x 10⁻13)</th>
<th>kφ (min⁻¹ x 10²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.650</td>
<td>8.90</td>
</tr>
<tr>
<td>22</td>
<td>1.650</td>
<td>8.73</td>
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<td>22</td>
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<td>7.48</td>
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<td>2.060</td>
<td>4.63</td>
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<td>25</td>
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<td>31</td>
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<td>419</td>
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<td>419</td>
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<tr>
<td>420</td>
<td>1.650</td>
<td>0.65</td>
</tr>
</tbody>
</table>

* All experiments run using 0.250 g of catalyst and a 10:100 torr mixture of benzene:deuterium reactants.

** Reactor evacuated one hour at 415°C, following NH₃ adsorption.
temperature of 420°C (expt. 152), the exchange sites were completely blocked, as illustrated in Figure 13. Evacuation for one hour at 420°C, following ammonia adsorption (expt. 163), restored less than 3% of the unpoisoned exchange activity. These results are roughly paralleled by the increasing rate of exchange of ammonia itself with D₂ at increasing temperatures, as shown in Figure 14. The exchange rate is very slow up to about 200°C, but then increases rapidly as the temperature is raised further.

The results of the last three experiments in Table IV, which various amounts of ammonia, smaller than the "lethal dose," were adsorbed at 420°C, are plotted in Figure 15. Here, \( k_\phi \) has been taken as 8.9 x 10⁻² \( \text{min}^{-1} \), the value in expt. 155. It is seen that the extrapolated site density from these data (0.7 x 10^{13}/cm²) is at least of the same order of magnitude as that obtained in Figure 10 and 11 from CO₂ poisoning.

D. Benzene-D₂ exchange on A-2 alumina - Other poisons

The effect of various other poisons on the benzene-D₂ exchange reaction at 25°C was also investigated, and these results are summarized in Table V. Nitrogen dioxide had only a marginal poisoning effect when added to the reaction at 25°C, but completely poisoned the exchange sites when it was preadsorbed at 415°C. Nitric oxide had virtually no effect when added at 25°C, preadsorbed at 415°C, or when a 1:1 mixture of NO:O₂ was preadsorbed at 415°C. Carbon monoxide likewise had no poisoning effect at 25°C, but reduced
FIGURE 13. Effect of Adsorption Temperature of a "Lethal Dose" of Ammonia on Benzene/D$_2$ Exchange Reaction on 0.250 g of A-2 Alumina at 250°C.
$k_{\phi} = 8.90 \times 10^{-2} \text{ min}^{-1}$

Molecules per cm$^2$ of Ammonia Preadsorbed at 420°C ($\times 10^{-13}$)

**FIGURE 15.** Benzene/D$_2$ Exchange on 0.250 g of A-2 Alumina at 25°C - Ammonia Pre-poisoning at 420°C
**TABLE V**

Benzene/D$_2$ Exchange on A-2 Alumina at 25°C - Various Poisons*

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Reaction Temp(°C)</th>
<th>Poison</th>
<th>Molecules/cm$^2$ (x 10$^{-13}$)</th>
<th>$k_\phi$(min$^{-1}$) (x 10$^2$)</th>
<th>$k_\phi,p$(min$^{-1}$) (x 10$^2$)</th>
<th>$k_\phi,p/k_\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>183</td>
<td>23</td>
<td>NO$_2$</td>
<td>1.65</td>
<td>6.53</td>
<td>5.00</td>
<td>.766</td>
</tr>
<tr>
<td>185</td>
<td>23</td>
<td>&quot;</td>
<td>2.97</td>
<td>6.25</td>
<td>4.02</td>
<td>.644</td>
</tr>
<tr>
<td>184</td>
<td>23</td>
<td>&quot;</td>
<td>1.65</td>
<td>-</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>176</td>
<td>22</td>
<td>(Preads. at 415°)</td>
<td>NO</td>
<td>1.65</td>
<td>8.45</td>
<td>7.71</td>
</tr>
<tr>
<td>177</td>
<td>21</td>
<td>&quot;</td>
<td>1.65</td>
<td>-</td>
<td>6.95</td>
<td>-</td>
</tr>
<tr>
<td>180</td>
<td>21</td>
<td>(Preads. at 415°)</td>
<td>&quot;</td>
<td>2.36</td>
<td>-</td>
<td>7.36</td>
</tr>
<tr>
<td>179</td>
<td>21</td>
<td>(Preads. at 415°)</td>
<td>1:1 NO:O$_2$</td>
<td>1.65</td>
<td>-</td>
<td>7.34</td>
</tr>
<tr>
<td>171</td>
<td>22</td>
<td>(Preads. at 415°)</td>
<td>CO</td>
<td>1.65</td>
<td>8.81</td>
<td>7.95</td>
</tr>
<tr>
<td>172</td>
<td>20</td>
<td>&quot;</td>
<td>1.65</td>
<td>-</td>
<td>2.72</td>
<td>-</td>
</tr>
<tr>
<td>173</td>
<td>21</td>
<td>(Preads. at 415°)</td>
<td>1:1 CO:O$_2$</td>
<td>1.65</td>
<td>-</td>
<td>0.00</td>
</tr>
<tr>
<td>130</td>
<td>29</td>
<td>CS$_2$</td>
<td>.330</td>
<td>12.97</td>
<td>0.00</td>
<td>.000</td>
</tr>
<tr>
<td>115</td>
<td>23</td>
<td>&quot;</td>
<td>.495</td>
<td>6.00</td>
<td>0.00</td>
<td>.000</td>
</tr>
<tr>
<td>131</td>
<td>22</td>
<td>&quot;</td>
<td>.165</td>
<td>5.40</td>
<td>0.002</td>
<td>.0004</td>
</tr>
<tr>
<td>132</td>
<td>24</td>
<td>&quot;</td>
<td>.165</td>
<td>3.49</td>
<td>0.001</td>
<td>.0003</td>
</tr>
</tbody>
</table>

* All experiments run using 0.250 g of catalyst and a 10:100 torr mixture of benzene: deuterium reactants.
the exchange rate by 2/3 (7.95 to 2.72 x 10^{-2} min^{-1}) when pre-
adsorbed at 415°C. A 1:1 mixture of CO:O_2 preadsorbed at
415°C completely poisoned the exchange sites. Carbon disul-
fide, when added to the reaction at 25°C, had an even stronger
poisoning effect than carbon dioxide. But unlike the results
with other poisons, the usual 520° O_2 pretreatment failed to
completely restore exchange activity, as seen from the k_φ
values for successive experiments, and when the reactor was
opened to replace the catalyst following expt. 132, a notice-
able odor of hydrogen sulfide was present.

E. Benzene-D_2 exchange on fluorided aluminas - CO_2 poison

The carbon dioxide poisoning experiments described
above for the A-2 alumina were repeated using 0.250 g samples
of the two fluorided aluminas, FA-1 and FA-2. Due to the
much slower reaction rates over these fluorided materials,
the reactions were run at 100°C for the FA-1 alumina and at
150°C for the FA-2 catalyst. The results are presented in
Tables VI and VII, and the corresponding site density plots
are shown in Figures 16 and 17. It is apparent from these
Figures that the extrapolated exchange site densities (0.025
x 10^{13}/cm^2 for FA-1 and 0.010 x 10^{13}/cm^2 for FA-2) for these
catalysts are much less than that of the unfluorided A-2
alumina. It is significant, however, that although the reac-
tion rates (at comparable temperatures) were much lower on
these catalysts, a certain fraction of the exchange activity
(5% for FA-1 and 15% for FA-2) could not be poisoned, even
when twice the "lethal dose" of CO_2 was added, a phenomenon
<table>
<thead>
<tr>
<th>Expt.</th>
<th>Reaction Temp(°C)</th>
<th>Molecules CO$_2$/cm$^2$ (x 10$^{-13}$)</th>
<th>kφ(min$^{-1}$) (x 10$^2$)</th>
<th>kφ,P(min$^{-1}$) (x 10$^2$)</th>
<th>kφ,p/kφ</th>
</tr>
</thead>
<tbody>
<tr>
<td>88</td>
<td>27</td>
<td>-</td>
<td>.325</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>89</td>
<td>70</td>
<td>-</td>
<td>.741</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>22</td>
<td>-</td>
<td>.260</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90a</td>
<td>100</td>
<td>-</td>
<td>1.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>97</td>
<td>100</td>
<td>.015</td>
<td>1.44</td>
<td>0.56</td>
<td>.390</td>
</tr>
<tr>
<td>96</td>
<td>100</td>
<td>.086</td>
<td>1.38</td>
<td>0.21</td>
<td>.155</td>
</tr>
<tr>
<td>94</td>
<td>100</td>
<td>.172</td>
<td>1.62</td>
<td>0.18</td>
<td>.110</td>
</tr>
<tr>
<td>92</td>
<td>100</td>
<td>.344</td>
<td>1.49</td>
<td>0.15</td>
<td>.100</td>
</tr>
<tr>
<td>149</td>
<td>100</td>
<td>.344</td>
<td>1.25</td>
<td>0.12</td>
<td>.097</td>
</tr>
<tr>
<td>93</td>
<td>100</td>
<td>.688</td>
<td>1.57</td>
<td>0.11</td>
<td>.073</td>
</tr>
<tr>
<td>95</td>
<td>100</td>
<td>1.204</td>
<td>1.45</td>
<td>0.09</td>
<td>.064</td>
</tr>
<tr>
<td>91</td>
<td>100</td>
<td>1.720</td>
<td>1.64</td>
<td>0.08</td>
<td>.051</td>
</tr>
<tr>
<td>97a</td>
<td>100</td>
<td>1.720 Preads.</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>98**</td>
<td>52</td>
<td>-</td>
<td>.392</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>-</td>
<td>.758</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-</td>
<td>1.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>-</td>
<td>2.77</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* All experiments run using 0.250 g of catalyst and a 10:100 torr mixture of benzene:deuterium reactants.

** Gave $E_a = 6.9$ kcal/mole
Extrapolated Site Density = 0.025 \times 10^{13}/\text{cm}^2

\text{FIGURE 16.} \quad \text{Deuterium Exchange Site Density of FA-1 Alumina by CO}_2\text{ Poisoning at } 100^\circ
<table>
<thead>
<tr>
<th>Expt.</th>
<th>Reaction Temp(°C)</th>
<th>Molecules CO₂/cm² (x 10⁻¹³)</th>
<th>k_φ(min⁻¹) (x 10²)</th>
<th>k_φ,P(min⁻¹) (x 10²)</th>
<th>k_φ,P/k_φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>150</td>
<td>-</td>
<td>0.550</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>102</td>
<td>152</td>
<td>-</td>
<td>0.597</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>107</td>
<td>155</td>
<td>.0045</td>
<td>0.792</td>
<td>0.356</td>
<td>.442</td>
</tr>
<tr>
<td>106</td>
<td>156</td>
<td>.009</td>
<td>0.735</td>
<td>0.286</td>
<td>.390</td>
</tr>
<tr>
<td>104</td>
<td>153</td>
<td>.180</td>
<td>0.806</td>
<td>0.282</td>
<td>.350</td>
</tr>
<tr>
<td>108</td>
<td>156</td>
<td>.270</td>
<td>0.863</td>
<td>0.254</td>
<td>.294</td>
</tr>
<tr>
<td>105</td>
<td>155</td>
<td>.360</td>
<td>0.909</td>
<td>0.231</td>
<td>.254</td>
</tr>
<tr>
<td>110</td>
<td>156</td>
<td>.900</td>
<td>0.810</td>
<td>0.121</td>
<td>.150</td>
</tr>
<tr>
<td>109</td>
<td>157</td>
<td>1.800</td>
<td>0.921</td>
<td>0.129</td>
<td>.140</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Reaction Temp(°C)</th>
<th>Molecules CO₂/cm² (x 10⁻¹³)</th>
<th>k_φ(min⁻¹) (x 10²)</th>
<th>k_φ,P(min⁻¹) (x 10²)</th>
<th>k_φ,P/k_φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>111**</td>
<td>79</td>
<td>-</td>
<td>0.185</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>103</td>
<td>-</td>
<td>-</td>
<td>0.354</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>129</td>
<td>-</td>
<td>-</td>
<td>0.605</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>154</td>
<td>-</td>
<td>-</td>
<td>0.913</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* All experiments run using 0.250 g of catalyst and a 10:100 torr mixture of benzene:deuterium reactants.

** Gave E_a = 6.3 kcal/mole
Extrapolated Site Density = $0.01 \times 10^{13}$/cm$^2$

Molecules of Carbon Dioxide Added per cm$^2$ ($\times 10^{-13}$)

FIGURE 17. Deuterium Exchange Site Density of FA-2 Alumina by CO$_2$ Poisoning at 150°
Slope = -3470 kcal/mol
\( E_a = 6.90 \text{ kcal/mole} \)

FIGURE 10. Arrhenius Plot for Benzene/D₂ Exchange Reaction on FA-1 Alumina
Slope = $-3.163 \text{ K}^{-1} = -\frac{E_a}{R}$

$E_a = 6.30 \text{ kcal/mole}$

**Arhenius Plot for Benzene/D$_2$ Exchange Reaction on FA-2 Alumina**

Figure 19.
never observed with the unfluorided alumina samples. Arrhenius plots of expts. 98 (Table VI) and 111 (Table VII) are shown in Figures 18 and 19, and gave activation energies for the benzene-D$_2$ exchange reaction of 6.9 kcal/mole on FA-1 and 6.3 kcal/mole on FA-2.

F. Isomerization/D$_2$ exchange of 1-butene on A-2 alumina

The other test reaction used in the present work was the isomerization/D$_2$ exchange of 1-butene, and the results of these experiments on A-2 alumina are given in Table VIII. Both n-butene isomerization (without skeletal rearrangement nor observable polymerization) and deuterium incorporation (without saturation to butane) occurred simultaneously. Results of a typical experiment (expt. 27) with no poison added are shown in Figures 20, 21, and 22. Figures 20 and 21 depict the extent of the isomerization reaction as plotted according to equation (9), and the product distribution, respectively, while Figure 22 shows the deuterium incorporation, as calculated from equation (1). The first-order isomerization curve in Figure 20 is linear up to 70% conversion of the 1-butene, indicating that no significant self-poisoning occurred during the reaction. Figure 21 shows that cis-2-butene is formed in excess of the trans isomer during the initial stages of the reaction, even though it is thermodynamically the less favorable of the two isomers [51]. As observed previously [60], kinetic, rather than thermodynamic, factors govern the initial course of the catalytic reaction.

The effect of addition of a "lethal dose" of carbon
TABLE VIII
Isomerization/D$_2$ Exchange of 1-Butene on A-2 Alumina*

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Butene:D$_2$ (torr)</th>
<th>Poison</th>
<th>Molecules/cm$^2$ (x 10$^{-13}$)</th>
<th>$k$(min$^{-1}$) (x 10$^3$)</th>
<th>$k_p$(min$^{-1}$) (x 10$^3$)</th>
<th>Effect of Poison on Exchange Reac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>70:288</td>
<td>None</td>
<td>-</td>
<td>4.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>100:408</td>
<td>&quot;</td>
<td>-</td>
<td>3.42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>33</td>
<td>102:398</td>
<td>&quot;</td>
<td>-</td>
<td>2.86</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>39</td>
<td>100:423</td>
<td>CO$_2$</td>
<td>1.65</td>
<td>2.70</td>
<td>1.94</td>
<td>Exchange Stopped</td>
</tr>
<tr>
<td>45</td>
<td>101:399</td>
<td>&quot;</td>
<td>1.65</td>
<td>3.55</td>
<td>2.72</td>
<td>&quot;</td>
</tr>
<tr>
<td>51</td>
<td>100:410</td>
<td>&quot;</td>
<td>3.30 (Preads.)</td>
<td>-</td>
<td>2.99</td>
<td>No Exchange Obs.</td>
</tr>
<tr>
<td>55</td>
<td>100:399</td>
<td>&quot;</td>
<td>1.65 (Preads.)</td>
<td>-</td>
<td>2.67</td>
<td>&quot;</td>
</tr>
<tr>
<td>56</td>
<td>100:402</td>
<td>SO$_2$</td>
<td>1.65</td>
<td>3.01</td>
<td>3.20</td>
<td>No Effect</td>
</tr>
<tr>
<td>61</td>
<td>100:402</td>
<td>NH$_3$</td>
<td>1.65</td>
<td>2.26</td>
<td>1.64</td>
<td>&quot;</td>
</tr>
<tr>
<td>65</td>
<td>100:401</td>
<td>Pyridine</td>
<td>0.33</td>
<td>2.50</td>
<td>2.30</td>
<td>&quot;</td>
</tr>
<tr>
<td>73</td>
<td>100:410</td>
<td>HCl</td>
<td>1.65</td>
<td>2.68</td>
<td>2.60</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

* All experiments run at 25°C, using 0.250 g of catalyst.
FIGURE 20. Isomerization Rate of a 100:408 torr Mixture of 1-Butene:D₂ on 0.250 g of A-2 Alumina at 25°C

\[ \ln \left( \frac{X_e}{X_e - x} \right) \]

\[ k = 0.00342 \text{ min}^{-1} \]
FIGURE 21. Product Distribution during Isomerization of a 100:408 torr Mixture of 1-Butene:D$_2$ on 0.250 g of A-2 Alumina at 25°C
FIGURE 22. Deuterium Incorporation during Isomerization of a 100:408 torr Mixture of 1-Butene:D₂ on 0.250 g of A-2 Alumina at 25°C
FIGURE 23. Isomerization Rate of a 101:399 torr Mixture of 1-Butene:D₂ on 0.250 g of A-2 Alumina at 25°C - CO₂ Poisoning
FIGURE 24. Product Distribution during Isomerization of a \(101:399\) torr Mixture of \(1\)-Butene:\(D_2\) on 0.250 g of A-2 Alumina at 25°C – \(CO_2\) Poisoning
FIGURE 25. Deuterium Incorporation during Isomerization of a 101:399 torr Mixture of 1-Butene:D$_2$ on 0.250 g of A-2 Alumina at 25°C - CO$_2$ Poisoning
dioxide during the reaction is illustrated for a typical run (expt. 45) in Figures 23, 24, and 25. As shown (Figures 23 and 24), the isomerization reaction was not greatly affected by the poison, but the exchange reaction was completely poisoned (Figure 25). Addition of a second quantity of CO$_2$ equal to the first produced no further effect on either reaction. The slopes of the exchange curves for both 2-butenes in Figure 25 are non-zero after poison addition because of the continued formation of these products from the reactant 1-butene which itself contained a high deuterium concentration. These positive slopes thus represent a redistribution of D-atoms through isomerization within the butene molecules and do not indicate further exchange with gaseous D$_2$. When a "lethal dose" of CO$_2$ was preadsorbed onto the catalyst prior to starting the reaction, the isomerization again proceeded normally, but no deuterium exchange whatever could be detected in any of the three butene isomers. Addition of a "lethal dose" of CO$_2$ during the reaction had no effect.

Experiments were also performed (runs 56, 61, 65, 73) in which "lethal doses" of sulfur dioxide, ammonia, pyridine, and hydrogen chloride were added during the reaction at 25°C, but in all four cases, only very small effects were observed on either the isomerization or exchange reaction rates (See Table VIII).

It is interesting to note that in all cases in which the catalyst was not prepoisoned with CO$_2$, the deuterium content of 1-butene always exceeded that of either of the
2-butene isomers (Figures 22 and 25), even in the initial stages of the reaction when the 1-butene reactant was in large excess. (As seen in Figure 21, for example, even after 150 minutes of reaction time, the gas mixture was still over 60% 1-butene). When an experiment was carried out using a reactant mixture of cis-2-butene:D₂, a situation in which 1-butene was never in excess, the difference in exchange rates between 1-butene and the 2-butenes was even more noticeable (Figure 26).

G. Temperature-programmed desorption experiments

1. 1-Butene adsorbate

The TPD experiments were carried out on a 0.250 g sample of A-2 alumina, using the technique described in a previous section (pp. 43-45). Table IX summarizes the results of the experiments in which the catalyst was exposed for 60 minutes to different 1-butene:D₂ mixtures, and, in some cases, to CO₂ pre-poisoning. The fourth column in this Table indicates whether the surface hydroxyls were in the form of -OH or -OD, and Φ₀, Φ₁, and Φ₂ represent the average number of deuterium atoms per hydrocarbon molecule in the gas phase, and in peaks A and B, respectively. Curve 2 in Figure 27 illustrates the desorption obtained in a typical run (expt. 220) on an unpoisoned surface. The two peaks, A and B, had desorption maxima at 75° and 280°C, respectively, and were trapped for analysis during the temperature ranges indicated by the bars. Curve 1 in Figure 27 shows the desorption chromatogram for an experiment (run 225) in which the catalyst
FIGURE 26. Deuterium Incorporation during Isomerization of a 100:400 torr Mixture of cis-2-Butene:D₂ on 0.250 g of A-2 Alumina at 25°C
TABLE IX

Temperature-programmed Desorption Experiments - 1-Butene Adsorbate

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Butene:D₂ Ratio in Adsorbate**</th>
<th>Molecules of CO₂ Ads./cm² (x 10⁻¹³)</th>
<th>Surface</th>
<th>φG</th>
<th>φA</th>
<th>φB</th>
<th>Total Butene Molecules Desorbed/cm² (x 10⁻¹³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>217</td>
<td>1:10</td>
<td>-</td>
<td>H</td>
<td>-</td>
<td>1.38</td>
<td>0.58</td>
<td>0.69</td>
</tr>
<tr>
<td>218</td>
<td>1:10</td>
<td>-</td>
<td>H</td>
<td>-</td>
<td>1.36</td>
<td>0.35</td>
<td>0.61</td>
</tr>
<tr>
<td>216</td>
<td>1:10</td>
<td>-</td>
<td>H</td>
<td>-</td>
<td>1.47</td>
<td>0.54</td>
<td>-</td>
</tr>
<tr>
<td>218</td>
<td>1:10</td>
<td>1.65</td>
<td>H</td>
<td>-</td>
<td>0.01</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>223</td>
<td>1:10</td>
<td>1.65</td>
<td>H</td>
<td>-</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>220</td>
<td>1:10</td>
<td>-</td>
<td>D</td>
<td>-</td>
<td>2.01</td>
<td>6.73</td>
<td>0.66</td>
</tr>
<tr>
<td>227</td>
<td>1:10</td>
<td>-</td>
<td>D</td>
<td>1.71</td>
<td>1.35</td>
<td>6.40</td>
<td>0.72</td>
</tr>
<tr>
<td>231</td>
<td>1:10</td>
<td>-</td>
<td>D</td>
<td>1.66</td>
<td>1.44</td>
<td>6.60</td>
<td>0.67</td>
</tr>
<tr>
<td>224</td>
<td>1:0</td>
<td>-</td>
<td>D</td>
<td>-</td>
<td>0.33</td>
<td>6.41</td>
<td>0.58</td>
</tr>
<tr>
<td>232</td>
<td>1:0</td>
<td>-</td>
<td>D</td>
<td>0.12</td>
<td>0.29</td>
<td>6.47</td>
<td>0.67</td>
</tr>
<tr>
<td>226</td>
<td>1:10</td>
<td>1.65</td>
<td>D</td>
<td>-</td>
<td>0.16</td>
<td>6.01</td>
<td>-</td>
</tr>
<tr>
<td>225</td>
<td>1:0</td>
<td>1.65</td>
<td>D</td>
<td>0.00</td>
<td>0.12</td>
<td>5.92</td>
<td>-</td>
</tr>
<tr>
<td>229</td>
<td>1:10</td>
<td>-</td>
<td>D</td>
<td>1.57</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1:0</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>0.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1:0</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
<td>0.24</td>
<td>6.13</td>
<td>0.56</td>
</tr>
</tbody>
</table>

* All experiments run using 0.250 g of catalyst.

** All adsorbate exposure times = 60 min at 25°C.
**FIGURE 27.** Desorptograms of 1-Butene on 0.250 g of A-2 Alumina
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Substance</th>
<th>Gas Phase (%)</th>
<th>Peak A (%)</th>
<th>Peak B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>231</td>
<td>Ethylene</td>
<td>0.0</td>
<td>0.0</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>n-Butane</td>
<td>6.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1-Butene</td>
<td>20.7</td>
<td>8.0</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td>t-2-Butene</td>
<td>48.7</td>
<td>63.0</td>
<td>44.3</td>
</tr>
<tr>
<td></td>
<td>c-2-Butene</td>
<td>24.5</td>
<td>28.8</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>1,3-Butadiene</td>
<td>0.0</td>
<td>0.3</td>
<td>2.3</td>
</tr>
<tr>
<td>226</td>
<td>Ethylene</td>
<td>-</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>(Preads.</td>
<td>1-Butene</td>
<td>-</td>
<td>0.6</td>
<td>3.8</td>
</tr>
<tr>
<td>CO₂)</td>
<td>t-2-Butene</td>
<td>-</td>
<td>5.7</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>c-2-Butene</td>
<td>-</td>
<td>2.1</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>1,3-Butadiene</td>
<td>-</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Carbon dioxide</td>
<td>-</td>
<td>91.6</td>
<td>79.7</td>
</tr>
</tbody>
</table>

* Second column represents percentage of hydrocarbon only.
had been pre-poisoned with a "lethal dose" of CO$_2$. The wide temperature range of CO$_2$ desorption effectively masked the appearance of peak B, but when the effluent was trapped over the same temperature range as was used in expt. 220 (200-350$^\circ$), the existence of peak B was confirmed.

Table X shows typical GLC analyses of products from the gas phase and from the two desorption peaks. The desorbed n-butenes were essentially in thermodynamic equilibrium corresponding to the temperature at which each peak maximum occurred. Small amounts of saturated (n-butane), cracked (ethylene), and dehydrogenated (butadiene) products were also observed. Much more CO$_2$ was adsorbed than hydrocarbon, as noted by the predominance of CO$_2$ in expt. 226 in which the catalyst had been pre-poisoned by a "lethal dose" of CO$_2$.

It is seen from Table IX that when the catalyst was in a hydrogenated condition, (expts. 216, 217, and 222), deuterium exchange into peak B was not very extensive, and that this exchange could be completely eliminated by preadsorption of carbon dioxide (expt. 218 and 223). When the catalyst was initially in a deuterated condition, however, the desorbed olefins in peak B contained large concentrations of D-atoms (expt. 220, 227, and 231), and the deuterium incorporation was only very slightly affected either by preadsorption of CO$_2$ (expt. 226) or by absence of gaseous D$_2$ from the adsorbate (expt. 224 and 232).

The appearance of deuterium atoms in the gas phase and peak A olefins, on the other hand, was dependent primarily
on the presence of gaseous $D_2$ in the adsorbate, regardless of the hydrogenated or deuterated condition of the surface (expts. 217, 220, 222, 216, 227, 231). Deuterium incorporation into the peak A material was almost completely eliminated either by preadsorption of CO$_2$ (expts. 218, 223, 225, and 226) or by the absence of gaseous $D_2$ (expts. 224 and 232). The appearance of deuterium in the gas phase olefins was completely blocked by CO$_2$ poisoning (expt. 225). The unpoisoned deuterium content of the gas phase material, however, always exceeded that of the peak A material whenever gaseous $D_2$ was present (expts. 227 and 231).

Experiment 229 was carried out to investigate the communication between the gas phase material and the adsorbed species A and B. The gas phase from the initial 1-butene:$D_2$ adsorbate was removed after a 60 minute exposure time and analyzed, and a 1-butene charge was admitted. After 60 minutes, the gas phase was again removed for analysis, and the TPD was carried out only until peak A was removed (175°C). The reactor was rapidly quenched to 25°C, evacuated, and the catalyst was contacted with another 1-butene charge. After 60 minutes, a complete desorptionogram (25-500°C) was run. The deuterium content of peak B was only slightly reduced (from 6.5 to 6.0) by the two dilutions with undeuterated 1-butene, indicating that little communication existed between the B-type material and the gas phase species. By contrast, the deuterium content of the type-A material was significantly reduced (from 1.4 to 0.5) by dilution, and some of the deuterium atoms removed from the surface appeared in the gaseous
**TABLE XI**

Temperature-programmed Desorption Experiments - Benzene Adsorbate*

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Benzene:D&lt;sub&gt;2&lt;/sub&gt; Ratio in Adsorbate</th>
<th>Adsorption Time (min)</th>
<th>Molecules of CO&lt;sub&gt;2&lt;/sub&gt; Ads./cm&lt;sup&gt;2&lt;/sup&gt; (x 10&lt;sup&gt;-13&lt;/sup&gt;)</th>
<th>Surface</th>
<th>( \phi_G )</th>
<th>( \phi_A )</th>
<th>( \phi_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>233</td>
<td>1:10</td>
<td>5</td>
<td>-</td>
<td>D</td>
<td>.243</td>
<td>.018</td>
<td>4.631</td>
</tr>
<tr>
<td>234</td>
<td>1:0</td>
<td>5</td>
<td>-</td>
<td>D</td>
<td>.014</td>
<td>.033</td>
<td>5.023</td>
</tr>
<tr>
<td>235</td>
<td>1:10</td>
<td>5</td>
<td>1.65</td>
<td>D</td>
<td>.001</td>
<td>.001</td>
<td>5.118</td>
</tr>
<tr>
<td>236</td>
<td>1:10</td>
<td>60</td>
<td>-</td>
<td>D</td>
<td>1.143</td>
<td>.166</td>
<td>5.204</td>
</tr>
<tr>
<td>237</td>
<td>1:10</td>
<td>180</td>
<td>-</td>
<td>D</td>
<td>1.938</td>
<td>.325</td>
<td>5.267</td>
</tr>
<tr>
<td>238</td>
<td>1:10</td>
<td>1440</td>
<td>-</td>
<td>D</td>
<td>1.155</td>
<td>.800</td>
<td>5.205</td>
</tr>
</tbody>
</table>

* All experiments run using 0.250 g of catalyst.
FIGURE 28. Desorptograms of Benzene on 0.250 g of A-2 Alumina
species ($\phi_G = 0.35$). However, the communication between gaseous species and type-A olefins was not rapid, since $\phi_G$ always exceeded $\phi_A$ when gaseous $D_2$ was present, and was always less than $\phi_A$ in the absence of $D_2$.

2. Benzene adsorbate

The results of TPD experiments using various benzene:$D_2$ mixtures as adsorbates are summarized in Table XI, and desorptograms are shown in Figure 28 for an unpoisoned surface (Curve 1, expt. 236) and for one that had been pre-poisoned with $CO_2$ (Curve 2, expt. 235). The desorptograms are almost identical to those obtained with 1-butene (Figure 27), except that peak A was much larger due to the large amount of physically adsorbed benzene (note scale on left-hand ordinate). Both peaks consisted only of benzene; no saturation or cracking products were observed for either peak.

Data in Table XI shows that the main features of deuterium incorporation into the gas phase and peaks A and B are very similar to those discussed above for 1-butene, except that the amount by which $\phi_G$ exceeded $\phi_A$ in the presence of gaseous $D_2$ was much more pronounced for benzene. Only after an exposure time of 24 hours (expt. 238) was an appreciable redistribution of deuterium between gas phase and type-A material observed, while deuterium incorporation into peak B was virtually unaffected by changes in adsorption time. Preadsorption of carbon dioxide again eliminated deuterium pickup by the gas phase and peak A olefins, but had no effect on the deuterium content of peak B.
H. Infrared experiments

Infrared studies were undertaken in an attempt to gain some information about the manner in which carbon dioxide poisons the deuterium exchange sites on alumina. All spectra were obtained using a 0.060 g wafer (25 mg/cm²) of A-2 alumina, and employing the technique described in a previous section (pp. 52-53). The spectrum obtained for the plain alumina sample, immediately following O₂ pretreatment, is shown for the frequency range 2000-1100 cm⁻¹ (5-9 microns) in Curve a of Figure 29. The results of all infrared experiments are summarized in Table XII.

When the sample was exposed to twice the "lethal dose" of carbon dioxide for five minutes at 25°C, followed by a five minute evacuation (expt. 268), the spectrum shown in Curve b of Figure 29 was obtained. The absorption bands at 1233, 1480, 1640, 1780, and 1820 cm⁻¹ are identical to those reported by Parkyns [106] for CO₂ adsorbed on alumina, and discussed in an earlier section (pp. 26-29). Adsorption of 1-butene onto the CO₂-containing sample (expt. 268) produced essentially no change in the spectrum of curve b. But when either 1-butene (expt. 269) or benzene (expt. 270) was adsorbed onto the catalyst prior to CO₂ adsorption, the 1233 and 1640 cm⁻¹ bands were reduced to less than half their previous intensity, while the 1480, 1780, and 1820 cm⁻¹ bands were virtually unchanged.

Exposure of the sample to twice a "lethal dose" of ammonia at 420°C (expt. 271) produced an intense absorption band at 1277 cm⁻¹ in the spectrum recorded at 25°C (curve c).
FIGURE 29. Infrared Spectra of A-2 Alumina with CO$_2$ and NH$_3$ Adsorbates


**TABLE XII**

Summary of Infrared Experiments on A-2 Alumina

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Adsorbate*</th>
<th>Ads. Temp (°C)</th>
<th>Surface</th>
<th>Infrared Bands Observed (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>268</td>
<td>CO₂</td>
<td>25</td>
<td>H</td>
<td>1233, 1480, 1640, 1780, 1820</td>
</tr>
<tr>
<td></td>
<td>1-Butene</td>
<td>25</td>
<td>H</td>
<td>1233, 1480, 1640, 1780, 1820</td>
</tr>
<tr>
<td>269</td>
<td>1-Butene</td>
<td>25</td>
<td>H</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>25</td>
<td>H</td>
<td>1480, 1780, 1820, Bands at 1233 and 1640 reduced to less than half their intensity in expt. 268</td>
</tr>
<tr>
<td>270</td>
<td>Benzene</td>
<td>25</td>
<td>H</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>25</td>
<td>H</td>
<td>1480, 1780, 1820</td>
</tr>
<tr>
<td>271</td>
<td>Ammonia</td>
<td>25</td>
<td>H</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>420</td>
<td>H</td>
<td>1277</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>25</td>
<td>H</td>
<td>1277, 1780, 1820</td>
</tr>
<tr>
<td>272</td>
<td>CO₂</td>
<td>25</td>
<td>D</td>
<td>1480, 1610, 1780, 1820</td>
</tr>
<tr>
<td>273</td>
<td>CO₂</td>
<td>110</td>
<td>H</td>
<td>1480 (Trace of 1233, 1640)</td>
</tr>
</tbody>
</table>

* All adsorptions involved exposure of 3.3 x 10¹³ molecules/cm² of adsorbate to the sample for five minutes, followed by a five minute evacuation.
Subsequent adsorption of CO$_2$ onto the ammonia-containing catalysts produced only the 1780 and 1820 cm$^{-1}$ bands and failed to affect the 1277 cm$^{-1}$ band of the adsorbed ammonia.

Adsorption of CO$_2$ onto a deuterated catalyst (expt. 272) caused the 1640 cm$^{-1}$ band to shift to 1610 cm$^{-1}$ (shown by the dotted band in Figure 29) and the 1233 cm$^{-1}$ band to disappear entirely from the observable portion of the spectrum (over 1000 cm$^{-1}$), while the 1480 cm$^{-1}$ band was unaffected by catalyst deuteration. The low intensity and broadness of the 1780-1820 cm$^{-1}$ band prevented an accurate determination of whether it was shifted or not, but it appeared likely that no shift occurred. Parkyns [106] observed essentially the same behavior for CO$_2$ adsorption on deuterated alumina. Finally, when CO$_2$ was adsorbed at 100°C (expt. 273), only the band at 1480 cm$^{-1}$ was observed in the 25°C spectrum (at a somewhat lower intensity than previously due to the smaller amount of adsorption); the other CO$_2$ adsorption bands were almost entirely absent.
IV. DISCUSSION

A. Conclusions from investigation

In order that the results of the present study be properly considered within the framework of the overall objective, viz., a study of the catalytic and surface properties of active alumina, it is useful to briefly summarize the significant conclusions drawn from the investigation prior to a more detailed discussion. Adsorption of benzene and n-butene on alumina occurs on at least two types of surface sites, A and B, having distinct heats of adsorption. One of these adsorbed forms (B) is strongly-held and does not participate in low-temperature (<150°C) surface reactions. The other, more weakly-held form (A) communicates to a limited extent with gas phase material and is a partial contributor to deuterium exchange reactions occurring at 25°C.

In addition, two different and independent kinds of catalytically-active sites exist on the surface of activated alumina at 25°C. One of these promotes double-bond migration and cis-trans rotation in olefins, while the other type catalyzes exchange of olefinic and aromatic hydrogen atoms with gaseous deuterium. The former sites are relatively insensitive to poisoning by carbon dioxide, while the activity of the latter sites can be completely poisoned by adsorption of sufficient carbon dioxide at 25°C or ammonia at 420°C. Little information was obtained about the nature of the isomerization sites due to their insensitivity to the various poisons used. The D₂ exchange sites, however, exist
on the surface with a site density of no greater than \(0.3 \times 10^{13}/\text{cm}^2\) and are probably associated with exposed \(\text{Al}^{3+}\) ions on the surface. It is likely that they consist of other sites in addition to the A-sites described above. Fluoridation of alumina greatly reduces the exchange site concentration, probably due to attachment of F-atoms to \(\text{Al}^{3+}\) ions.

Adsorption of carbon dioxide on alumina is complex and involves the formation of several different adsorbed species having a wide range of adsorption energies. It is likely that only one of these adsorbed forms is responsible for poisoning the \(\text{D}_2\) exchange sites on alumina. The exact nature of this active form remains elusive, but it appears to be associated with an infrared band at \(1480 \text{ cm}^{-1}\) in the spectrum of adsorbed carbon dioxide. Poisoning of the exchange sites by adsorption of ammonia at \(420^\circ\text{C}\) apparently occurs by attachment of an \(\text{NH}_2^-\) species to the active sites.

B. Dual-site nature of alumina

It is evident from the results of the 1-butene isomerization/exchange process (Table VIII, Figures 20-25) that at least two completely different and independent kinds of catalytically-active sites exist on the surface of alumina at \(25^\circ\text{C}\). As seen in Figure 23, the sites that promote isomerization (double-bond migration and cis-trans rotation) of the n-butene are relatively insensitive to poisoning by carbon dioxide, since the isomerization process proceeds virtually unchanged after poison addition. The sites catalyzing exchange with gaseous deuterium, on the other hand,
are completely poisoned by the addition of a "lethal dose" of CO₂, as shown in Figure 25.

This result is consistent with the observation that the isomerization and exchange reactions on alumina appear to occur independently of each other at 25°C. If the two processes were simultaneous, i.e., if the incorporation of a D-atom were a necessary step in the 1-butene isomerization mechanism, then during the initial stages of the overall reaction the two 2-butenes would contain at least one D-atom per molecule. For independent occurrence of the two processes, on the other hand, the deuterium content of all three butene isomers should approach zero at zero reaction time. Examination of Figures 22 and 25 reveals that the latter situation, in fact, exists, in agreement with results obtained by previous investigators [60, 61, 63] who found that butene isomerization on alumina proceeds by an intra-, rather than an inter-molecular mechanism.

Little information could be gained about the isomerization sites due to their lack of sensitivity to any of the various "poisons" used in the present study (See Table VIII). The deuterium exchange sites, however, are apparently identical to those that catalyze the benzene-D₂ exchange reaction, since a few cursory 1-butene/D₂ experiments using various amounts of CO₂ poison smaller than the "lethal dose" appeared to give fractions of poisoned activity similar to those in Figure 10. The comparison was not direct, since individual exchange rate constants cannot be determined for the n-butene system, but the correlation was evident.
Additional information about these exchange sites was obtained from various of the other experimental results and will be discussed below.

C. Adsorption of benzene and n-butene on alumina

The results of the temperature-programmed desorption experiments (Tables IX and XI, Figures 27 and 28) indicate that both benzene and the n-butenes are adsorbed on alumina at 25°C on two types of sites, A and B, having heats of desorption of approximately 20 and 40 kcal/mole, respectively (these values are calculated from equation 11 of Ref. 32, utilizing the rate of temperature increase, temperatures at the desorption maxima, and an assumed pre-exponential factor of $10^{14}$ sec$^{-1}$). Contrary to original expectations, however, these adsorption sites do not correspond to the two kinds of catalytic sites evidenced by the 1-butene isomerization/exchange results. The high temperature (290°C) required for desorption of the material on sites-B precludes its participation in either the isomerization or D$_2$ exchange reactions at 25°C. As shown by the results of expt. 299 in Table IX, communication between material adsorbed on the B-sites and gas phase material is very slight at 25°C. Virtually all the D-atoms acquired by the B-type hydrocarbon are obtained from surface deuteroyxls, when these are present, during the desorption process itself. Moreover, this deuterium acquisition appears to be insensitive to the presence or absence of adsorbed CO$_2$, although in the case of a pre-poisoned surface, a considerable amount of carbon
dioxide desorbs before desorption of the B-type material begins, as seen in Figures 27 and 28. The isomerized olefins in the desorbate simply reflect thermal equilibration of the desorbing surface species.

Hydrocarbons adsorbed on the A-sites are held less strongly than those on the B-sites and communicate to a limited extent with gas phase material. Acquisition of D-atoms by the A-type material is dependent primarily on the presence of gaseous $D_2$ and is relatively insensitive to the state of the surface hydroxyls. Prior adsorption of carbon dioxide, however, almost completely eliminates the appearance of deuterium in the desorbed A-type material. These sites thus appear to be identical to those that catalyze the $D_2$ exchange reactions of benzene and the n-butenes at 25°C, since the same poisoning effect by CO$_2$ was observed for these reactions as in the TPD results, and the occurrence of a reaction at all necessitates communication between adsorbed and gas phase material. In addition, a separate experiment (not shown in any of the Tables) revealed that the rate of benzene-$D_2$ exchange at 25°C was the same over both a deuterated and hydrogenated surface.

However, if the A-sites were the only ones responsible for the $D_2$ exchange reactions, then the gas phase hydrocarbon would reflect an equilibrium with the material adsorbed on these sites and could contain no more deuterium, on the average, than the desorbed A-type material. As seen in Tables IX and XI, however, whenever gaseous deuterium was present in the adsorbate (on an unpoisoned surface), the gas
phase hydrocarbon always contained more deuterium than the peak A olefins. (The values of \( \phi_A \) for benzene in Table XI are lowered somewhat by the presence of unreactive physically-adsorbed material, but the effect is evident). The only reasonable way in which \( \phi_C \) can exceed \( \phi_A \) is by contribution from \( D_2 \) exchange that occurs on a third type of site, E. These sites are evidently susceptible to poisoning by \( CO_2 \) in much the same fashion as the A-sites, as seen in Table IX and XI, indicating that the two types of sites are probably quite similar. Failure to observe these E-sites in the TPD desorptograms suggests that the heats of adsorption of benzene and the n-butene on them are probably quite low, and that equilibrium between material adsorbed on these sites and the gas phase hydrocarbon may be much more rapid than for the A-sites. If the latter situation, in fact, exists, it may explain the catalytic importance of these sites.

Finally, the sites that promote isomerization of the n-butene appear to be quite different and independent from either the A- or E-sites, since the isomerization sites are virtually unaffected by \( CO_2 \), and the isomerization and \( D_2 \) exchange reactions of the n-butene are evidently unrelated processes, as discussed above. For these reasons, it appears likely that isomerization of the n-butene occurs on a fourth type of site, I, on the alumina surface. The heat of adsorption of the n-butene on these sites is evidently quite low, as for the E-sites, since they also escaped detection by the TPD technique. Whether adsorption of benzene also occurs on these sites is a moot point since a detectable
isomerization-type reaction is not possible for this molecule.

As mentioned previously, no further information about these I-sites could be obtained by the methods used in the present study due to their inertness to the various poisons used. The $D_2$ exchange sites (A and E), however, have been at least partially characterized by the results of the various poisoning experiments and infrared data, and these results will be considered in the discussion that follows.

D. Characterization of $D_2$ exchange sites on alumina

Information about the $D_2$ exchange sites was obtained indirectly, principally by observing the effects of various "poisons" on the benzene- and 1-butene-$D_2$ reactions, since at least a portion of the sites that adsorb the poisoning material must necessarily also be responsible for promoting the catalytic reaction.

1. Carbon dioxide adsorption on alumina

In agreement with preliminary findings by previous investigators [84], adsorption of carbon dioxide on alumina appears to be quite complex and results in the formation of several types of adsorbed species. This phenomenon is reflected in the desorptograms (Figures 27 and 28) of a $CO_2$-poisoned surface which reveal the wide range of adsorption energies for the $CO_2$-desorption process. Since it is unlikely that even extensive site heterogeneity would result in such a broad range of desorption energies [32], it is probable that adsorption occurs on several different types
of sites at 25°C.

The results shown in Tables II and III and in Figures 10 and 11, however, make it clear that not all of these CO₂-adsorption sites are responsible for catalyzing the D₂ exchange reactions. Since the temperature range employed in these experiments (0-100°C) is a negligible one with regard to the stability of the alumina surface (recall discussion in Part I), it is unlikely that the exchange site concentration actually varies with temperature, as it appeared originally. In reality, what occurs is that at higher temperatures (100°C) the CO₂ molecules preferentially adsorb on the sites having the highest heat of adsorption, and these are evidently the catalytically-active sites. At lower temperatures (0°C, 25°C) adsorption of the poison occurs on non-active sites as well, thus causing the apparently higher site densities observed.

These results are entirely consistent with those of Larson and Hall [84] who studied the poisoning effect of CO₂ on the CH₄-CD₄ equilibration on alumina at 25°C. They found that of the several forms of adsorbed carbon dioxide, only the most strongly-held (highest heat of adsorption) poisoned the equilibration. It is evident, therefore, that the determination of exchange site densities by the CO₂ poisoning technique can only be used to establish an upper limit on the true (A + E) site concentration, and that this limit (at 100°C) is no greater than approximately 0.3 x 10¹³ sites/cm².

The precise nature of the exchange sites remains
somewhat elusive, although Peri [114] has observed that carbon dioxide, benzene, and 1-butene are all strongly chemisorbed on the so-called "a-sites" of alumina which consist of an exposed Al$^{3+}$ ion with an O$^-$ ion nearest neighbor. Larson and Hall [84] have noted, however, that on a 90% dehydroxylated alumina surface, these a-sites are 10 times as numerous as the observed D$_2$ exchange sites. They believe that only high-energy a-sites, such as those at domain boundaries, for example, are involved in the catalytic reaction. It appears likely, therefore, that the exchange sites are in some way associated with surface Al$^{3+}$ ions having a particular surrounding environment of O$^-$ and/or hydroxyl ions.

Further, indirect, information about the exchange sites may possibly be gleaned from the results of the infrared experiments shown in Table XII. The absorption bands observed for CO$_2$ in the first spectrum of expt. 268 are very similar to those obtained by Parkyns [106] who assigned them to various postulated surface species, as discussed previously in Part I (pp. 26-29). The 1780 and 1820 cm$^{-1}$ bands were assigned to the stretching vibrations of very similar linear species, and it was originally thought [123, 129] that the kinetic behavior of the 1780 cm$^{-1}$ band paralleled the poisoning effect of carbon dioxide on the D$_2$ exchange sites. However, the disappearance of these bands on heating to 106°C and their absence from the spectrum of CO$_2$ adsorbed at 110°C (expt. 273, Table XII) show that these adsorbed species, whatever their nature, are not responsible for poisoning of the exchange sites, since the poisoning effect of CO$_2$
is still intact at 100°C, as shown previously (Figure 11).

The 1233, 1480, and 1640 cm\(^{-1}\) bands (as well as a band at 3605 cm\(^{-1}\) not observed in the present work due to scattering limitations) were all believed by Parkyns to be due to a monomeric surface bicarbonate (HCO\(_3\)) entity. Assignment of the 1233 cm\(^{-1}\) band to the C-O-H bending frequency, the 1640 cm\(^{-1}\) band to the asymmetric HCO\(_3\) vibrational mode, and the 3605 cm\(^{-1}\) band to the O-H stretching frequency were all fairly straightforward, as shown by comparison with similar spectra of crystalline KHCO\(_3\). Assignment of the 1480 cm\(^{-1}\) band to the symmetric HCO\(_3\) vibrational mode was considerably less satisfactory, however, since the expected frequency was at approximately 1340 cm\(^{-1}\). The assignment was finally made when Parkyns plotted the intensities of the 1233, 1480, and 3605 cm\(^{-1}\) bands vs. the 1640 cm\(^{-1}\) band intensity for various amounts of adsorbed CO\(_2\) and observed that the three lines were linear and passed through the origin. Parkyns believed that this result confirmed that all four bands were due to the same surface species. Similar plots were obtained from the data of the present study, but it is believed that they do not necessarily prove that all plotted bands arise from the same surface entity. Barring interconversion and/or rearrangement of the adsorbed species, similar results would be expected from any of the infrared bands of an adsorbed compound when all adsorptions are made at the same temperature, as they were in Parkyns' study. It is possible, therefore, that the 1480 cm\(^{-1}\) band may be due to some other adsorbed species of CO\(_2\).
This observation is amplified by the results of the other infrared experiments shown in Table XII. If all three bands, 1233, 1480, and 1640 cm\(^{-1}\), were due to the same species, their intensities would be expected to increase or decrease in unison under various adsorption conditions. Adsorption of 1-butene after CO\(_2\) adsorption (expt. 268) failed to affect the CO\(_2\) spectrum (Peri [114] observed displacement of CO\(_2\) from alumina by 1-butene, but he monitored the titration by observing the decrease in the 2370 cm\(^{-1}\) band of physically-adsorbed CO\(_2\) which is of no catalytic significance). However, when either 1-butene (expt. 269) or benzene (expt. 270) was adsorbed prior to adsorption of CO\(_2\) (a situation that parallels the addition of CO\(_2\) poison during the exchange reactions), the 1233 and 1640 cm\(^{-1}\) bands were almost entirely absent from the CO\(_2\) spectrum, while the intensity of the 1480 cm\(^{-1}\) was virtually unaffected. Similarly, when CO\(_2\) was adsorbed at 110°C (expt. 273), only a trace of the 1233 and 1640 cm\(^{-1}\) bands was observed, but the 1480 cm\(^{-1}\) band intensity was only slightly (20%) reduced. Finally, although not conclusive in itself, adsorption of CO\(_2\) on a deuterated surface (expt. 272) caused the 1640 cm\(^{-1}\) band to shift to 1610 cm\(^{-1}\) and the 1233 cm\(^{-1}\) band to disappear entirely (actually it shifts to 975 cm\(^{-1}\) which is below the transmission limit of alumina [106]), but left the 1480 cm\(^{-1}\) band unchanged.

Taken together, these infrared results clearly indicate that the 1480 cm\(^{-1}\) band adsorbed CO\(_2\) is not necessarily associated with the 1233 and 1640 cm\(^{-1}\) bands of the
bicarbonate entity, but may be due to an entirely different surface species. The precise nature of this species could not be determined from the present study, but it is probably not a simple O=C=O or O=C=O moiety, since the Lewis-acid nature of the unmodified carbon dioxide molecule would not favor a strong interaction with the acidic Al\textsuperscript{3+} structure. Additional study of this problem is clearly indicated.

2. Ammonia adsorption on alumina

As seen in Tables I and VIII, ammonia has virtually no poisoning effect on the benzene-D\textsubscript{2} or 1-butene-D\textsubscript{2} exchange reactions at 25\textdegree{}C, but when preadsorbed at 420\textdegree{}C (Table IV), a "lethal dose" of ammonia completely poisons the exchange sites. Peri has observed [112] that ammonia adsorbs on alumina at 25\textdegree{}C principally as molecular NH\textsubscript{3}, and that adsorption occurs on several different types of sites, similar to the situation with carbon dioxide. It is apparent, therefore, that either none of the adsorption sites are the active exchange sites, or, more likely, that molecular NH\textsubscript{3} is unable to displace adsorbed benzene or 1-butene from the active sites.

At 420\textdegree{}C, Peri [112] found that the principal mode of ammonia adsorption on alumina is by the formation of amide and, to a lesser extent, imide ions by interaction with surface oxide ions:

\[
\text{NH}_3 + O = \xrightarrow{400\degree{}C} \text{NH}_2^- + \text{OH}^- \quad (10)
\]

\[
\text{NH}_3 + O = \xrightarrow{400\degree{}C} \text{NH}^= + \text{H}_2\text{O} \quad (11)
\]
Since the TPD experiments (Tables IX and XI) have shown that the OH entity is very labile above 200°C, it appears likely that the NH$_2^-$ species is responsible for the poisoning effect of ammonia adsorbed at 420°C. This would at least be consistent with the active site postulate of exposed Al$^{3+}$ ions, since the electron-rich NH$_2^-$ species should interact strongly with the acidic Al$^{3+}$ entity, and the site density obtained in Figure 15 is not too different from the value obtained by CO$_2$ poisoning in Figures 10 and 11. The NH$_2^-$ adsorption is apparently a very strong one, since the active form of CO$_2$ is unable to displace it at 25°C, as shown by experiment 271 in Table XII.

3. Other poisons

None of the other materials used as poisons for the D$_2$ exchange reactions (with the exception of carbon disulfide and the rather erratic results for pyridine) had a significant effect on the process at 25°C. Evidently, HCl, NO, NO$_2$, CO, and SO$_2$ either do not adsorb at all on alumina at 25°C, or they are unable to displace adsorbed benzene or 1-butene from the active exchange sites. The effects of high-temperature adsorption of these materials was not investigated extensively, but NO$_2$ (expt. 184, Table V) apparently forms some species at 415°C that is capable of poisoning the exchange sites, in a manner similar to ammonia. Perhaps this interaction involves combination with a surface oxide ion to form a nitrate entity:

\[ \text{NO}_2 + \text{O}^= \xrightarrow{400^\circ} \text{NO}_3^= \quad (12) \]
Infrared examination of NO₂ adsorbed at high temperatures may prove informative.

Carbon monoxide (expt. 172, Table V) probably reacts with surface oxide ions at 415°C to form a CO₂-type species, since when excess O₂ was present in the adsorbate (expt. 173), the partial poisoning effect of CO alone was complete. The CO₂ entity formed by the interaction then poisons the active sites in a manner similar to molecular carbon dioxide. Previous workers [92] have also observed that carbon monoxide adsorbed on alumina at high temperatures (>350°C) was recoverable upon desorption only as carbon dioxide.

4. Fluoridation of alumina

Fluoridation of alumina greatly reduces the D₂ exchange site concentration, as seen in Tables VI and VII and in Figures 16 and 17. The original belief [14, 45, 47] that fluoridation involved a simple replacement of surface -OH groups by F-atoms appears unlikely, therefore, since the TPD experiments (Tables IX and XI) have shown that the low-temperature D₂ exchange reactions do not involve surface hydroxyls. The postulate of Hughes et al. [69], discussed in Part I, that F-atoms become attached directly to Al³⁺ ions is consistent with the assignment of the active exchange sites to some form of this entity. Hughes' mechanism also predicts the formation, in some cases, of -OH groups adjacent to the Al-F linkages. As noted previously, due to the close proximity of the strongly electron-withdrawing F-atoms, the -OH groups formed by this process would be expected to possess considerable Brönsted acidity, in contrast to the normal hydroxyls
on the aluminia surface. These -OH groups might readily undergo exchange with gaseous D₂ at 25°C, and, being different from the usual exchange sites, could account for the small percentage of "unpoisonable" exchange activity observed in Figures 16 and 17.

Further examination of these fluorided catalysts by the TPD technique and infrared study to determine the effect of fluoridation on CO₂ adsorption, for example, would be a useful extension of the present work.

E. Mechanism of hydrocarbon-D₂ interaction with alumina

The pertinent results of the present study can be summarized by the postulated site distribution and isomerization/exchange mechanism shown for 1-butene in Figure 30. The mechanism is identical for benzene, except for interaction with the I-sites. Upon initial exposure of a "clean" alumina surface to gaseous benzene or n-butene, adsorption of the hydrocarbon occurs first on those sites having the highest heat of adsorption (B-sites) [32]. After saturation of the B-sites, adsorption proceeds to the A-sites, and finally to the E- and I-sites. Residual adsorbate remains in the gas phase and equilibrates to a greater or lesser extent with certain of the adsorbed species. This postulate is supported by the observation that during the various benzene-D₂ reactions, no exchange whatever occurred during approximately the first four minutes after exposure of the catalyst to the reactant mixture. Only a decrease in total gas phase material was detected during this time, indicating
FIGURE 30. Postulated Site Distribution and Mechanism of Isomerization/D2 Exchange on Activated Alumina
the occurrence of the initial adsorption process.

After saturation, material adsorbed on the B-sites experiences virtually no communication with the gas phase hydrocarbon, as indicated by the relative lengths of the arrows in Figure 30, but undergoes exchange with surface -OH or -OD during subsequent desorption at 200-300° [34]. The A-type material equilibrates to a limited extent with the gas phase and also undergoes a very small amount of exchange with surface -OD during the latter stages of its desorption at 100-130°C. The principal mode of deuterium incorporation into both the A- and E-type hydrocarbons, however, is via a Rideal-type mechanism with gaseous D₂. The A- and E-sites are apparently quite similar and may both be associated with surface Al³⁺ ions. Differences in surrounding environments of O⁻ ions and general extent of coordination may cause the apparent difference in heats of hydrocarbon adsorption and exchange activity of the two sites. In any case, the E-sites are probably the ones responsible for promoting the benzene-D₂ and 1-butene-D₂ exchange reactions, since pre-poisoning with CO₂ does not prevent adsorption of hydrocarbon onto the A-sites but appears to block occupancy of the E-sites entirely. Finally, concurrent isomerization of the n-butenes occurs on the I-sites, and this process is completely insensitive to CO₂-poisoning and is unrelated to the D₂ exchange processes occurring on the other sites.
V. SUMMARY

The surface of activated alumina is apparently quite complex. Benzene, n-butenes, and probably other unsaturated hydrocarbons as well are adsorbed on at least two types of surface sites. In addition, two kinds of catalytically-active sites exist on the surface. One of these catalyzes isomerization of light olefins and is relatively insensitive to poisoning by carbon dioxide. The other promotes exchange of olefinic and aromatic hydrogen atoms with gaseous deuterium and can be completely poisoned by adsorption of sufficient carbon dioxide, as well as by certain other materials such as ammonia and carbon monoxide at various temperatures of adsorption. These deuterium exchange sites occur with a surface concentration of no greater than \(0.3 \times 10^{13}/\text{cm}^2\).

Carbon dioxide also adsorbs in more than one form on the alumina surface, but only one of these forms, apparently associated with an infrared band at 1480 cm\(^{-1}\), poisons the deuterium exchange sites. Fluoridation of the surface has much the same effect as carbon dioxide poisoning, but results in a small fraction of "unpoisonable" exchange activity, possibly due to formation of labile hydroxyl groups on the surface.
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