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Oxidative dehydrogenation of butenes over zinc ferrite catalysts

Park, Tae-Jin, Ph.D.

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OXIDATIVE DEHYDROGENATION OF BUTENES
OVER ZINC FERRITE CATALYSTS

by

TAE-JIN PARK

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

DOCTOR OF PHILOSOPHY

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HOUSTON, TEXAS
OCTOBER 1986
ABSTRACT

OXIDATIVE DEHYDROGENATION OF BUTENES
OVER ZINC FERRITE CATALYSTS

by

Tae-Jin Park

The oxidative dehydrogenation (OXD) of butene over a zinc ferrite catalyst was studied in a batch recirculation and microcatalytic pulse reactor system at temperatures between 300 and 400°C. Mechanistic features of the reaction were examined using deuterium labeled butene and 18O-labeled carbon dioxide experiments. Solid state changes in the catalyst were examined through x-ray powder diffraction and Mössbauer spectroscopy.

Reaction products consist of 1,3-butadiene, carbon dioxide, water, and butene isomers. At higher reaction temperatures, a small amount of carbon monoxide was observed. Kinetic expressions were constructed for both OXD and deep oxidation reactions based on a two site Langmuir-Hinshelwood model assuming dissociative adsorption for oxygen on one site and competitive adsorption by butene and butadiene on the other. Preliminary values for the kinetic parameters were evaluated from initial reaction rate data and were refined to fit the integral data obtained as a function of time. The activation energies for OXD and deep oxidation are 34.1 and 30.6 Kcal/mole, respectively.

The OXD of perdeuterated butene is slower than that of undeuterated butene, which indicates a significant kinetic isotope effect of 2.7 at 350°C. A
similar effect was observed for isomerization of cis-2-butene to 1-butene by double bond shift (1.4 at 350°C). Apparently, carbon-hydrogen bond cleavage is involved in the rate limiting step for both reactions.

Microcatalytic pulse experiments carried out in the absence of gas phase oxygen indicated that the lattice oxygen does not participate in the reaction and that the migration of bulk oxygen to the surface of the catalyst is very slow under these conditions. A similar result was observed in $^{18}$O exchange experiments with C$^{18}$O$_2$.

The experimental data are consistent with an oxidation-reduction cycle involving Fe$^{2+}$/Fe$^{3+}$ interconversion. Butene and oxygen molecules may adsorb into surface anion vacancies associated with an iron cation. The absence of intermolecular hydrogen-deuterium exchange during the isotopic tracer experiments indicates that the OXD and isomerization reaction rates are much greater than surface diffusion of hydrogen and/or deuterium.

The catalytic activity of zinc ferrite increases greatly when it is exposed to a high temperature under the reaction environment. Solid state studies using x-ray diffraction and Mössbauer spectroscopy indicated that the zinc ferrite phase decomposes into zinc oxide and iron oxides. Iron oxides thus formed are considered to be responsible for the enhancement of the catalytic activity.
ACKNOWLEDGMENTS

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I am joined by Dr. Hightower and the Chemical Engineering Department in expressing gratitude to The Robert A. Welch Foundation for the financial support of my work at Rice University.
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I. INTRODUCTION

GENERAL

The shortage of natural rubber during the World War II enhanced the development and production of synthetic rubbers. As a raw material for those synthetic rubbers, butadiene has gained an important role in the chemical industry. The major fraction of butadiene production has been from steam cracking ethylene plants where butadiene is a co-product representing 20-40% of the C₄ cut.¹ Besides this production, two major catalytic processes have been used commercially to produce butadiene. The first is direct dehydrogenation over chromia/alumina or promoted iron oxide catalysts, viz.

\[
\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3 \rightarrow \text{CH}_=\text{CH}-\text{CH}=\text{CH}_2 + \text{H}_2 \quad \Delta H=28\text{kcal/mole (1)}
\]

Although the reaction is relatively selective, it suffers from being thermodynamically limited, endothermic, and coke-forming.²

A second approach, oxidative dehydrogenation (OXD) of butene, involves addition of oxygen to the feed hydrocarbon stream to remove the hydrogen as water, viz.

\[
\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_2=\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \quad \Delta H=-30\text{kcal/mole (2)}
\]

This process was first invented by Hearne³ over bismuth molybdate which had been used for the partial oxidation of propylene to acrolein.

With the formation of stable hydrogen compounds in the OXD reaction, the reaction equilibrium shifts toward complete dehydrogenation. The equilibrium constant for the OXD of 1-butene at 480°C is 1.6x10¹² which is dramatically larger than the 9.0x10⁻³ value found for normal dehydrogenation at the same temperature.⁴ In other words, this reaction is essentially irreversible, high per
pass conversion can be acquired, and recycling of the unreacted reactants is not necessary.

In addition to the favorable equilibrium change, the exothermicity of the process yields energy savings in the form of decreased steam requirements. The steam in the OXD process is used primarily for temperature control, while it is used as an energy carrier for providing the required heat of reaction in the non-OXD process.

Furthermore, the OXD process can be carried out in the temperature range of 400 to 500°C which is substantially lower than the 600-700°C range required for the traditional dehydrogenation reaction. But, this process is not without its disadvantages. Since the complete oxidation to CO₂ and H₂O is thermodynamically much more favored than the desired reaction (Kₑₚ at 480°C is 4.2x10⁻¹⁸²), a catalyst which can provide good selectivity is essential for this process to be commercially viable.

Several kinds of catalysts have been claimed to be effective, and some commercial processes have been reported based upon those catalysts. The first catalyst used for the OXD reaction was bismuth-molybdate⁵ which has been widely used as a partial oxidation catalyst for hydrocarbons. Phillips Petroleum⁶,⁷ has been particularly active in the investigation of materials containing phosphate groups, while Petro-Tex⁸,⁹ has developed most of the ferrite catalysts. Various kinds of mixed metal oxides have also been claimed to be effective.¹⁰,¹¹

Iron oxides are active for this reaction. However, since α-Fe₂O₃ (hematite) shows very poor selectivity and γ-Fe₂O₃ (maghemite) and Fe₃O₄ (magnetite) are unstable under reaction conditions¹², they have not been used commercially.
The poor selectivity is in sharp contrast to the high activity these iron oxides show for oxidizing olefins.

COMMERCIAL PROCESSES

Phillips Process

In 1974, Phillips announced that they were operating a commercial plant whose capacity was 140,000 tons/yr at Borger, Texas. Per-pass butadiene yields in the pilot plant were about 70% as compared with only about 20-22% in Phillips' earlier non-OXD process using an iron oxide catalyst. Typically, when the steam/oxygen/butene mole ratio is 35/1/1, butene conversion is in the range of 75 to 80% and the selectivity to butadiene is about 88 to 92%.

A mixture of steam, air, and normal butenes is passed over a fixed catalyst bed at temperatures of 480 to 600°C. They propose that, as the butenes are dehydrogenated, the released hydrogen reacts with oxygen from the air to form water. Steam and air fed to the reactor make possible continuous, in situ catalyst regeneration. The steam further serves as a means of controlling reactor temperature by acting as a heat sink, as it absorbs the heat released by both the OXD and complete oxidation reactions.

Over the ranges investigated with their pilot plant, residence time and reactor effluent temperature exert strong effects on butene conversion; the oxygen/butene ratio and steam/butene ratio are less important. Reactor effluent temperature and oxygen concentration in the reactor effluent are respectively 607°C and 7.5% in all cases. Higher steam ratios and shorter residence times increase butadiene selectivities. Residence time exerts a strong influence on butene conversion, while higher steam ratios favor higher butene conversions.
at constant residence time.

**Petro-Tex Process**\(^{14}\)

In this process which is based on a ferrite catalyst, the reactor system is insulated and almost adiabatic. The primary variables are oxygen/butene ratio, steam/butene ratio, inlet temperature, space velocity, and pressure. The oxygen/butene ratio is the most important variable because the yield of butadiene obtained is directly related to the oxygen level used.

Feed purity is also important because many of the impurities found in mixed butene streams are reactive and consume oxygen in their conversion to oxygenated compounds or carbon oxides. Isobutene is the most troublesome impurity because 80% of the isobutene in the feed is converted primarily to combustion products. Byproducts include acetylene compounds (e.g. vinylacetylene and methyl acetylene) and oxidation or combustion products (e.g. formaldehyde, acetaldehyde, acrolein, furan, and carbon oxides). The n-butene isomers differ slightly in their reactivity and selectivity for butadiene formation. Cis-2-butene is the most reactive and most selective isomer when operated at the optimum steam/butene ratio of 16-18 and with an \(\text{O}_2/\text{butene}\) ratio of 1/1.65. The per pass conversion was typically 65%, with a selectivity of 93%; these conditions result in a per pass yield of 60%.

**British Petroleum Process**\(^{15}\)

Over a catalyst based on tin and antimony oxides, 1-butene undergoes the OXD reaction more rapidly than either of the 2-butene isomers. This relative reactivity is presumably due to the fact that 1-butene forms an allylic
intermediate on the catalyst surface more rapidly than the 2-butenes. Such bond cleavage is a primary step in formation of butadiene.

For large scale development work, a crude C_4 raffinate (approximately 80% n-butenes) which remained after extraction of butadiene and iso-butene, was used as feed. When air and steam were added to give a C_4/air/steam ratio was 13/60/27, the yield of butadiene was 50-60%.

During fixed-bed reaction, a carbonaceous material is very slowly deposited on some sections of the porous oxide catalyst, thus lowering the selectivity. After a substantial period on stream (several days), it is necessary to regenerate the catalyst activity by removing these carbonaceous deposits. This is easily done in situ by burning off the carbon in a controlled manner with air, the catalyst being completely restored to its previous activity.

**Nippon Zeon Process**

The main characteristic of the Nippon Zeon process is the use of a mixture of n-butene/butane (about 66/34 mole %) as feed mixed with offgas as the reaction diluent. The offgas results from recovery of crude butadiene from the C_4 fraction of a naphtha cracker effluent. The use of the mixed reactant and offgas in the process is based on the desire to minimize feed and diluent costs.

Since the feed is a multi-component mixture of hydrocarbons, those catalysts which are equally active for different isomers are preferred. Even though multicomponent oxide catalysts based on Bi, Mo, Fe, or Cr are very active,\textsuperscript{17,18} the catalytic activity varies greatly depending upon the type of the
isomers in the starting butene. To overcome this deficiency, the Nippon Zeon company improved the properties of the catalyst by adding still other components (e.g. Cd\textsuperscript{10} and Pb\textsuperscript{11}) which make the catalyst almost equally active for all n-butene isomers.

When a multi-tube reactor is used in this process, n-butene conversion is 85%. Butane in the reactant mixture is inactive. Since the oxygen/butene ratio can be made larger (0.8-1.2), the process is safe being out of the explosion limit for the mixture. No recycling is necessary, since per pass conversion is high. Substitution of steam gives almost the same reaction result as offfgas. When the conversion is 90.6%, selectivity may be as high as 90.2-91.6%.

**OXD CATALYSTS**

**Bismuth Molybdate**

Early studies\textsuperscript{19-22} showed that the OXD reactions of aliphatic monoolefins such as propene and butene over bismuth molybdate catalysts proceed through allyllic intermediates. This conclusion was based on analysis of results from kinetic experiments using\textsuperscript{13}C-, \textsuperscript{14}C-labeled, or deuterated reactants.\textsuperscript{19} When acrolein or acrylonitrile, obtained by oxidation or ammoxidation of [1- or 3-\textsuperscript{13}C-]propene over such catalysts as Bi\textsubscript{2}O\textsubscript{3}-MoO\textsubscript{3}\textsuperscript{19}, Bi-Mo-P-O\textsuperscript{20,21} and Cu\textsubscript{2}O\textsuperscript{22}, was analyzed, half of the \textsuperscript{13}C in the acrylonitrile was found in the CN-group and the other half in the C\textsubscript{2}H\textsubscript{3}-group. This result points to a symmetric intermediate, such as an allylic species, in the ammoxidation reaction.

A model that has been suggested\textsuperscript{23} to explain the dehydrogenation of 1-butene involves a first extraction of an allylic hydrogen to give a methyl
allyl radical followed by a second extraction occurring at the methyl group. An isotope effect of \( k_\text{d}/k_\text{h} = 0.7 \) is required to fit the data from an experiment using deuterated butene (1-butene-3d). This compares with the value of 0.55 for the isotope effect in the oxidation of propene at the same temperature (450°C). Since both reactions show primary kinetic isotope effects, the first dehydrogenation must be the rate-determining step. The formation of an allylic species from propene over a zinc oxide catalyst was actually observed by use of infrared and mass spectroscopy.

Batist et al. measured the rate of oxidative dehydrogenation of 1-butene in the presence of oxygen and the rate of catalyst \( (\text{Bi}_2\text{MoO}_6) \) reduction with 1-butene in absence of gaseous oxygen. They found the initial rates of butadiene production were almost the same. From this observation, they concluded that the rate of reaction is controlled by the rate of catalyst reduction and therefore involves a redox mechanism.

Isotopic tracer \( (^{18}\text{O}) \) experiments conducted by Keulks and Wragg et al. indicate the participation of lattice oxide ions in the OXD of propylene. The oxygen incorporated into the product acrolein is derived from the lattice of the catalyst instead of coming from the gas phase. In addition, rapid diffusion of oxygen from the surface into the bulk and from the bulk to the surface was observed.

The mechanism of the selective oxidation of olefins on oxide catalysts can be summarized as follows:

1. Following physical adsorption, the first step of the reaction is the dissociative chemisorption of an olefin molecule with the abstraction of a \( \beta \)-hydrogen to form an allylic species.
2. This dissociative chemisorption is the rate determining step.

3. In the case of the OXD of 1-butene to butadiene the rate of the reaction is equal to the initial rate of reduction of the catalyst with 1-butene in the absence of oxygen, which is in agreement with the reduction-oxidation mechanism of Mars and Van Krevelen.\textsuperscript{30}

While complete agreement has not yet been reached with regard to the exact nature of the active sites, it does seem relatively well established that the OXD reaction occurs via a dual-site mechanism.\textsuperscript{31}

Bi–O polyhedra act as centers for the first hydrogen abstraction and formation of the allylic species. Mo–O polyhedra act as centers for the second hydrogen abstraction, which results in the formation of an allylic fragment \( \pi \)-bonded to the lattice oxygen. In other words, Bi-sites are responsible for activity, while Mo-sites determine the selectivity.\textsuperscript{29}

One evidence supporting the bismuth center as a site of propylene activation comes from the analysis of the rates of formation and product distribution of propylene oxidation over bismuth oxide, bismuth molybdate, and molybdenum oxide.\textsuperscript{31} Bismuth molybdate is highly active and selective for the conversion of propylene to acrolein. However, the interaction of propylene with its component oxides yields quite different results. Swift et al.\textsuperscript{32} and White and Hightower\textsuperscript{33} observed that, in the absence of oxygen, propylene is converted to 1,5-hexadiene over bismuth oxide at a high rate with moderate selectivity, whereas molybdenum oxide is known as a fairly selective but less active catalyst for acrolein formation. The formation of 1,5-hexadiene over bismuth oxide can be explained if the adsorption of propylene on a bismuth site yields a \( \pi \)-allylic species. Two of these allylic intermediates can then combine
to give 1,5-hexadiene.

These observations over bismuth molybdate catalysts suggest a reaction scheme in which the allylic species is formed initially at a bismuth center and then reacts further at a molybdenum site to produce acrolein. Thus, once the allylic complex is formed, the MoO polyhedra are highly active and selective for acrolein formation.

A somewhat different scheme was proposed by Matsuura and Schuit.\textsuperscript{34} They attempted to elucidate the active adsorption sites on $\gamma$-bismuth molybdate by measuring the adsorption equilibria of butene, propylene, oxygen, water, butadiene, acrolein, and ammonia. Their work led to the complicated assignment of two different types of adsorption sites, viz:

1. a single site adsorbs butadiene in a slow but strong adsorption and also acts as the adsorption site for $H_2O$ and $1/2 O_2$ in the reduced state (A center), which is connected with the presence of bismuth.

2. a combination of three sites, two of which adsorb 1-butene, cis-2-butene but also butadiene in a fast but weak adsorption, the third one adsorbing trans-2-butene in a single site adsorption (B center). These centers are related to molybdenum.

The conversion of butene to butadiene was postulated to be a bifunctional process that involves the simultaneous cooperation of A and B centers. Combustion, on the other hand, proceeds independently on isolated A centers.

Of the three stable bismuth molybdate phases called $\alpha, \beta,$ and $\gamma$ (Bi/Mo = 2/3, 1/1, 2/1), the $\beta$-phase exhibits maximum activity.\textsuperscript{35} OXD of n-butenes on Bi-Mo catalysts proceeds according to a redox mechanism, in which adsorbed butene interacts with surface oxygen in the catalyst lattice. Under conditions
where oxygen is absent from the gas phase, oxygen is depleted from the bulk of the catalyst and moves toward the surface.

Work of Batist et al.\textsuperscript{36} indicates that the $\gamma$-phase may be the active one. This composition corresponds to the koehlinite structure\textsuperscript{37} which can be considered as a stacking of planes alternately containing, respectively, \((\text{BiO}^-)_2n\) and \((\text{MoO}_4^{2-})_n\). The mechanism for butadiene production over bismuth molybdate proceeds as follows:

\begin{align}
\text{C}_4\text{H}_8 + \Box + \text{O}^- & \rightleftharpoons \text{C}_4\text{H}_7 + \text{OH}^- & (3) \\
\text{Mo}^+6 + \text{C}_4\text{H}_7^- & \rightarrow \text{Mo} = \text{C}_4\text{H}_7^+5 & (4) \\
\text{Mo} = \text{C}_4\text{H}_7^+5 + \text{O}^- & \rightarrow \text{Mo}^+4 + \Box + \text{OH}^- + \text{C}_4\text{H}_6^- & (5) \\
2\text{OH}^- & \rightleftharpoons \text{O}^- + \Box + \text{H}_2\text{O} & (6) \\
\text{O}_2 + 2\Box + 2\text{Mo}^+4 & \rightarrow 2\text{O}^- + 2\text{Mo}^+6 & (7)
\end{align}

In these steps, the symbol $\Box$ denotes an anion vacancy and Mo=C$_4$H$_7$\textsuperscript{+5} represents a $\pi$-allyl complex between the Mo\textsuperscript{+6} and the allyl carbanion (C$_4$H$_7$\textsuperscript{-}). Later studies by Batist et al.\textsuperscript{38} on supported bismuth molybdate catalysts also indicated high activity for the $\beta$-phase.

The role of bismuth seems to be to provide rapid formation of allylic species by chemisorption, providing the means for enhancing the rate-controlling dissociative absorption step which abstracts the first hydrogen from an olefin. Molybdenum plays a role in abstracting the second hydrogen in a selective fashion without oxidizing the molecule to CO$_2$.

The catalytic oxidation of butene to butadiene is first order in butene and independent of oxygen and products.\textsuperscript{39} The reaction is quite selective in the range of 450-550°C. The cis- and trans-2-butene isomers are less reactive than 1-butene, and isomerization by double-bond shift is not rapid.
Wolfs and Batist\textsuperscript{40} patented multicomponent molybdate catalysts whose general formulae are $\text{Me}^{\text{II}}_a\text{Me}^{\text{III}}_b\text{Bi}_c\text{Mo}_d\text{O}_e$ in which $\text{Me}^{\text{II}}$ is Ni, Co, Mg, or Mn and $\text{Me}^{\text{III}}$ is Fe, Cr, or Al where the ratio $\text{Bi}/\text{Mo} = 1/12$. This group is remarkable because it contains only a small amount of a cation ($\text{Bi}^+$) which is believed to be the essential component for high activity. Catalytic activity and selectivity are connected with $\text{Bi}_2\text{MoO}_6$ and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ present as an outer layer on a nucleus formed by $\text{Me}^{\text{II}}\text{MoO}_4$ (with $\beta$-CoMoO$_4$ structure) and $\text{Me}^{\text{III}}_2(\text{MoO}_4)_3$. The formation of $\text{Bi}_2\text{MoO}_6$ is promoted by $\text{Me}^{\text{III}}$ in the sequence $\text{Fe} > \text{Cr} > \text{Al}$. Moreover, $\text{Bi}_2\text{MoO}_6$ is activated by addition of Fe. A catalyst based on this formulation is believed to be used in the Nippon Zeon process.\textsuperscript{16}

**Tin Phosphate**

Catalysts have also been made for OXD of butenes to butadiene employing tin phosphate.\textsuperscript{41} The original catalyst contained a ratio of $\text{P}/\text{Sn} = 1/1.5$, but since then other catalysts containing Li have been developed and used commercially since 1970 by the Phillips Petroleum Co.

The fundamental mechanism of OXD over the tin phosphate catalysts has not received much attention in the literature. The catalyst appears to be amorphous, but upon heating the rutile structure of $\text{SnO}_2$ can be detected.\textsuperscript{41}

Marak et al.\textsuperscript{42} used X-ray photoelectron spectroscopy to show that lattice oxygen is the source of reactive oxygen on the catalyst surface which promotes the butane OXD reactions. As lattice oxygen is removed from the surface, the catalytic behavior is influenced by the ability of bulk lattice oxygen to migrate to the surface thereby maintaining both a supply of reactive oxygen on the
surface and a surface oxide layer which inhibits coking. Approximately 90% of the oxygen removed by reduction with H₂ or hydrocarbons is derived from subsurface layers. Chickering's work⁴³ on this catalyst indicates that a Mars-Van Krevien model may be applied to the kinetic data. This model implies that a redox cycle is established for one or more of the metal species.

A somewhat different result was obtained by Yin⁴⁴ from microcatalytic pulse experiments over tin phosphate and lithium tin phosphate catalysts. The result of this experiment indicates that the extent of the participation of subsurface layer in the OXD of butene is very low. Since Yin's experiments were conducted at relatively low temperatures, the decreased participation of lattice oxygen was likely due to the slow diffusion under these conditions.

**Ferrites**

Following the disclosure of Bajars et al.⁴⁵ that magnesium ferrite was an active and selective catalyst for conversion of butenes to butadiene, a number of studies were made by the Petro-Tex group using ferrite spinels for this reaction. The ferrites claimed to be active for this reaction include strontium, barium, zinc, nickel, calcium, cadmium, cobalt, and manganese ferrites either independently or in combination with one another.

Most of these ferrite catalysts are spinels, which are named after the mineral spinel MgAl₂O₄ and have well-defined crystal structures. The general formula of spinel is AB₂O₄, where, typically, B may be iron (ferrite), chromium (chromites), or cobalt (cobaltites). The spinel lattice is a face-centered cubic oxygen matrix with metal cations distributed in the tetrahedral (A-site) or octahedral (B-site) interstices(Fig. 1).⁴⁶
Figure 1. Unit cell of spinel structure. The positions of the ions in only two octants are shown. The solid lines indicate the fourfold and sixfold coordination of the respective metal ion positions. Large circles represent oxygen ions, the small solid circles are metal ions in octahedral sites, and the small clear circles depict metal ions in tetrahedral sites.⁴⁶
Spinels are classified as "normal" when all the A cations occupy octahedral sites. The inverse spinel structure corresponds to a defective one since all crystallographically identical sites within the unit cell are not occupied by the same cations. Normal and inverse spinels are limiting cases, and various degrees of inversion or even complete randomization are sometimes observed. For example, zinc ferrite is normal, magnesium and manganese are partially inverse, and cobalt and nickel ferrites are almost completely inverse. Barium and strontium ferrites have perovskite-like structures instead of spinel.\textsuperscript{46}

Later, Kehl and Rennard at Goodrich-Gulf Chemicals have continued studying and developing the ferrite based catalysts; they have patented the application of mixtures containing magnesium\textsuperscript{8} and zinc chromium ferrites\textsuperscript{9} (MgCrFeO$_4$ & ZnCrFeO$_4$) which are claimed to be superior to magnesium and zinc ferrites.

Since these catalysts are employed under reducing conditions, preactivation by reducing gas is suggested prior to use. It is likely that Fe$^{2+}$ is present in the working catalyst. This cation would tend to occupy the octahedral sites favoring n-type semiconductivity.

Rennard and Kehl\textsuperscript{47} proposed a mechanism:

\[
\begin{align*}
\square + C_4H_8 + Fe^{3+} + O_{L}^{-2} & \rightleftharpoons C_4H_7Fe^{2+} + OH^- \\
C_4H_7Fe^{2+} + O_{ads}^- & \rightarrow C_4H_6 + Fe^{3+} + OH^- \\
2OH^- & \rightleftharpoons O_{L}^{-2} + H_2O + \square \\
1/2 O_2(g) & \rightarrow O_{ads}^{-}
\end{align*}
\]

Here \(\square\) is an anion vacancy adjacent to an Fe$^{3+}$ ion, \(O_{ads}^-\) is an adsorbed oxygen radical ion, \(O_{L}^{-2}\) is a lattice oxygen, and \((C_4H_7-Fe)^{3+}\) is a complex
involving Fe$^{+3}$ and an allylic radical.

The reversal of step 1 (eq. 8) would give rise to double-bond isomerization in the presence of gas phase oxygen. Since in the presence of oxygen the rate of isomerization is much less than the rate of dehydrogenation, the reversal of step 1 must be slower than step 2. Either step 1 or 2 could be rate controlling.

This mechanism has five main features;

1. it does not require reduction to an oxidation state less than Fe$^{+2}$;
2. in the absence of gas-phase oxygen, butadiene will be formed only until the adsorbed oxygen is consumed, and there will be only a corresponding surface reduction to Fe$^{+2}$;
3. since either step 1 or 2 could be rate controlling, this model would predict that the formation of butadiene should be zero order in oxygen;
4. it predicts that if reversal of step 1 is solely responsible for the isomerization, then there should be no steady-state isomerization in the absence of oxygen;
5. and it predicts that the kinetics for butadiene formation should be consistent with a two-site adsorption model.

A study by Gibson and Hightower$^{48}$ showed similar results over a magnesium ferrite catalyst. They modified this mechanism slightly to explain their experimental results (Figure 2). In the same study, they proposed that irreversible catalyst deactivation was due to formation of a small portion of anion vacancies together with an increase in the number of Fe$^{+2}$ sites at the expense of Fe$^{+3}$ sites on the catalyst.$^{49}$
Figure 2. Proposed Mechanism for OXD of Butenes over Ferrite Catalysts
Cares and Hightower\textsuperscript{50} conducted studies on the OXD of butenes using \(\text{CoFe}_2\text{O}_4\) and \(\text{CuFe}_2\text{O}_4\). The kinetics are not simple, but the reaction orders are less than one for both oxygen and butene and are negative for the product butadiene. They observed a primary kinetic isotope effect in experiments using deuterated butenes. This effect indicates that carbon-hydrogen bond cleavage might be the rate determining step.

A kinetic model was developed for the OXD of 2-butene to butadiene over \(\text{ZnCrFeO}_4\) by Sterrett and McIlvried.\textsuperscript{51} A semiempirical two-site rate model was found to fit the experimental results most successfully. The experiment was carried out in a plug flow reactor in which the reaction temperature was varied from 316 to 360\(^\circ\)C. Operating conditions generally involved steam/butene mole ratios near 20 and an oxygen/butene mole ratio of 2:3.

The rate of \(\text{CO}_2\) formation was found to follow zero-order kinetics experimentally with respect to both hydrocarbon and oxygen. However, they suggested that a term of the form \(P_{\text{O}_2}/(1 + K_{\text{O}_2} P_{\text{O}_2})\) would be necessary since the rate must approach zero as the partial pressure of oxygen approach zero. They did not explain clearly why \(K_{\text{O}_2} P_{\text{O}_2}\) term (associative adsorption) was used instead of \(\sqrt{K_{\text{O}_2} P_{\text{O}_2}}\) (dissociative adsorption). Meanwhile, the rate expression for the formation of butadiene \((r_{\text{BD}})\) includes two terms. The first term represents the rate of butadiene formation from butene and the second term accounts for the disappearance of butadiene by combustion. The butadiene formation term is derived based on a two site Langmuir-Hinshelwood rate model.

\[
r_{\text{BD,1}} = k_1 \frac{K_{\text{BP}} P_B^n}{1 + K_{\text{BP}} + K_{\text{BD BP}} P_{\text{BD}}} \cdot \frac{K_{\text{O}_2} P_{\text{O}_2}}{1 + K_{\text{O}_2} P_{\text{O}_2}} \tag{12}
\]
Computer simulation showed that the $K_B P_B$ term in the denominator was negligible and that $n$ had a very small value of 0.142. The ratio $P_{BD}/(P_{BD} + P_B)$ appears in the deep oxidation term of the butadiene rate equation, because butene and butadiene compete about equal for deep oxidation sites; their rates of deep oxidation are about equal.

After adjustment of required parameters by computer calculations, the final rate expressions were written as follow:

\[
\begin{align*}
\tau_{BD} &= \frac{5.98 \times 10^{12} \exp(-33,400/RT) \; P_B^{0.142} \; P_O^2}{(1 + 415 \; P_O)(1 + 285 \; P_{BD})} \\
&\quad \times \frac{2.41 \times 10^7 \exp(-20,800/RT) \; P_O \; P_B}{(1 + 1800 \; P_O)(P_{BD} + P_B)} \\
&\quad \frac{2.41 \times 10^7 \exp(-20,800/RT) \; P_O}{1 + 1800 \; P_O}
\end{align*}
\]  

(13)  

(14)

From these rate expressions, it is noticed that the activation energy for butadiene formation is much higher than that for carbon dioxide. Thus, butadiene production is favored at high temperature.

Massoth and Scarpiello\textsuperscript{52} investigated the behavior of several ferrite catalysts without the use of steam as a diluent and concluded that the OXD involves a redox cycle, with the cation reducing to a lower valence state due to reaction with olefin, followed by reoxidation with oxygen. In the case of zinc chromium ferrite, the redox cycle involves Fe$^{2+}$/Fe$^{3+}$ interconversion. Iron oxide itself exhibits activity but rapidly declines owing to over-reduction beyond the +2 state. Addition of chromium and zinc causes the iron to be less susceptible to deep reduction, at the same time forming a more stable spinel lattice.
Structural analyses indicated that ZnFe$_2$O$_4$ and ZnCrFeO$_4$ possess mainly the octahedral spinel zinc ferrite and a small amount of $\alpha$-Fe$_2$O$_3$.$^{53}$ The ferrite is likely the primary active phase with $\alpha$-Fe$_2$O$_3$ serving as a promoter phase to enhance the activity. As the $\alpha$-Fe$_2$O$_3$ phase in the catalyst decreases, its activity drops, yet its selectivity for butadiene formation remains unchanged. Incorporation of chromium seems to promote stability of the $\alpha$-Fe$_2$O$_3$ phase. This result matches well with the earlier observation by Gibson.$^{49}$ Alkhazov et al.$^{54}$ also reported that the addition of iron to a bismuth molybdate catalyst increases its activity. They suggested that the activity increase is due to weakening of the bonding of oxygen adsorbed on the catalyst.

Several authors$^{55-61}$ have studied the behavior of pure iron oxides as catalysts for butene OXD reaction since they regard iron oxides as the active components of the ferrite catalysts and the other oxides (zinc, magnesium, or chromium) as promoters which enhance the selectivity and/or stability of the catalyst.

Sazonova et al.$^{55}$ concluded that at equal proportions of oxygen and butenes the catalyst under equilibrium conditions is Fe$_3$O$_4$ (magnetite). Under these conditions much better conversion and selectivity were obtained than with large excess of oxygen. In the latter case complexes with an excess of oxygen are formed on the catalyst which is now $\alpha$-ferric oxide. Since there are two crystalline forms of Fe$_2$O$_3$, $\alpha$- and $\gamma$-, it may well be that reduction in catalytic activity is associated with the presence of $\alpha$-Fe$_2$O$_3$ rather than $\gamma$-Fe$_2$O$_3$ which is isomorphous with the spinel structure.

According to Misono et al.$^{56}$, $\alpha$-Fe$_2$O$_3$ can be reduced by carbon monoxide
(or hydrogen) and reoxidized by nitrous oxide (or oxygen) to a controlled extent to produce $\gamma$-Fe$_2$O$_3$ which is remarkably active and selective for the OXD reaction. Moreover, under reaction conditions, Fe$_3$O$_4$ is oxidized to $\gamma$-Fe$_2$O$_3$ while $\alpha$- and $\gamma$-Fe$_2$O$_3$ remain unchanged. $\gamma$-Fe$_2$O$_3$, initially synthesized in the original catalyst, as well as $\gamma$-Fe$_2$O$_3$ formed from Fe$_3$O$_4$ under the reaction conditions, is very active and selective for the reaction. It was concluded that the oxygen species responsible for this reaction is lattice oxygen from $\gamma$-Fe$_2$O$_3$ and that the reaction proceeds by the redox cycles of $\gamma$-Fe$_2$O$_3 \rightleftharpoons \gamma$-Fe$_2$O$_{3-x}$ ($0 < x < 0.2$).

Actually, $\alpha$-Fe$_2$O$_3$ is quite an active catalyst, but it has very low selectivity at high conversion and high reaction temperature. At temperatures below about 350°C, $\gamma$-Fe$_2$O$_3$ has both high activity and selectivity, however, since the thermal stability of $\gamma$-Fe$_2$O$_3$ is low, it is converted to the $\alpha$- form above about 350°C. Because most industrial processes operate near 500°C, promoters have been added to obtain the desired selectivity by preserving the crystallographic forms of the iron oxide. 12

Using temperature programmed desorption and reaction of cis-2-butene over $\alpha$-Fe$_2$O$_3$, Kung et al. 58 found two different oxidation sites. That is, branching of the OXD and deep oxidation takes place on adsorption of butene in the absence of gas-phase oxygen. Moreover, the number of active sites of $\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$, and ZnFe$_2$O$_4$ was calculated by measuring the quantities of desorbed products, with the assumption that each and every active site produces only one molecule of reaction product. Comparison of these results suggests that zinc ferrite is a more selective oxidation catalyst because it has a
higher density of selective oxidation sites and a lower density of combustion sites.\textsuperscript{59} The fact that the more selective $\gamma$-$\text{Fe}_2\text{O}_3$ has more combustion sites was not explained.

In another study by Yang, et al.\textsuperscript{60}, the effect of preadsorbed and gas phase oxygen on the selective OXD of butene to butadiene on $\alpha$-iron oxide was investigated using adsorption-desorption and a pulse reaction technique. They found that irreversibly adsorbed oxygen did not affect the butene OXD reaction. However, the presence of gas phase oxygen significantly reduced the production of butadiene and increased the production of carbon dioxide. This decrease in butadiene production was due to the high reactivity of adsorbed butadiene precursors toward weakly adsorbed oxygen. Therefore, under steady-state conditions, the rate of production of butadiene is determined by the competition between the desorption of butadiene and the degradation of the precursors by oxygen. The same experiment over $\gamma$-$\text{Fe}_2\text{O}_3$\textsuperscript{61} showed that the precursor is not susceptible to degradation by gas-phase oxygen. The difference is probably due to the ability of $\alpha$-$\text{Fe}_2\text{O}_3$ to activate oxygen more readily than $\gamma$-$\text{Fe}_2\text{O}_3$. This is supposed to be the main reason why butadiene selectivity is much higher for $\gamma$- than for $\alpha$-$\text{Fe}_2\text{O}_3$.

**POSSIBILITIES FOR FUTURE DEVELOPMENT**

The best OXD catalysts for olefin-to-diene conversion appear to involve iron in both the tervalent and divalent states (or vacancies) for the adsorption of hydrocarbon and oxygen, respectively. Further research could therefore be directed toward variations in spinel ferrites which provide adjustment of such parameters as $\text{Fe}^{3+}/\text{Fe}^{2+}$ cation ratios as well as varying the absolute
concentrations of these ions and vacancies.\textsuperscript{46}

Another possible application of the OXD process is for the production of styrene from ethylbenzene for which direct dehydrogenation is currently used. Various kinds of catalysts, mostly based on metal oxides such as iron oxide, have been patented.\textsuperscript{62,63}

Variations in the application of ferrites involve the use of halogen, sulfur dioxide, or sulfur as hydrogen acceptors instead of (or together with) oxygen. With the use of these compounds, much better conversion and/or selectivity can be obtained at milder conditions. For example, styrene can be produced from ethylbenzene over a nickel-calcium phosphate catalyst with sulfur dioxide at 97\% conversion and 89\% selectivity.\textsuperscript{64} Meanwhile, these processes have disadvantages such as the loss of the expensive hydrogen acceptor, corrosion of equipment, and the formation of halogen- or sulfur-containing by-products.

The ferrite catalysts are capable of promoting OXD of a large variety of organic compounds to obtain the corresponding unsaturated derivatives. Possible processes include the following\textsuperscript{65}:

1) methacrolein or methacrylic acid from isobutyl aldehyde or isolactic acid
2) stilbene from toluene by oxidative dehydrodimerization
3) p-xylene from isobutylene
4) ethylbenzene/styrene from vinyl cyclohexene
5) coproduction of methacrolein/butadiene from mixed C\textsubscript{4} hydrocarbons

Copper chromite catalysts can be used for selective hydrogenation of unsaturated compounds and particularly of dienes since the cubic spinel phase of the catalyst contains some occluded hydrogen species which are able to
hydrogenate dienes in the absence of gaseous hydrogen.\textsuperscript{66}

A process to synthesize ethylene by oxidative dehydrocoupling of methane has been studied using various metal oxide catalysts.\textsuperscript{67} Manganese oxide was found to be the most effective oxidizing agent when used with sodium as a promoter and phosphorus as a stabilizer.\textsuperscript{68} A commercial process\textsuperscript{69} is patented in which the catalyst particles continuously recirculate between two zones, one for methane contact and another for contact with oxygen. The metal oxide is reduced in the first zone and regenerated in the second.

Another OXD of methane to methanol and formaldehyde was reported by Liu and Lunsford\textsuperscript{70} over a silica-supported molybdenum catalyst. Nitrous oxide is used as an oxidant and steam is added to enhance the conversion. At a conversion of 3%, the combined selectivity to methanol and formaldehyde is 78%, with carbon monoxide as the principal by-product.

Other possible applications of ferrite spinels are ammonia synthesis, the water gas shift reaction,\textsuperscript{71,72} and synthesis of hydrocarbons from CO and H\textsubscript{2}\textsuperscript{73} for which processes iron catalysts have been found effective.

\textbf{OBJECTIVES}

The objectives of this research were the following:

a) To develop rate expressions for both the OXD and deep oxidation reactions by performing kinetic experiments.

b) To obtain information about the reaction mechanisms using deuterium-labeled butene experiments.

c) To measure the participation of catalyst lattice oxygen in the surface reactions with microcatalytic pulse experiments.
d) To determine the effect of minor components of the catalyst on the catalytic activity and selectivity by studying the solid state properties of the catalyst.
II. EXPERIMENTAL

CATALYSTS

The two zinc ferrite catalysts used in the present study were supplied by the Columbian Chemicals Company. Both are commercial zinc ferrite catalysts, Mapico Tan 10 and 15, which have same chemical composition (Fe$_2$O$_3$ 66%, ZnO 33%). The iron oxides, $\alpha$-Fe$_2$O$_3$ (hematite), $\gamma$-Fe$_2$O$_3$ (maghemite), and Fe$_3$O$_4$ (magnetite), were supplied by Fisher Scientific (hematite) and Alfa Products (maghemite and magnetite).

GASES

Airco Industrial Gases grade 4.5 helium (min. 99.995% pure) was used without further purification as the chromatographic carrier gas in all experiments. The n-butene isomers and 1,3-butadiene were all Phillips research grade (butenes, 99.8%; 1,3-butadiene; 99.85%) and were each purified before use by freezing with liquid nitrogen and outgassing several times. Airco Industrial Gases Extra Dry grade oxygen (99.6%) was used without further purification. All the gases were checked by gas chromatography, and no impurities were detected except in trans-2-butene which had about 0.2% impurity (probably n-butane).

The deuterium labeled 2-butene-d$_8$ (99 atom% deuterium) was a mixture of the trans- and cis- isomers provided by Merck, Sharp and Dohme Isotopes Ltd. The isomers were separated prior to use by fractionation in a propylene carbonate gas chromatographic column at 0°C (vide infra). The composition of the resulting cis-2-butene was 89.7% C$_4$D$_8$ and 10.3% C$_4$D$_7$H. The $^{18}$O-
labeled carbon dioxide was obtained from MSD Isotopes and contained 99.85 atom% $^{18}$O.

**APPARATUS**

**Reactor System**

The reactor system (Figure 3) could be used as either a batch recirculation reactor or a microcatalytic pulse reactor. Only a pair of stopcocks (S31 & S34) had to be reversed to make the conversion. The batch recirculation reactor mode was used for the kinetic and deuterium-labeled butene experiments, while the microcatalytic mode was used for the butene pulse and $^{18}$O$_2$ exchange experiments. The system is a vacuum / low pressure apparatus constructed of Pyrex glass utilizing a Welch Duo-Seal fore pump (FP) and a mercury diffusion pump (D) to maintain a pressure below $10^{-6}$ torr in condensible gases. The pressure is measured by a McLeod gauge (MG). All the stopcocks are high vacuum glass stopcocks lubricated with Dow Corning vacuum silicone grease.

All reactant gases are kept in storage bulbs (B1 - B6) for ready access prior to use, and the purities of the gases are checked by gas chromatography occasionally. The amount of the stored gases are monitored by the manometers (M1 - M6) attached to each bulb. The traps T1 and T2 (cooled to -78°C) are used to prevent the mercury from diffusing into the reactor system and to purify the reactant gases by repeated freeze-pump-thaw cycles.

When the reactor system is in the recirculation mode, the reactant mixture is recirculated in the loop by the recirculation pump (PUMP) in the counterclockwise direction through the reactor bed (R), ice-watertrap (T4), pump, and a mixing volume (T3). The total volume of the loop is about 500 ± 10
cm$^3$, and the pressure is measured by a mercury manometer (M8).

The recirculation pump is a double action positive displacement pump containing a glass piston with an iron core and four glass check valves. The piston is moved by alternate switching of power to two externally mounted solenoids. The frequency of the switching determines the pumping rate, which can be varied from approximately 200 to 1000 cm$^3$/min using an electronic pump controller.

A bypass section, formed by stopcocks S32 and S33, permits recirculation of gas mixtures without flow over the reactor (R) for the premixing of reactant gases before the initiation of reaction.

The reactor, including S35, may be inserted into or removed from the recirculation loop through the use of two 10/30 standard glass ground joints. The reactor bed has a volume of approximately 2 cm$^3$, and the catalyst is held in place between two glass wool plugs. A glass thermowell is mounted inside the reactor to permit placement of a thermocouple within the catalyst bed. The temperature in the bed is measured by a Chromel-Alumel thermocouple attached to a Leeds & Northrup Electromax V PID temperature indicating controller. For the continuous monitoring of the temperature, an OmegaLine 640 temperature recorder is connected to the same thermocouple.

Reactant gases are introduced into the storage bulbs through the stopcocks S13, S12, S11, and the corresponding stopcocks S5 - S10. Samples are admitted into the recirculation loop through S14.

During kinetic runs, samples of the reactant mixture are expanded into the sampling loop between S24 and S26 and swept from the loop into a gas chromatograph by the helium carrier gas for analysis. The gas chromatograph
consists of a fractionation column, a thermal conductivity detector, a detector power supply, and an integrator. The column is a 1/4 inch x 35 feet copper tube packed with propylene carbonate (25 wt.%) supported on 60/80 mesh Chromosorb W (AW). An ice-water bath is used to keep the column temperature at 0°C. The detector and the power supply were purchased from the Antek Instruments Co. The detector filament current is 100 mA and the temperature is 80°C. Output of the detector is monitored by 3390A Hewlett Packard Reporting Integrator.

Individual components from the G.C. effluent can be collected in removable sample tubes attached to the G.C. outlet as the compounds emerge from the detector. The components of interest have the following relative sensitivity factors (area/amount) and retention times (min.): oxygen, 1.000, 7.98; carbon monoxide, 1.253, 8.30; carbon dioxide, 1.253, 10.15; 1-butene, 2.080, 15.18; trans-2-butene, 2.147, 17.29; cis-2-butene, 2.176, 19.85; and butadiene, 2.001, 27.03. Since the sensitivities and retention times changed as the filament grew old and the flow rates of helium varied slightly, the sensitivities and retention times were measured occasionally and the calibration table was adjusted. At an inlet pressure of 15 psig, the helium carrier gas flow rate was 60 cc(NTP)/min for the sample stream; it was 12 cc/min for the reference stream.

For the microcatalytic pulse experiments, the pulse doser between S36 and S37 was filled with a reactant or CO₂ in either of the two ways: through S15 from a storage bulb, or through T1. By reversing the stopcocks, the contents were swept through the reactor by the helium carrier gas and into the GC system for analysis. In the CO₂ exchange experiments, the effluent from the GC detector was collected in a sample tube and analyzed by a mass
A Consolidated Electrodynamics Corporation Model 21-104 mass spectrometer was used for gas analysis in the deuterium-labeled butene and C$^{18}$O$_2$ exchange experiments. The mass spectrometer was equipped with a sample volume (3313 cm$^3$) and an MKS Baratron electronic manometer. Vacuum in the inlet system was maintained by an oil diffusion pump with a mechanical fore pump. The analyzer was kept under a high vacuum (10$^{-7}$ torr) by a Varian Vac Ion pump. During all experiments, an anode current of 10 mA and a nominal ionization voltage of 10 volts were employed.

Specific surface areas for catalysts used in this study were determined by the nitrogen BET method using a Micromeritics AccuSorb 2100E analyzer.

**X-Ray Diffraction Equipment**

The x-ray diffraction and the Mössbauer spectroscopy experiments were carried out at the Haldor Topsøe labs in Denmark. The X-ray patterns were recorded on a Philips PW 1050 vertical goniometer equipped with a variable slit, a graphite diffracted-beam monochromator, a Xe-filled proportional counter, and a strip chart recorder. The radiation used was CuK$_{a1,2}$ generated in an x-ray tube running at 40kV and 40mA. A complete XRD pattern was obtained by line scanning at a speed of 2$^\circ$ (2$\theta$) per minute while the spinel lattice constants were obtained by slowly scanning the (553)-line at a speed of 1/4$^\circ$ (2$\theta$) per minute.

**Mössbauer Spectroscopy**

All spectra were obtained by use of a conventional Mössbauer
spectrometer operating in the constant acceleration mode. The Doppler velocity is obtained by attaching the source to a drive rod which is part of an electromechanical velocity transducer (Wissenschaftliche Elektronik MVT-2000). The driving force of the shaft is produced by a current through the so-called drive coil and another coil, the pick-up coil feeds back the induced current corresponding to the actual velocity of the source or adsorber. This signal is then compared in the electronic drive unit (Wissenschaftliche Elektronik MR-350) with the desired velocity wave form provided by the digital function generator (Wissenschaftliche Elektronik DGF-1200) and the resulting error signal is amplified and is used as input to the drive coil. Also, it is possible to add different pulse shapes to the drive signal in order to minimize the error signal.

Although the error signal could be reduced to about 0.2% of the reference signal for most of the velocity scale, this does not assure that oscillations at the source will be detected by the pick-up coil. A calibration spectrum of metallic iron is able to disclose this error.

The gamma ray detection is carried out using a Kr-CO₂ filled proportional counter tube with a Be-window (Reuter-Stokes, RS-P3-1605-261) powered by a stabilized high-voltage power supply (Nuclear Data ND 253). The output signals of the counter are amplified in a low noise charge sensitive preamplifier (Nuclear Data ND 401), and subsequently amplified and shaped in a line amplifier (Nuclear Data ND 510). The signals of interest are then selected in a single channel analyser (SCA, Nuclear Data ND 602), which gives a standard pulse, when a pulse, whose amplitude corresponds to the 14.4 keV gamma rays, is received. The selection of a proper window for the SCA is done by use of the
analog to digital converter (ADC, Nuclear Data ND 575); the pulses from the amplifier are stored in the ADC operating in coincidence mode in which a window is quickly selected by use of an oscilloscope.

A 2048 channel multi channel analyser (MCA, Nuclear Data 100) operating in the multiscaler-mode is used for storage of the gamma ray counts. The pulses from the SCA are addressed in one of the four groups (each having 512 channels). A repetitive velocity scan is used which admits investigation of the entire velocity spectrum simultaneously. In the MSC-mode (multiscaling or time-mode) the channel address of the analyser is advanced sequentially at a constant rate. Pulses from the SCA are added to the channel which is open. The total scan through all 512 channels is repeated at a frequency of 10c/s, determined by analog signals from the drive unit. The drive rod is slaved to move back and forth at the same frequency synchronously with the channel advance, and with constant acceleration in each half period. This leads to a linear connection between the channel address and the velocity of the rod. In this way a full Mössbauer spectrum is recorded in each half period, being symmetric (ideally) about the center channel. The addition of the two counter parts in the data treatment improves the statistics and furthermore, the parabolic curvature of the background due to the varying source and detector distance will disappear. However, non-linearities of the velocity/channel address relationship will introduce a slight line broadening, when two spectra are added. Finally, the counts in the channels forming the Mössbauer spectrum were transferred to main frame computer (PRIME 750) where data analyses were carried out.
EXPERIMENTAL PROCEDURES

Kinetic Runs in Recirculation System

Before each reaction, the catalyst was pretreated for at least 1 hr at 500°C in 100 torr of recirculating oxygen. Any water, carbon dioxide or hydrocarbons were removed from the flowing stream by thermostating T3 at liquid nitrogen temperature. After the oxygen treatment, the system was evacuated at the reaction temperature (usually 300-400°C) for an hour. To prevent the reactor from being contaminated by the condensate in the trap T3, the reactor stopcocks (S32 & S33) were closed while the trap was being evacuated. The vacuum was kept under $10^{-6}$ torr in noncondensible gases. During the evacuation through S3, S4, and S14, T1 was thermostated at -78°C using a dry ice - acetone trap to prevent mercury vapor from diffusing into the loop.

After pretreatment of the catalyst, the stopcocks S32 and S33 were switched to the bypass position, and the butene reactant was introduced into the loop; its pressure was measured by M8. The butene was then frozen in T4 with a liquid nitrogen trap, and oxygen was introduced into the loop. The amount of oxygen was measured again by M8. The liquid nitrogen trap was removed, the recirculation pump was activated, the butene was vaporized, and the reactants were mixed. Once the butene and oxygen were mixed, extreme care was exercised to avoid a possible explosion of the mixture (explosive region: approximately 5 to 33% butene at room temperature).

During this preparation period, the Electromax V temperature controller which was described earlier (p.28) for the reactor was activated and the isothermal reaction temperature was reached. To initiate a reaction, stopcocks
S32 and S33 were rotated to the reaction positions and the reactant mixture began to flow over the catalyst. Since the butene OXD and deep oxidation reactions are highly exothermic, it was very difficult to obtain an isothermal reaction condition. By starting the reaction at low temperature and adjusting the set point of the reactor temperature controller carefully, the reaction temperature could be controlled within \( \pm 1^\circ C \) about 5 minutes after initiation of the reaction. A typical reaction temperature profile is given in Figure 4. Before and during the reaction, samples were drawn at certain time intervals from the system for gas chromatographic analysis.

**Deuterium-Labeled Butene Experiments**

These experiments were performed following the exactly same procedure as used in the kinetic runs, except that the butene reactant was a mixture of 50 torr undeuterated cis-2-butene and 50 torr perdeuterated cis-2-butene. As each hydrocarbon component eluted from the gas chromatograph detector, it was collected in a sample tube at liquid nitrogen temperature. Following evacuation of helium, each tube was warmed to room temperature and its contents expanded into the mass spectrometer for isotopic analysis.

**Microcatalytic Pulse Experiments**

The butene pulse and \( \text{C}^{18}\text{O}_2 \) exchange experiments were carried out in the microcatalytic reactor mode. In both series of experiments, the doser between S36 and S37 was filled to 124 torr \( (1.73\times10^{19} \text{ molecules}) \) of the desired reactant. The helium carrier gas pressure and flow rate in all experiments were 15 psig and 40 cm\(^3\) (NTP)/min, respectively. In most cases, fresh catalyst
Figure 4. Typical Reaction Temperature Profile
samples were used at the beginning of each series of experiments in order to obtain reproducible results. When pretreatment was required, it could easily be done by switching the system to the recirculation mode.

Since a single helium flow mode was used, the same helium carrier gas stream flowed over the catalyst bed and into the gas chromatographic column. In the C^{18}O_2 exchange reaction, effluent CO_2 was collected in a sample tube and the isotopic composition of the content was analyzed in the mass spectrometer.

**TREATMENT OF DATA**

**Kinetic Experiments**

Data collected in the kinetic experiments in the recirculation system included the compositions and partial pressures of the product mixture as a function of the reaction time. The results were analyzed to determine the "initial" reaction rates and to test several proposed kinetic models. In most experiments, the first sample was taken 15 minutes after initiation of the reaction, and the initial reaction rate was calculated as the average amount of products formed per unit reaction time. Since the conversion was very low (less than 5%) for the first sample, the partial pressures of the reactants could be assumed to be nearly constant.

Several kinetic expressions were derived from models and tested by comparing the experimental data with the calculated values based on the proposed models by numerical integration. Models investigated included power-law, two site Langmuir-Hinshelwood, Rideal-Eley, and Mars Van Krevelen models.
The reaction rate expressions finally suggested could not be integrated by standard means since they were coupled non-linear differential equations. Therefore, an approximation was made by assuming that partial pressures of reactants and the reaction rates are constant over a small increment of residence time. This simplification made the change in the partial pressure of a specific compound equal to the reaction rate multiplied by the incremental residence time. Using this relation allowed one to estimate the initial partial pressure for the next incremental residence time. For most calculations, 1 min/increment was used, since no more than 0.5% difference (avg. less than 0.1%) was observed when the increment was reduced by half. Parameters obtained from the analysis of the "initial" reaction rates were adjusted slightly to give the best fit for experimental data obtained as a function of time.

**Deuterium-Labeled Butene Experiments**

The samples from deuterium-labeled butene experiments were separated into each hydrocarbon component by the gas chromatograph, and the isotopic composition was determined for each component by mass spectroscopy. Using the Hall and Hightower\textsuperscript{68} method, isotope effects were calculated for both isomerization and butadiene formation reactions, since both of the reactions were found to be intramolecular. The method is based on the following assumptions:

a. Product butene molecules containing less than four deuterium atoms originate from the d\textsubscript{5} species; molecules containing more than four deuterium atoms originate from d\textsubscript{8} species. The d\textsubscript{4} products originate
from both directions equally.

b. Product butadiene molecules containing less than three deuterium atoms originate from light starting materials, and those containing more than three deuterium atoms originate from heavy starting materials. The d₃ species is produced equally from both directions.

c. The concentration of the trans- and 1-butene isomers is always small, such that the reverse isomerization reactions are negligible compared to the cis- to trans- and cis- to 1-butene reactions.

d. An average isotope effect is considered rather than specific effects for each dᵢ species.

An isotope effect for isomerization is defined as

\[
\text{I.E. isom} = \frac{\sum_{i=0}^{3} N_{ip} + \frac{1}{2} N_{4p}}{\sum_{i=5}^{8} N_{ip} + \frac{1}{2} N_{4p}} \quad (15)
\]

\[
\sum_{i=0}^{3} N_{ir} + \frac{1}{2} N_{4r} \quad / \quad \sum_{i=5}^{8} N_{ir} + \frac{1}{2} N_{4r}
\]

and an isotope effect for OXD is defined as

\[
\text{I.E. OXD} = \frac{\sum_{i=0}^{2} N_{ip} + \frac{1}{2} N_{3p}}{\sum_{i=4}^{6} N_{ip} + \frac{1}{2} N_{3p}} \quad (16)
\]

\[
\sum_{i=0}^{3} N_{ir} + \frac{1}{2} N_{4r} \quad / \quad \sum_{i=5}^{8} N_{ir} + \frac{1}{2} N_{4r}
\]

where r refers to reactant and p to products, i.e. butene isomers for isomerization and butadiene for the OXD reaction.

Microcatalytic Pulse Experiments

Two different types of experiments were performed in the microcatalytic pulse system. The first was an isotope exchange experiment in which C¹⁸O₂
was pulsed over the catalyst. Its labeled oxygen could exchange with unlabeled oxygen on the catalyst surface and/or in the bulk of the solid. The extent of the exchange was calculated by analyzing the isotopic composition of effluent CO₂ with the mass spectrometer. In the second type of experiment, butene isomers were pulsed over the catalyst without gas phase oxygen and the reaction product mixture was analyzed by gas chromatography. These experiments were designed to provide information about the mobility and reactivity of the catalyst lattice oxygen.

In the exchange experiments, the total exchangeable oxygen ($\Sigma_{\infty}$) can be calculated from the cumulative amount of exchanged oxygen ($\Sigma_j$) for each pulse $j$ by assuming that exchange equilibrium is achieved between the catalyst surface and the gas phase.⁴³ A relationship between the $1/\Sigma_j$ and $1/j$ is given by the equation

$$
1/\Sigma_j = 1/\Sigma_{\infty} \left[ \frac{(1 + a)^j}{\{i + a\} - 1} \right]
$$

(17)

where, $a = 2n/\Sigma_{\infty}$ (n = number of C$^{18}$O₂ molecules / pulse). A detailed mathematical derivation is given in the Appendix. This equation can be linearized by a Taylor series expansion when $a<<1$ to give

$$
1/\Sigma_j = 1/\Sigma_{\infty} + (1/2n) \left(1/j\right).
$$

(18)

Thus, from a linear plot between $1/ \Sigma_j$ and $1/j$ we obtain a slope $S = 1/2n$ and an intercept $I = 1/ \Sigma_{\infty}$.

Since some of the assumptions made to derive the equations 17 and 18 were not realistic and the slope $S = 1/2n$ did not agree with experimental data, another equation was derived without the equilibrium exchange assumption. With the assumption that the isotopic compositions of the catalyst surface and the gas phase are constant throughout the catalyst bed for each pulse (CSTR
assumption), another relationship between $1/\Sigma_j$ and $1/j$ can be derived, viz.

$$\frac{1}{\Sigma_j} = \frac{1}{\Sigma_\infty} \left[ 1 - \{1 - (\Sigma_1/\Sigma_\infty)^j\} \right]$$  \hspace{1cm} (19)

When $\Sigma_1/\Sigma_\infty << 1$, the equation can be linearized to give

$$\frac{1}{\Sigma_j} = \frac{1}{\Sigma_\infty} + \left(\frac{1}{\Sigma_1}\right) \frac{(1/j)}{1}.$$  \hspace{1cm} (20)

Equation 20 is essentially the same as equation 18 except that the slope is different. Noteworthy is the observation that both the inexact equation 18 and the more realistic equation 20 both have intercepts of $1/\Sigma_\infty$.

While most of the calculations throughout this study involved using equation 20, in some cases the linear plot method was used because it proved to be quite an acceptable and simpler method for calculating the approximate values of $\Sigma_\infty$.

The preceding linear plot method was used to calculate the total amount of removable oxygen ($\Sigma_\infty$) in the catalyst from the cumulative amount of removed oxygen ($\Sigma_j$) for the production of butadiene. In the calculation of the $\Sigma_j$, it was assumed that one oxygen is removed from the catalyst for every butadiene molecule formed. Even though the linear plot method cannot be mathematically justified for the butene pulse experiments, it is regarded that this method is acceptable for the calculation of the approximate values of $\Sigma_\infty$, considering the similarity between the $\text{C}^{18}\text{O}_2$ and butene pulse experiments.
III. RESULTS

KINETIC EXPERIMENTS

General

When a reactant mixture of butene and oxygen was introduced into the batch recirculation system and reacted over a catalyst, three reactions, isomerization, oxidative dehydrogenation, and deep oxidation, produced butene isomers, butadiene, and carbon oxides. Unless the reaction was carried out at a very high temperature, e.g. above 500°C, no other products were observed. Typical results of a reaction are plotted in the Figure 5 showing the changes of the partial pressures of reactants and products with reaction time.

Since the OXD and deep oxidation reactions are highly exothermic, a large temperature excursion (exotherm) was observed when the initial reaction temperature was high (e.g. >400°C). The excursion often exceeded 100°C. Even if the reaction were initiated at a low temperature (e.g. 300°C), there was still an exotherm, but it was usually less than 10°C. Most kinetic experiments were performed at low reaction temperatures to avoid the high exotherm. When there was a small exotherm, the reaction temperature stabilized within ±1°C of the set point in less than 10 minutes after initiation of the reaction (See Figure 4, p.35).

To obtain reproducible results, most kinetic experiments were performed under a “standard” set of conditions. The “standard” condition implies the use of a reactant mixture of 200 torr butene and 100 torr oxygen, and 0.125 g of fresh Tan 15 catalyst at 350°C. After 4 hours’ reaction, 10% conversion and 60% selectivity were obtained from a typical reaction where conversion is
Figure 5. Typical Kinetic Run
(rxn temp. = 330°C, Tan 15 0.125g)
(CO₂, BD, c-2-B, 1-B : x10)
defined as

\[
\text{Conversion (\%)} = \frac{(P_{BD} + \frac{1}{4} P_{CO2})_t}{(P_B)_t = 0} \times 100
\]  

(21)

the corresponding selectivity is determined from the equation

\[
\text{Selectivity (\%)} = \left( \frac{P_{BD}}{P_{BD} + \frac{1}{4} P_{CO2}} \right) \times 100.
\]  

(22)

The conversion and selectivity obtained in this study were low compared with values reported for industrial processes presumably because the reaction was carried out at low temperatures without steam over a long contact time.

Specific surface areas of the catalysts, as determined by a nitrogen BET method, are very close to each other except for $\gamma$-Fe$_2$O$_3$, which has an exceptionally higher specific surface area of 100.4 m$^2$/g (Table 1). The BET "C" values and heats of adsorption ($\lambda_1$) are listed also. Since Tan 15 has a higher surface area than Tan 10, it was used as the catalyst throughout this study unless otherwise stated.

\begin{table}
\caption{Surface Area of Catalysts}
\begin{tabular}{|c|c|c|c|}
\hline
Catalyst & Surface Area (m$^2$/g) & C & $\lambda_1$(Kcal/mole) \\
\hline
Tan 10 & 6.4 & 214 & 2.16 \\
Tan 15 & 8.3 & 248 & 2.18 \\
$\alpha$-Fe$_2$O$_3$ & 10.1 & 206 & 2.15 \\
$\gamma$-Fe$_2$O$_3$ & 100. & 153 & 2.11 \\
Fe$_3$O$_4$ & 6.4 & 64 & 1.97 \\
\hline
\end{tabular}
\end{table}
Effect of Catalyst History

Using "standard" reaction mixtures and catalyst, a series of reactions were performed at different initial reaction temperatures. The exotherms, conversions, and selectivities observed after 15 minutes' reaction are recorded in Table 2. No large exotherm (temperature excursion) was seen at 360°C in the first reaction when a virgin catalyst was used (reaction #1). The catalyst was given the usual pretreatment in O₂, evacuated, and prepared for a second reaction at a slightly higher temperature. At an initial temperature of 380°C, there was a large exotherm of 119°C (#2) and in just 15 minutes about 74% of reactant the O₂ was consumed. The calculated conversion and selectivity (based on the amount of trans-2-butene and products) were 21% and 73%, respectively.

<table>
<thead>
<tr>
<th>Rxn #</th>
<th>Initial Temp. (°C)</th>
<th>Exotherm (°C)</th>
<th>Conv. (%) @ 15 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>360</td>
<td>11</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>380</td>
<td>119</td>
<td>21.4</td>
</tr>
<tr>
<td>3</td>
<td>370</td>
<td>102</td>
<td>21.3</td>
</tr>
<tr>
<td>4</td>
<td>360</td>
<td>91</td>
<td>22.3</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>105</td>
<td>22.7</td>
</tr>
</tbody>
</table>

Several more reactions were successively carried out at lower initial reaction temperatures (reactions #3 at 370°C, 4 at 360°C, and 5 at 350°C). In reaction #5 when the temperature was even lower than in reaction #1, an unexpectedly high exotherm (105°C) was observed.
Another series of experiments were performed over the other catalyst (Tan 10) and same result was observed (Table 3). When the results of the reactions #2 and #5-7 are compared, it is apparent that both catalysts have higher activities than the corresponding virgin catalysts after exposure to the high exotherm in presence of the reaction mixture.

<table>
<thead>
<tr>
<th>Rxn #</th>
<th>Initial Temp. (°C)</th>
<th>Exotherm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>323</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>359</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>365</td>
<td>230</td>
</tr>
<tr>
<td>4</td>
<td>365</td>
<td>185</td>
</tr>
<tr>
<td>5</td>
<td>356</td>
<td>155</td>
</tr>
<tr>
<td>6</td>
<td>355</td>
<td>150</td>
</tr>
<tr>
<td>7</td>
<td>345</td>
<td>130</td>
</tr>
</tbody>
</table>

To examine the cause of the enhancement of the catalytic activity, the fresh Tan 15 catalyst was heat-treated for 2 hours at temperatures up to 800°C in air or under a N₂ environment, but no change in the catalytic activity was found. Thus, it seems that the activity enhancement cannot be accomplished with heat alone.

**X-ray Diffraction and Mössbauer Spectroscopy**

To explore the reason why the catalytic activity changes, virgin and used catalysts were examined by X-ray powder diffractometry and Mössbauer
spectroscopy; spectra obtained on the two types of material were compared.

Three samples of zinc ferrite catalysts were prepared and subjected to X-ray powder diffraction analysis. These include a fresh sample of Tan 15 (#1, Figure 6), one used repeatedly and exposed to a high exotherm (#2, Figure 7), and another used only once at a low reaction temperature without being exposed to a high exotherm (#3, Figure 8). The samples #1 and #3 were almost identical, showing spinel zinc ferrite \( (a_0=8.442\text{Å}, \text{literature value } = 8.441\text{Å}) \) plus about 1.5 wt.% \( \alpha\text{-Fe}_2\text{O}_3 \) and ca. 0.2 wt.% ZnO. An XRD spectrum for \( \alpha\text{-Fe}_2\text{O}_3 \) is shown in Figure 9 as a reference to identify the peak positions. No \( \alpha\text{-Fe}_2\text{O}_3 \) is seen in #2, while the amount of ZnO has increased to about 2.5 wt.%; this sample was found to be magnetic by noting its response to a magnet moved outside the sample container. Since the amount of ZnO increased, the amount of free iron oxide should also have increased; however, no \( \alpha\text{-Fe}_2\text{O}_3 \) was observed. It is probable that \( \alpha\text{-Fe}_2\text{O}_3 \) has changed into \( \text{Fe}_3\text{O}_4 \) or \( \gamma\text{-Fe}_2\text{O}_3 \) which is magnetic and which cannot be detected by XRD when it exists as a small amount in presence of a large excess of zinc ferrite.

At the same time, zinc ferrite may decompose into \( \text{Fe}_3\text{O}_4 \) and ZnO. When the catalyst is exposed to a high exotherm, it is under a reductive environment at high temperature. The calculations of equilibrium constants (Table 4) show that the reaction #8 can proceed at high temperature under a reductive gas (butene) environment to produce \( \text{Fe}_3\text{O}_4 \) from zinc ferrite. Most of the data in the Table 4 were calculated from free energy data given in an API report.\(^{69} \) It should be mentioned that \( \text{Fe}_3\text{O}_4 \) thus formed can reversibly change into \( \gamma\text{-Fe}_2\text{O}_3 \) or \( \gamma\text{-Fe}_2\text{O}_3-x \ (0<x<1/3) \) both of which have essentially spinel structures.\(^{57} \)
Figure 6. XRD of Fresh Zinc Ferrite (Tan 15)
Figure 7. XRD of Used Zinc Ferrite (Tan 15)
(used repeatedly and exposed to high exotherm)
Figure 8. XRD of Used Zinc Ferrite (Tan 15)
(used once and not exposed to high exotherm)
Table 4. Related Reactions and Equilibrium Constants

\[
\begin{align*}
t-C_4H_8 & \rightarrow C_4H_6 + H_2 & \quad (1) \\
t-C_4H_8 + \frac{1}{2} O_2 & \rightarrow C_4H_6 + H_2O & \quad (2) \\
t-C_4H_8 + 6O_2 & \rightarrow 4CO_2 + 4H_2O & \quad (3) \\
CO + \frac{1}{2} O_2 & \rightarrow CO_2 & \quad (4) \\
ZnO + Fe_2O_3 & \rightarrow ZnFe_2O_4 & \quad (5) \\
3Fe_2O_3 & \rightarrow 2 Fe_3O_4 + \frac{1}{2} O_2 & \quad (6) \\
3ZnFe_2O_4 & \rightarrow 2 Fe_3O_4 + 3ZnO + \frac{1}{2} O_2 & \quad (7) \\
3ZnFe_2O_4 + C_4H_8 & \rightarrow 2 Fe_3O_4 + 3ZnO + C_4H_6 + H_2O & \quad (8)
\end{align*}
\]

<table>
<thead>
<tr>
<th>Rxn #</th>
<th>( \log K_p )</th>
<th>Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298</td>
<td>400</td>
</tr>
<tr>
<td>1</td>
<td>-15.3634</td>
<td>-9.9166</td>
</tr>
<tr>
<td>3</td>
<td>448.5853</td>
<td>334.7507</td>
</tr>
<tr>
<td>4</td>
<td>45.0435</td>
<td>32.4096</td>
</tr>
<tr>
<td>5</td>
<td>0.343</td>
<td>0.326</td>
</tr>
<tr>
<td>8</td>
<td>-11.4027</td>
<td>-6.0236</td>
</tr>
</tbody>
</table>
Similar conclusions can be obtained from the Mössbauer spectra (Figures 10 - 13). A Mössbauer spectrum of used zinc ferrite (Figure 10) showed some small peaks which were not found in a fresh zinc ferrite (Figure 11). The small peaks matched quite well with those of iron oxides (Figure 12 & 13). However, it is not very clear which iron oxide is responsible for these small Mössbauer peaks, since the iron oxides, α-Fe₂O₃, γ-Fe₂O₃ and Fe₃O₄ all exhibit very similar spectra and the amount of the iron oxide was very small. When a used α-Fe₂O₃ catalyst was examined by Mössbauer spectroscopy, its spectrum was exactly the same as that from a fresh α-Fe₂O₃ sample.

**Mixed Catalysts**

Various amounts (5, 10, 20%) of Fe₃O₄ were mixed with zinc ferrite (Tan 15). The mixtures were used to observe the effect of the presence of Fe₃O₄. The addition of Fe₃O₄ enhanced the catalytic activity and selectivity of zinc ferrite (Table 5). This observed enhancement could not be due to increased surface area of the mixed catalyst, since Fe₃O₄ actually has a slightly lower specific surface area (6.40 m²/g) than Tan 15 catalyst (8.31 m²/g).

<table>
<thead>
<tr>
<th>Table 5. Conversions and selectivities over mixed catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>0%</td>
</tr>
<tr>
<td>5%</td>
</tr>
<tr>
<td>10%</td>
</tr>
<tr>
<td>20%</td>
</tr>
</tbody>
</table>

* : %conversion / %selectivity (15 min.)
E : large exotherm
Figure 10. Mössbauer Spectrum of used Zinc Ferrite
Figure 11. Mössbauer Spectrum of Fresh Zinc Ferrite
Figure 12. Mössbauer Spectrum of Fresh Fe₂O₃
**Initial Reaction Rates**

As a first step to derive reaction rate equations, the initial reaction rates were calculated by analyzing the first sample taken 15 minutes after the initiation of each reaction. An attempt was made to fit the data to evaluate the activation energies for butadiene and carbon dioxide formation by defining the initial rate equations

\[ R_{BD}^0 = A_1 \exp(-E_1/RT) \]  \hspace{1cm} (23)

and

\[ R_{CO2}^0 = A_2 \exp(-E_2/RT). \]  \hspace{1cm} (24)

Since the partial pressures were always the same, they do not appear explicitly in equations 23 and 24 because the conversion for the first sample was always less than 3%; the purpose of this "initial" rate study was to provide initial estimates of the activation energies. The "standard" reaction mixture (200 torr of butene and 100 torr of oxygen) was used throughout this "initial" rate study.

As is seen in Figure 14, the data were not consistent and depended upon the history of the catalysts. In contrast, when a series of reactions were performed over the same catalyst sample, quite consistent results were obtained.

A series of reactions were performed over three catalysts with different histories using reactant mixtures of the same composition. From the Arrhenius plot (Figure 14) of these data, the values of \( A_1 \) and \( E_1 \) for each catalyst were calculated. Even though the \( A_1 \)'s varied, the \( E_1 \) values were very close to each other; the average value was 14.2 kcal/mole for used catalysts which had been exposed to high exotherms. This value is quite different from the reported values of 33.4 kcal/mole\(^5\) and 35.2 kcal/mole\(^4\) reported for similar catalysts.
Figure 14. Initial Rate of OXD Reaction over Fresh and Used Zinc Ferrite

- + △ ○ : used catalyst 0.125 g
- ◊ : fresh catalyst 0.125 g
- × : fresh catalyst 0.250 g
However, when the reactions were done over the virgin catalyst only, i.e. the catalyst was replaced with a fresh sample prior to each reaction, the initial reaction rates for the OXD reaction and deep oxidation reactions were much slower but were quite reproducible. The activation energy $E_1$ for the OXD reaction was $28.2 \pm 2.8$ kcal/mole which is much closer to the values reported for similar catalysts by the other authors$^{4,51}$. The uncertainty associated with $E_1$, $\pm 2.8$ kcal/mole, arises from two sources. The first is inherent in the linear least squares method. It involved estimating the differences between the experimental points and the regression line and was found to be 6.4% of $E_1$. A second uncertainty is caused by the unstable temperature at initiation of the exothermic reaction. From the typical temperature profile shown in Figure 4, a calculation was made that involved integrating the reaction rate constant over the 15 minute period, the corrected rate was only 3.2% different from the uncorrected value. A combination of these two resulted in the final uncertainty for $E_1$, 9.8% or 2.8 kcal/mole.

After the activation energies had been determined, the reaction orders of butene and oxygen were studied by varying the partial pressures one at a time and noting the effect on the “initial” reaction rate. As listed in Table 6, a series of reactions (B) were performed in a batch recirculation system changing the partial pressure of butene while another series (O) were done changing that of oxygen.

The dependency of the OXD and deep oxidation rates on the partial pressure of butene could be expressed by equations 25 and 26 which are derived based on a Langmuir-Hinshelwood mechanism.
Table 6. Reaction Order Experiments

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Partial Pressure of Reactants (torr)</th>
<th>Product Formation (torr)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Butene</td>
<td>O₂</td>
</tr>
<tr>
<td>B-1</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>B-2</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>B-3</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>B-4</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>B-5</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>O-1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>O-2</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>O-3</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>O-4</td>
<td>100</td>
<td>75</td>
</tr>
<tr>
<td>O-5</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

* reaction time = 15 minutes

\[
\begin{align*}
\dot{r}_{BD} &= 2.613 \times 10^{-12} \frac{P_B}{1 + 1.35 \times 10^{-2} P_B} \text{ mole/cm}^2\text{sec} \quad (25) \\
\dot{r}_{CO_2} &= 6.283 \times 10^{-12} \frac{P_B}{1 + 1.14 \times 10^{-2} P_B} \text{ mole/cm}^2\text{sec} \quad (26)
\end{align*}
\]

\(P_{O_2} = 50 \text{ torr, } 350^\circ C, \text{ Tan 15 0.125 g)}\)

The experimental rate data and the calculated curves are compared in Figure 15.
Figure 15. Butene Dependency of Initial Reaction Rate
($P_{O_2} = 50$ torr, $350^\circ$C, Tan 15 0.125g)

curves: calculated from eqs. 25, 26
points: experimental data
The oxygen dependency of the deep oxidation reaction could also be fit quite well by equation 27 whose derivation is based on a dissociative Langmuir-Hinshelwood model (Figure 16).

\[
 r_{CO_2} = 5.296 \times 10^{-12} \frac{\sqrt{P_{O_2}}}{1 + 0.123 \sqrt{P_{O_2}}} \text{ (mole/cm}^2\text{sec)} \tag{27}
\]

\( P_B = 100 \text{ torr}, 350^\circ\text{C, Tan 15 0.125 g) \}

However, the oxygen dependency for butadiene formation could not be explained with a simple equation. The reaction appears to be near zero-order in oxygen unless the oxygen partial pressure is reduced to quite a low level. Surprisingly, the “initial” reaction did not terminate even in the absence of gas phase oxygen as may be seen in Figure 16. The best fit was obtained by the equation

\[
 r_{BD} = 1.05 \times 10^{-12} + \frac{\sqrt{P_{O_2}}}{1 + 3.15 \times 10^{-2} \sqrt{P_{O_2}}} \text{ (mole/cm}^2\text{sec)} \tag{28}
\]

in which the first term may be related to removal of surface oxygen and the second term to gas phase oxygen. In other words, the first term describes a “stoichiometric” reaction in which the catalyst is reduced through removal of the surface oxygen.

When the two dependencies are combined, the rate equations reduce to

\[
 r_{BD} = 3.58 \times 10^{-15} \frac{P_B}{1 + 1.35 \times 10^{-2} P_B} \\
 \left( 7.84 + \frac{\sqrt{P_{O_2}}}{1 + 3.15 \times 10^{-2} \sqrt{P_{O_2}}} \right) \text{(mole/cm}^2\text{ sec)} \tag{29}
\]

\[
 r_{CO_2} = 2.64 \times 10^{-14} \frac{P_B}{1 + 1.14 \times 10^{-2} P_B} \frac{\sqrt{P_{O_2}}}{1 + 0.123 \sqrt{P_{O_2}}} \text{ (mole/cm}^2\text{ sec)} \tag{30}
\]

\( (350^\circ\text{C, Tan 15 0.125g}) \)
Figure 16. Oxygen Dependency of Initial Reaction Rate
($P_B = 100$ torr, $350^\circ C$, Tan 15 0.125g)
**Rate Equations.**

An attempt was made to develop a kinetic expression that will fit the kinetic experimental data using the information obtained in the initial reaction rate study. A pair of rate expressions for OXD and deep oxidation of butene were constructed by modifying the initial reaction rate equations 29 and 30 with the following assumptions.

a. The rate constants for deep oxidation of butadiene and all of the n-butenes are the same.

b. When butadiene is present in the reaction mixture, it adsorbs on the catalyst surface competitively with the n-butenes and has the same adsorption equilibrium constant. As a result, butadiene inhibits the butene OXD.

c. The adsorption equilibrium constants are temperature independent.

\[ R_{CO2} = k_2' \frac{P_B + P_{BD}}{1 + K_B(P_B + P_{BD})} \frac{\sqrt{P_{O2}}}{1 + \sqrt{K_{O2}P_{O2}}} \]  \hspace{1cm} (31)

The butadiene formation rate can be expressed as a difference between the rate of formation of butadiene from butene by OXD and its disappearance to CO₂ by deep oxidation. Thus, using the Langmuir-Hinshelwood mechanism we have

\[ R_{BD} = R_{BD}' - R_{BD}'' \]  \hspace{1cm} (32)

\[ R_{BD}' = k_1 \theta_B \theta_{O2} = k_1 \frac{K_B^{PB}}{1 + K_B^{PB} + K_B^{BD}P_{BD}} \left( k_s + \frac{\sqrt{K_{O2}P_{O2}}}{1 + \sqrt{K_{O2}P_{O2}}} \right) \]  \hspace{1cm} (33)

\[ R_{BD}'' = R_{CO2} \frac{P_{BD}}{P_{BD} + P_B} = k_2 \frac{P_{BD}}{1 + K_B' (P_{BD} + P_B)} \frac{\sqrt{K_{O2}P_{O2}}}{1 + \sqrt{K_{O2}P_{O2}}} \]  \hspace{1cm} (34)
The final equations with the constants obtained from a computer fit of the data are the following:

\[
R_{CO2} = 1.42 \times 10^7 \exp(-30,640/RT) \frac{P_B + P_{BD}}{1 + 1.14 \times 10^{-2}(P_B + P_{BD})} \frac{\sqrt{P_{O2}}}{1 + 0.02 \sqrt{P_{O2}}}
\]

\[
R_{BD} = 3.66 \times 10^9 \exp(-34,050/RT) \frac{1}{1 + (P_{BD}/P_B)^{(7.84 + \frac{\sqrt{P_{O2}}}{1 + 3.15 \times 10^{-2}\sqrt{P_{O2}}})}}
\]

\[
- 1.42 \times 10^7 \exp(-30,640/RT) \frac{P_{BD}}{1 + 1.14 \times 10^{-2}(P_B + P_{BD})} \frac{\sqrt{P_{O2}}}{1 + 0.02 \sqrt{P_{O2}}}
\]

(35) (36)

These equations were numerically integrated by the method described earlier (See p. 34) and the calculated values were compared with a set of experimental data (Figure 17 - 20).

**Catalyst Deactivation**

Most kinetic experiments were run for 4 hours. Over this period, the activity of the catalyst was assumed to be constant. To test this, several reactions were carried out for variable lengths of time (15, 45, 90, 150, and 240 minutes) and terminated. Following each reaction, the reactor system was quickly evacuated, another reactant mixture was prepared, and a new reaction was run over the same catalyst. After 15 minutes, a sample was taken and analyzed. The catalyst activities for deep oxidation and OXD were compared for the first and second experiments by measuring the amounts of CO$_2$ and butadiene formed in 15 minutes (Table 7).
Figure 17. Butene OXD over Zinc Ferrite
(t-2-B 200, O2 100, 377°C, fresh Tan 15 0.125g)
Figure 18. Deep Oxidation of Butene over Zinc Ferrite
(t-2-B 200, O2 100, 377°C, fresh Tan 15 0.125g)
Figure 19. Butene OXD over Zinc Ferrite
(t-2-B 200, O2 100, 340-377°C, fresh Tan 15 0.125g)
Figure 20. Deep Oxidation of Butene over Zinc Ferrite
(t-2-B 200, O2 100, 340-377°C, fresh Tan 15 0.125g)
Table 7. The Change of the Catalytic Activity

<table>
<thead>
<tr>
<th>Time on Stream (min.)</th>
<th>0</th>
<th>15</th>
<th>45</th>
<th>90</th>
<th>150</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial OXD Rate*</td>
<td>2.51</td>
<td>2.14</td>
<td>2.20</td>
<td>2.31</td>
<td>2.29</td>
<td>2.42</td>
</tr>
<tr>
<td>Initial Deep Oxidation Rate**</td>
<td>1.43</td>
<td>1.57</td>
<td>1.64</td>
<td>1.58</td>
<td>1.65</td>
<td>1.64</td>
</tr>
</tbody>
</table>

* (butadiene $10^{-12}$ mole/cm$^2$sec)
** (1/4 CO$_2$ $10^{-12}$ mole/cm$^2$sec)

( Temp.= 350°C, t-2-butene 200 torr, O$_2$ 100 torr, fresh Tan 15 0.125g)

As can be seen in the table, the initial rates for an unregenerated catalyst sample after varying lengths of time on stream are within 15% the same as the initial rates on a fresh catalyst. These data confirm the assumption that the activity of catalyst did not change significantly over the reaction period of 4 hrs.

**Batch Recirculation Reaction without Gas Phase Oxygen**

Butene was exposed to the catalyst in the absence of gas phase oxygen in the batch recirculation system to examine the reaction of surface oxygen and migration of lattice oxygen to the catalyst surface. The formation of CO$_2$ was almost negligible but the isomerization reaction was very fast (Figure 21). About 1.5 hours after initiation of the reaction, no further changes in the gas phase were observed. At 1.5 hours, the amount of oxygen consumed for the production of butadiene was in the range of 60 to 80% of 1 monolayer oxygen (one O atom removed per butadiene molecule produced) assuming each surface oxygen occupies about 10Å$^2$. The amount of butadiene produced increased slightly when the initial partial pressure of butene was increased, but it leveled
Figure 21. Butene OXD without gas phase $O_2$

($350^\circ C$, 1 g Tan 15)
off when the butene partial pressure exceeded 50 torr (Figure 22).

**DEUTERIUM-LABELED BUTENE EXPERIMENTS**

An experiment was conducted at 360°C using a reactant mixture containing 50 torr undeuterated cis-2-butene, 50 torr deuterated cis-2-butene, and 50 torr oxygen. Before and after the experiment a couple of reactions were done using undeuterated butene and O₂ under the same reaction conditions. Between the reactions, the catalyst was pretreated by the standard procedure. The results from the reactions are compared in Figures 23 and 24. The two undeuterated butene experiments (#1 and #3) show essentially the same results, but the second experiment with the mixture of perdeuterated and undeuterated butene shows much slower reaction. From this observation, we can conclude that there is a significant isotope effect for this reaction. To investigate the effect quantitatively, the isotopic composition of the product mixture was analyzed; the results are tabulated in Table 8. The reactions appear to be intramolecular since very little H/D scrambling was observed. Had rapid scrambling to statistical equilibrium occurred, the maximum d₄ concentration would be observed at the d₄ (butenes) or d₃ (butadiene) species.

From these data, the isotope effects for isomerization and OXD were calculated using equations 15 and 16 (p. 36). As shown in Table 9, the isotope effects are significant for isomerization to 1-butene and OXD to butadiene. The isotope effect for cis/trans rotation to produce trans-2-butene, however was, essentially negligible. The presence of isotope effects indicates that C–H bond cleavage is involved in the rate determining steps of both OXD and double
Figure 22. Butene OXD without Gas Phase $O_2$
(350°C, 1 g Tan 15)
Figure 23. Isotope Effect on Conversion

(360°C, Tan 15 0.25g)
Figure 24. Isotope Effect on Selectivity
(360°C, Tan 15 0.25g)
Table 8. Isotopic Composition Data During Deuterium Labeling Experiments

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Mole Fraction of Isotopic Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (Hydrocarbons)</td>
<td></td>
<td>$d_0$ $d_1$ $d_2$ $d_3$ $d_4$ $d_5$ $d_6$ $d_7$ $d_8$</td>
</tr>
<tr>
<td>cis-2-butene</td>
<td>1.0</td>
<td>.469 - - - - - .072 .459</td>
</tr>
<tr>
<td>After 24 hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-2-butene</td>
<td>.649</td>
<td>.410 .012 - - - - .096 .482</td>
</tr>
<tr>
<td>1-butene</td>
<td>.080</td>
<td>.488 .093 - - - .020 .033 .273 .093</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>.127</td>
<td>.466 .032 .002 - - -.017 .165 .318</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>.068</td>
<td>.611 .110 .018 .012 .045 .085 .119 - -</td>
</tr>
<tr>
<td>1/4 CO₂</td>
<td>.076</td>
<td></td>
</tr>
</tbody>
</table>

(360°C, Undeuterated c-2-butene 50 torr, Deuterated c-2-butene 50 torr,
O₃ 50 torr, Tan 15 0.25g)

**Binomial Distribution for H : D = 1 : 1**

| Butenes        | .004 .031 .110 .219 .272 .219 .110 .031 .004 |
| 1,3-butadiene  | .016 .093 .235 .312 .235 .093 .016 - -        |
Table 9. Isotope Effect of Isomerization and OXD Reactions

<table>
<thead>
<tr>
<th>Reaction time (hr)</th>
<th>1-Butene</th>
<th>trans-2-Butene</th>
<th>1,3-Butadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I.E.</td>
<td>I.E.</td>
<td>I.E.</td>
</tr>
<tr>
<td>4</td>
<td>1.499</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>1.492</td>
<td>0.953</td>
<td>2.580</td>
</tr>
<tr>
<td>12</td>
<td>1.429</td>
<td>0.976</td>
<td>2.676</td>
</tr>
<tr>
<td>24</td>
<td>1.348</td>
<td>0.970</td>
<td>2.837</td>
</tr>
<tr>
<td>Average</td>
<td>1.442</td>
<td>0.987</td>
<td>2.698</td>
</tr>
</tbody>
</table>

I.E. : Isotope Effect
φ : Atoms exchanged / molecule

reactants : perdeuterated cis-2-butene 50 torr
undeuterated cis-2-butene 50 torr
O₂ 50 torr

reaction temperature : 360°C

catalyst : Tan 15, 0.25 g
bond migration. Similar conclusions were reached by Gibson and Van Kleek.

MICROCATALYTIC PULSE EXPERIMENTS

Butene Pulse Experiments

A series of butene pulse experiments were conducted on several kinds of catalysts to evaluate the participation of lattice oxygen in the OXD reactions. When zinc ferrite was used, the formation of CO$_2$ was almost negligible (less than 0.1% of the butene reactant). Considerable butadiene was formed in the first pulse, but progressively lesser amounts were found as the surface oxygen was depleted in successive pulses. In contrast, the isomerization reaction rate remained almost constant which indicates that this reaction is not affected by the oxygen species on the catalyst. Figure 25 shows typical results of a butene pulse experiment.

The consumption of the surface oxygen was calculated from the formation of butadiene for which oxygen is required. The cumulative amount of oxygen consumed in each pulse is plotted in Figure 26, and the total amount of oxygen consumed at infinite pulses ($\Sigma_{\infty}$) was calculated using the conventional linear plot method (Figure 27) which is expressed by equation 20.

For zinc ferrite at 400°C, $\Sigma_{\infty}$ was $8.4 \times 10^{19}$ O/g-cat. which corresponds to 1.01 monolayer. Since the specific surface area of the catalyst was 8.31 m$^2$/g, if we assume each O-species occupies a surface area of 10Å$^2$, then 1 monolayer of O-species corresponds to $8.31 \times 10^{19}$ O-species. On the other hand, 1 monolayer represents only about 0.83% of the entire O-species in the
Figure 25. Composition of rxn. prod. mixture
(400°C, Tan 15 0.25g, c-2-B 0.151 mmole)
Figure 26. Surface Oxygen Consumption for Butadiene Production
(400°C, Tan15 0.25g)
Figure 27. Effect of Catalyst Amount on Butadiene Formation
(400°C, Tan 15 0.25g)
bulk. When another pulse experiment was carried out using half the amount of the same catalyst (0.125 g) to test for artifacts that might arise from transport effects, almost same result was obtained (Figure 27).

When the value of \( \Sigma_{\infty} \) calculated using 6 pulses and 12 pulses were compared (Figure 28), the difference was only about 10%; 12 gave a slightly higher value. Since it seemed that 6 pulses were sufficient to obtain reasonably accurate results, all subsequent pulse experiments were performed with only 6 pulses unless otherwise stated.

A butene pulse experiment was performed over a virgin zinc ferrite catalyst at 380°C. Afterwards, the catalyst was pretreated following the standard procedure. Another pulse experiment was repeated over the used and pretreated catalyst under the same conditions. The results from the two experiments are essentially the same as is shown in Figure 29.

Several more experiments were performed at various temperatures with different butene isomers. In each series the value of \( \Sigma_{\infty} \) was determined; the results are plotted in Figure 30. It is apparent that the total amount of available oxygen (\( \Sigma_{\infty} \)) increased as the temperature was elevated and reached a maximum at about 420°C. This increase was presumably due to the migration of lattice oxygen to the surface of the catalyst since the rate of oxygen migration would be expected to increase as the temperature was raised. The decrease at temperatures above 420°C may be due to the catalyst's becoming coked at the higher temperature.

In the temperature range 400 to 420°C, 1-butene showed about same reactivity as cis-2-butene, however, at lower temperatures 1-butene seemed to be slightly more reactive than cis-2-butene. Some experiments with trans-2-
Figure 28. Effect of Number of Pulses
(380°C, Tani15 0.25g)
Figure 29. Comparison of Fresh and Used Catalysts
(380°C, Tan 15 0.125g)
Figure 30. Temperature Dependency of $\Sigma_\infty$.
butene gave almost same results as cis-2-butene. It may be concluded that the surface oxygen species participate in the reaction to a much greater extent than do lattice oxygen species, the migration of lattice oxygen to the surface being a very slow process under these conditions. The total amount of reactive oxygen is in the range of 1 monolayer.

After six butene pulses had been passed over a catalyst, oxygen pulses were injected to examine the reoxidation of the catalyst. The oxygen of the first two or three pulses was almost completely consumed for the reoxidation of the catalyst (Figure 31); beyond the sixth pulse, no more oxygen was lost to the catalyst. Moreover, the total amount of consumed oxygen was very close to the amount of oxygen removed from the catalyst. From this observation, it was concluded that the catalyst surface oxidizes very quickly.

Butene Pulse over Iron Oxides

Similar butene pulse experiments were performed over iron oxide catalysts in the absence of gas phase O_2. The results obtained from these experiments were compared with those for Tan 15 catalyst (Table 10).

<table>
<thead>
<tr>
<th>Pulse Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tan 15</td>
<td>24.8/0.2*</td>
<td>15.2/0.1</td>
<td>11.3/0.0</td>
<td>9.1/0.0</td>
<td>7.5/0.0</td>
<td>5.9/0.0</td>
</tr>
<tr>
<td>α-Fe_2O_3</td>
<td>29.7/6.6</td>
<td>46.1/6.8</td>
<td>58.6/7.2</td>
<td>62.2/6.3</td>
<td>64.8/6.2</td>
<td>60.8/5.2</td>
</tr>
<tr>
<td>Fe_3O_4</td>
<td>118.0/1.6</td>
<td>23.6/0.2</td>
<td>15.2/0.1</td>
<td>12.5/0.0</td>
<td>11.5/0.0</td>
<td>10.9/0.0</td>
</tr>
</tbody>
</table>

* Production of butadiene / (1/4 CO_2), 10^{-7} mole
Figure 31. Reoxidation of Reduced Catalyst by Oxygen Pulses
(380°C, Tan 15 0.25g)
As was expected, iron oxides showed higher activity and lower selectivity compared with zinc ferrite. \( \alpha-\text{Fe}_2\text{O}_3 \) was the most active one. A large amount of butadiene was produced even after several monolayers of oxygen were removed from the catalyst (Figure 32). The total amount of removed oxygen in 6 pulses was equivalent to 4.5 monolayers. However, the selectivity (80-90%) was considerably lower than zinc ferrite whose selectivity was virtually 100% in absence of gas phase oxygen.

Although a similar result was observed over \( \text{Fe}_3\text{O}_4 \) (Figure 33), this material produced considerably more butadiene but much less \( \text{CO}_2 \) than was observed over \( \alpha-\text{Fe}_2\text{O}_3 \) in absence of gaseous oxygen. For the first pulse about 0.6% of the butene was completely oxidized; in subsequent pulses, \( \text{CO}_2 \) formation was almost negligible (less than 0.1%). It is apparent that \( \text{Fe}_3\text{O}_4 \) is much more selective than is \( \alpha-\text{Fe}_2\text{O}_3 \) for the OXD reaction. Since \( \text{Fe}_3\text{O}_4 \) exhibited both high activity and good selectivity, 10% \( \text{Fe}_3\text{O}_4 \) was added to zinc ferrite and the mixed catalyst was used for a butene pulse experiment. As is shown in Figure 34, the butadiene production was enhanced by about 60%. When the used mixed catalyst was pretreated by the standard procedure and used again, the activity increased remarkably while maintaining quite good selectivity.

\[ \text{C}^{18}\text{O}_2 \text{ Pulse Experiments} \]

A series of \( \text{C}^{18}\text{O}_2 \) pulse experiments were conducted in the microcatalytic system over 0.25g of Tan 15 catalyst. The labeled \( \text{CO}_2 \) molecules exchanged their oxygen atoms with the unlabeled surface atoms. Mass spectral analysis of the product \( \text{CO}_2 \) allowed one to calculate the number of oxygen atoms
Figure 32. Butene Pulse Experiment over $\alpha$-Fe$_2$O$_3$
($380^\circ$C, $\alpha$-Fe$_2$O$_3$ 0.125 g, c-2-B 0.151 mmole)
Figure 33. Butene Pulse Experiment over Fe$_3$O$_4$

(380°C, Fe$_3$O$_4$ 0.125g, c-2-B 0.151 mmole)
Figure 34. Effect of $\text{Fe}_3\text{O}_4$ Addition to Zinc Ferrite
exchanged (\(\Sigma_f\)) for each pulse and to determine the total number of exchangeable oxygen atoms by the linear plot method (\(1/\Sigma\) vs. 1/pulse number, equation 20). Figure 35 shows the results of the exchange experiments conducted at 320, 350 and 380°C. Detailed numerical results are presented in the Table 11.

Since the calculated \(\Sigma_{\infty}\) values were in the range only 1 to 2 monolayers, the mobility of lattice oxygen was determined to be very low. These \(\Sigma_{\infty}\) values are about two times larger than the values obtained from butene pulse experiments where the catalyst oxygen was chemically removed during the reduction process.

As discussed in the butene pulse section, the total amount of exchangeable oxygen (\(\Sigma_{\infty}\)) changed depending upon the reaction temperature. This was probably because the lattice oxygen mobility increases as the temperature is increased.

An equation which can explain the linear plot method was derived (Appendix) by modeling the exchange reaction with the following assumptions,

1. isotopic compositions of gas phase and catalyst surface are constant throughout the catalyst bed and a pulse (CSTR-like behavior),

2. all oxygen atoms on the catalyst surface are equally active.

In Figure 36, the experimental data are compared with the values calculated by the use of the derived equation 19. When the amount of exchanged oxygen in the first pulse is much smaller than the total amount of exchangeable oxygen, equation 19 can be linearized to give the equation 20 which explains the linear plot method (see p.34). Figure 37 demonstrates the effect of the non-linearity of the exact equation on the difference between the values calculated by the
Figure 35. Calculation of $\Sigma_\infty$ by Linear Plot Method
(Tan 15 0.25g)
### Table 11. C$^{18}$O$_2$ Exchange Experiment (350°C)

<table>
<thead>
<tr>
<th>Pulse #</th>
<th>C$^{16}$O$_2$</th>
<th>C$^{16}$O$^{18}$O</th>
<th>C$^{18}$O$_2$</th>
<th>O-exchanged/ CO$_2$ molecule</th>
<th>Cumulative O-exchanged</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.060</td>
<td>.222</td>
<td>.718</td>
<td>.342</td>
<td>.52 x 10$^{19}$</td>
</tr>
<tr>
<td>2</td>
<td>.028</td>
<td>.175</td>
<td>.797</td>
<td>.231</td>
<td>.86 x 10$^{19}$</td>
</tr>
<tr>
<td>3</td>
<td>.022</td>
<td>.143</td>
<td>.835</td>
<td>.187</td>
<td>1.15 x 10$^{19}$</td>
</tr>
<tr>
<td>4</td>
<td>.013</td>
<td>.124</td>
<td>.863</td>
<td>.150</td>
<td>1.37 x 10$^{19}$</td>
</tr>
<tr>
<td>5</td>
<td>.011</td>
<td>.109</td>
<td>.880</td>
<td>.131</td>
<td>1.57 x 10$^{19}$</td>
</tr>
<tr>
<td>6</td>
<td>.007</td>
<td>.097</td>
<td>.896</td>
<td>.111</td>
<td>1.75 x 10$^{19}$</td>
</tr>
</tbody>
</table>

(350°C, Tan 15 0.25g, C$^{18}$O$_2$ 0.151 mmole)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Sigma_{\infty}$ (O-exchangeable)</th>
<th>$\Sigma_{\infty}$ (Monolayers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>2.60 x 10$^{19}$</td>
<td>1.25</td>
</tr>
<tr>
<td>350</td>
<td>3.13 x 10$^{19}$</td>
<td>1.51</td>
</tr>
<tr>
<td>380</td>
<td>4.09 x 10$^{19}$</td>
<td>1.97</td>
</tr>
</tbody>
</table>
Figure 36. Comparison of Experimental Data and Calculated Values
Figure 37. Comparison of $\Sigma_\infty$ Values from Exact Eq. 19 and Linearized Eq. 20
two equations.

In Table 12, the values of $\Sigma_{\infty}$ calculated by the approximate linear plot method of equation 20 are compared with values determined by the original equation 19.

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Linearized eq. $\Sigma_{\infty}$ (eq. 20)</th>
<th>Original eq. $\Sigma_{\infty}$ (eq. 19)</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.465</td>
<td>1.585</td>
<td>Tan 15</td>
</tr>
<tr>
<td>2</td>
<td>1.859</td>
<td>1.238</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.507</td>
<td>1.018</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5.953</td>
<td>4.056</td>
<td>Fe$_3$O$_4$</td>
</tr>
</tbody>
</table>

(Unit, Monolayer)

The values are close, but the original equation gives about 1/3 lower values (higher intercept) than does the linearized equation.

A C$^{16}$O$_2$ pulse experiment was conducted over a catalyst whose oxygen had been exchanged by C$^{18}$O$_2$ pulses. The purpose of this experiment was to verify the fact that the mobility of oxygen is low by recovering the $^{18}$O with $^{16}$O. After six pulses 38.9% of exchanged oxygen ($^{18}$O) was recovered, and the calculated $\Sigma_{\infty}$ value indicates that about 60% of the labeled oxygen could have been recovered in an infinite number of pulses (Figure 38). About 5 hours were required to conduct both the labeling and recovering experiments. These results clearly indicate that the oxygens laid down on the surface (<2%) do not scramble to a significant extent with unlabeled oxygen from the bulk (>98%).
Figure 38. Oxygen Exchange and Recovery
Diffusion of oxygen into the bulk of the catalyst must be quite slow under these conditions.
IV. DISCUSSION

Activity of Catalyst

As a first step of the kinetic experiments, an initial reaction rate study was performed in a batch recirculation system to estimate activation energies and to determine the oxygen and butene dependencies of the OXD and deep oxidation reactions. When the initial reaction rate data were collected and analyzed, they were found to be inconsistent and dependent on the history of the catalyst. Since both OXD and deep oxidation reactions are exothermic, a large temperature excursion ("exotherm") was observed when a reaction was initiated at a high temperature (e.g. 400°C). Once a catalyst was exposed to such a large exotherm, its activity increased considerably.

A similar result was found by Massoth and Scarpiello. They reported that the initial reaction rate of butene over a fresh ZnCrFeO₄ catalyst was many times slower than over an aged catalyst. In some of the early patents it also was claimed that ferrite catalysts can be "activated" prior to the use by reducing them with butene or a butene rich butene/oxygen mixture at or above the reaction temperature (400-500°C). A couple of experiments showed that an activated catalyst gave 60% conversion and 80% selectivity while the same catalyst gave only 52% conversion and 72% selectivity without the activation procedure. To explore the cause of this enhancement in catalytic activity, two samples of catalyst were heated to a very high temperature (e.g. 800°C) under air and nitrogen environments, respectively. The resulting catalysts did not show any change in activity. Thus, a high temperature and reaction mixture environment are presumably required simultaneously for the enhancement of the
catalyst activity. Since no significant difference was observed between the surface areas of fresh and used catalysts, this enhancement does not seem to be related to the surface area of catalyst.

The activity change was further investigated by X-ray powder diffraction (XRD) and Mossbauer spectroscopy. As was described in the Results section (p. 46), the fresh catalyst had about 0.2 wt.% ZnO and 1.5 wt.% $\alpha$-Fe$_2$O$_3$ as minor components with the major component being zinc ferrite. A diffractogram of a used catalyst, which had been subjected to low temperatures only, did not show significant differences when compared with that of a fresh catalyst. However, an "exposed" catalyst showed no $\alpha$-Fe$_2$O$_3$ phase while the amount of ZnO increased to about 2.5 wt.%. At the same time, this sample was found to be magnetic by visually noting its response to movement of an external magnet. These observations suggested that the exposed catalyst may have $\gamma$-Fe$_2$O$_3$ or Fe$_3$O$_4$, which are magnetic and have a spinel structure. Unfortunately, these components cannot be detected by XRD when only a small amount exists in the presence of a large amount of zinc ferrite as the major component.

Aliev, et al.$^{76}$ investigated phase transformations that occurred when a sample of ZnO-Fe$_2$O$_3$ was exposed to a reaction medium. The $\alpha$-Fe$_2$O$_3$ phase was converted into Fe$_3$O$_4$, whereas the zinc ferrite did not undergo any change. Since the conversion of $\alpha$-Fe$_2$O$_3$ into Fe$_3$O$_4$ had practically no influence on the catalytic activity of the catalyst, it was presumed that the spinel phase was responsible for the activity of zinc ferrite catalyst.

Misono, et al.$^{56}$ studied the OXD of butenes over $\alpha$- and $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$. Under the reaction conditions, the structures of $\alpha$- and $\gamma$-Fe$_2$O$_3$ remained unchanged, while Fe$_3$O$_4$ was oxidized to $\gamma$-Fe$_2$O$_3$. $\gamma$-Fe$_2$O$_3$ originally present,
as well as $\gamma$-Fe$_2$O$_3$ formed from Fe$_3$O$_4$ under the catalytic conditions, was very active and selective for the reaction. They discovered from X-ray diffraction data that the fresh catalyst contained a minor amount of uncombined oxides in addition to the spinel structure. And, from magnetic susceptibility and Mössbauer studies, it was found that Fe$^{+3}$ and Cr$^{+3}$ cations present in the free-oxide phase are able to diffuse into the spinel lattice more readily in a hydrocarbon atmosphere than in air.$^{47}$

When a reaction is initiated at a high temperature and a large exotherm is observed, CO$_2$ is produced at a very high rate. Consequently, the amount of oxygen present in the reaction mixture decreases very rapidly while butene decreases at a much slower rate. Under such severe conditions of high temperature and highly reductive environment, zinc ferrite, which is quite stable under milder reaction conditions, may decompose into ZnO and Fe$_3$O$_4$. Then, Fe$_3$O$_4$ may reoxidize to $\gamma$-Fe$_2$O$_3$-$x$ ($0 \leq x \leq 1/3$) while the catalyst is pretreated prior to another reaction.

From these observations and thermodynamic data (see p.51, Table 4), it is proposed that an exposed catalyst has $\gamma$-Fe$_2$O$_3$-$x$ ($0 \leq x \leq 1/3$) as a minor component. It may be produced from Fe$_3$O$_4$ and the decomposition of zinc ferrite. According to electrical conductivity measurements by Gibson$^{49}$ and Van Kleeck$^4$, magnesium and manganese ferrites exist in almost fully oxidized states under reaction conditions. Thus, $x$ may be very close to zero.

It is generally admitted that Fe$^{+2}$/Fe$^{+3}$ interconversion is very important in the OXD of butene. Existence of a small amount of the $\gamma$-Fe$_2$O$_3$-$x$ phase may enhance the interconversion and thus improve the catalyst activity. It should also be noted that too much $\gamma$-Fe$_2$O$_3$-$x$ phase may enhance deep oxidation
rather than the OXD. Thus, it is recommended that the amount of $\gamma$-$\text{Fe}_2\text{O}_3$ in the catalyst be adjusted to produce the most effective catalyst.

**Activation Energy**

Activation energies for OXD and deep oxidation were estimated from initial reaction rates (Table 13).

<table>
<thead>
<tr>
<th></th>
<th>used catalyst</th>
<th>virgin catalyst</th>
<th>Sterrett$^{41}$</th>
<th>Van Kleeck$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$ (kcal/mole)</td>
<td>14.2</td>
<td>28.2</td>
<td>33.4</td>
<td>35.2</td>
</tr>
<tr>
<td>$E_2$ (kcal/mole)</td>
<td>15.3</td>
<td>30.7</td>
<td>20.8</td>
<td>37.5</td>
</tr>
</tbody>
</table>

Over a used catalyst, the activation energies of $E_1$ (OXD) and $E_2$ (deep oxidation) are 14.2 and 15.3 Kcal/mole which are considerably lower than values reported by Sterrett et al.$^{41}$ and Van Kleeck$^4$ for similar catalysts. Sterrett et al. obtained their data for ZnFeCrO$_4$. Furthermore, they used steam in their experiment along with the butene/oxygen reaction mixture. Van Kleeck's experimental results with a manganese ferrite are very similar to those of this study. The disagreement is presumably due to the existence of $\gamma$-$\text{Fe}_2\text{O}_3$ in the "exposed" catalyst for which the Fe$^{2+}$/Fe$^{3+}$ interconversion is relatively easier than in ferrite catalysts.

However, when only fresh catalyst samples were used for the experiment, the activation energy $E_1$ for OXD was found to be 28.2 kcal/mole, which is close to the values reported by the other researchers (Table 13). An Arrhenius plot of these experimental results is very similar to such a plot of Van Kleeck's data (Figure 39).
Figure 39. Comparison of Initial OXD Rate over Zinc and Manganese Ferrites
Meanwhile, $E_2$ for the deep oxidation reaction was 30.7 kcal/mole which is close to Van Kleck's value but quite different from Sterrett's value. This difference may be due to the different catalyst and/or the use of steam. Sterrett et al.\textsuperscript{51} claimed that the ZnCrFeO$_4$ was more selective than ZnFe$_2$O$_4$ and they used a large amount of steam in the reactant mixture. The presence of steam almost certainly affected the results of the kinetic experiments, but that effect was not investigated in this study.

**Rate Equations**

Most authors have reported that the OXD reaction is zeroth order for oxygen and near first order for butene. Both of these observations can be accounted for by the two site Langmuir-Hinshelwood model derived from the initial rate data. Moreover, this same model does a reasonably good job explaining the kinetics of both OXD and deep oxidation reactions. The butene dependency of butadiene and CO$_2$ formation reactions could be modeled by a $K_B P_B(1+K_B P_B)$ term very closely.

The oxygen dependency of CO$_2$ formation could be modeled equally well with either $\sqrt{K_{O2}P_{O2}/(1+\sqrt{K_{O2}P_{O2}})}$ or $K_{O2}P_{O2}/(1+K_{O2}P_{O2})$ by choosing suitable adsorption equilibrium constants. Since the dissociative adsorption is more reasonable, the expression $\sqrt{K_{O2}P_{O2}/(1+\sqrt{K_{O2}P_{O2}})}$ was adopted.

The oxygen dependency of butadiene formation has been reported to be zero order by several authors\textsuperscript{47,48,52} over ferrite catalysts. However, experimental results showed quite clearly that the oxygen dependency is not zero order since the rate drops significantly as the partial pressure of gas phase oxygen approaches zero (see Figure 16). It is noteworthy that the
dependency is almost zero order unless the amount of oxygen is much less than the stoichiometric ratio.

Actually, the oxygen dependency can be modeled best by using two terms, viz:

\[ r_{OXD} = k_1 + \frac{K_{O2}P_{O2}}{(1 + \sqrt{K_{O2}P_{O2}})} \]  \hspace{2cm} (37)

The constant \( k_1 \) reflects the contribution of catalyst lattice oxygen on or near the catalyst surface and the second term describes the contribution of the dissociatively adsorbed oxygen from gas phase. These equations imply that the catalyst lattice oxygen can contribute to the formation of butadiene but not to the formation of CO\(_2\).

Final rate equations were constructed based on a two site Langmuir-Hinshelwood model. One of the two sites is for dissociative adsorption of oxygen and the other is for the competitive adsorption of butene and butadiene.

The final equations fit the experimental data quite well, with suitable constants, except the formation of carbon dioxide in the initial 15 minutes at various reaction temperatures (see Figure 20). The experimental values were 10-20% higher than the predicted values. This may have been caused by CO\(_2\) formation being higher due to the unstable reaction temperature at the initiation of the reaction.

The rate expressions have a few weak points, as follow:

1. The temperature dependency of the adsorption equilibrium constants are neglected.

2. The rate expressions were compared with the experimental data obtained in low conversion range only.

3. The role of steam was not studied.
The temperature dependencies of the adsorption equilibrium constants were lumped into the other rate constants since it was impossible to isolate their contribution under the conditions employed in this research. In the temperature range studied, the rate expressions worked fairly well as semiempirical equations. The experiments were carried out at a low temperature and conversion range to avoid high exotherms and to maintain isothermal conditions. By using steam, data could have been collected at higher conversions and the role of steam examined, but such experiments were not attempted in this study because the reaction system was built with Pyrex glass and greased stopcocks that could not be heated.

The change of catalyst activity with time on stream was difficult to monitor since the system was not a flow reactor. By performing several consecutive reactions over the same catalyst without any treatment of the catalyst between the two runs, the change of the catalyst was examined (see Table 7, p. 70). It was clear that there was no drastic change in the catalyst activity.

**Mechanism**

The mechanism proposed by Massoth and Scarpiello for OXD on ferrite catalysts was shown earlier in the "Introduction" part (Figure 2, p.16). Such a mechanism can also explain our data. Butene adsorbs on an anion vacancy and oxygen on another anion vacancy in the form of a radical ion, $O^-$. Hydrogen abstraction occurs in two steps. The first is homolytic and produces a $\text{C}_4\text{H}_7$ allyl fragment $\pi$-bonded to the $\text{Fe}^{\text{III}}$ ion and an $\text{OH}^-$ group from $O^-$ and
the H atom. The second is heterolytic, H⁺ attaching to the lattice O⁻² and leaving a C₄H₆⁻-Fe⁺³ complex. This complex dissociates with reduction of the Fe⁺³ to Fe⁺² and desorption of butadiene. The hydroxyl groups combine to give water and regenerate the lattice O⁻² and the bare active center, Fe⁺² associated with two anion vacancies. Reoxidation of Fe⁺² to Fe⁺³ occurs when gas phase oxygen is adsorbed as O⁻, completing the cycle. This mechanism is consistent with the proposed kinetic expressions since it suggests two adsorption sites. One is for competitive adsorption of butene and butadiene. The other is for dissociative adsorption of oxygen.

The results of the deuterium labeled butene experiments provide some additional information about this mechanism. The isotope effects for both OXD (2.7) and isomerization by double bond shift (cis-2-butene to 1-butene, 1.4) clearly indicate that both of these reactions involve hydrogen abstraction in rate-limiting steps. Since the effect is substantial especially for the OXD reaction, it is possible that both of the hydrogen abstractions may be slow steps. The lack of significant H/D scrambling in the butadiene and butene isomers suggests that when butene molecules adsorb on active sites, they remain associated with the site throughout the reaction. Surface migration of the allylic intermediate must be slow compared with the rate of reaction. The lower selectivity observed with deuterated butene implies that the deep oxidation may be affected less by the isotope effect.

**Participation of Lattice Oxygen in the Reaction**

Lattice oxygen from the bulk of bismuth molybdate catalysts has been reported to participate in the OXD of butene.²⁸,²⁹ On the other hand, it is
generally regarded that only surface oxygen participates in the reaction over ferrite catalysts.\textsuperscript{48,52} Butene or $\text{C}^{18}\text{O}_2$ pulse experiments in a microcatalytic reactor system provide some answers for dilemma.

From the results of both butene and $\text{C}^{18}\text{O}_2$ pulse experiments, it is clear that only surface oxygen participate in the reaction and that migration of oxygen atoms from the bulk of the catalyst to the surface is very slow.

Another butene OXD experiment without gas phase oxygen in the batch recirculation system provided the same conclusion. However, some migration of oxygen was observed at high temperature (e.g. over 400\textdegree C).

$\text{C}^{18}\text{O}_2$ pulse experiments, with the recovery of the exchanged oxygen, also support this conclusion. However, the oxygen migration rate appears to be faster than in the butene pulse experiments. This is probably due to the difference in nature between oxygen removal (butene OXD) and exchange ($\text{C}^{18}\text{O}_2$) reactions, since the oxygen removal creates some vacancies in the crystalline structure while the exchange reaction leaves the structure of the catalyst chemically unaltered.

Most pulse experiments involved six pulses only. The $\Sigma_{\infty}$ (total reactive or exchangeable oxygen) values were calculated by the linear plot method. The method had been justified by a mathematical manipulation with an equilibrium assumption. This assumes that an equilibrium of isotopic composition can be easily reached between the catalyst surface and CO$_2$ in the gas phase. Since the derivation includes some unrealistic assumptions of equilibrium exchange and very small pulse size, another equation was derived without these assumptions. The linear plot method could be justified with the latter equation, since both give nearly the same results. Thus, the method is relatively accurate for the estimation of $\Sigma_{\infty}$. 
Reoxidation of the reduced catalyst surface is very fast. This observation is in good agreement with the observation from the electrical conductivity experiments.\textsuperscript{48,50} Results from both experiments indicated that the surface of the catalyst remains almost fully oxidized during all these reactions in the presence of gaseous oxygen.
V. SUMMARY

A pair of rate equations have been developed for both butadiene and carbon dioxide formation over a zinc ferrite catalyst based on a two site Langmuir-Hinshelwood model. These rate equations fit the experimental data quite well and explain the zero order dependency of butadiene formation with respect to oxygen unless the amount of oxygen is much less than the stoichiometric ratio.

Butadiene is formed without gas phase oxygen by reaction with catalyst lattice oxygen while CO₂ formation is negligible. Only surface oxygen participates in the reaction, and the migration of bulk oxygen to the surface is very slow. The reduced surface can be rapidly reoxidized by gas phase oxygen. The rate equations are consistent with a mechanism in which butene and oxygen are adsorbed onto the two independent sites on the surface of the catalyst. Oxidation of the hydrocarbon then proceeds through an Fe⁺³ ↔ Fe⁺² redox cycle on the surface; reoxidation of the reduced Fe⁺² is by gas-phase oxygen. Butene is dehydrogenated after adsorption and both the butene fragment and the removed hydrogen are immobile at reaction temperature. The isotope effect indicates that hydrogen abstraction is involved in rate-limiting steps of both the OXD and double-bond migration reactions.

The phase composition of the catalyst changes with the reaction. This could cause the enhancement in the catalytic activity presumably due to the formation of a γ-Fe₂O₃₋ₓ (0 ≤ x ≤ 1/3) phase at high temperatures under the reductive environment.
APPENDIX

Oxygen Exchange Between C^{18}O_2 and Catalyst Surface

Exchange of O atoms from a CO_2 molecule with those on the catalyst surface can be modeled by the reactions

\[
\begin{align*}
\text{Gas phase} & \quad \text{Surface} \\
1) & \quad ^{18}\text{O} \leftrightarrow ^{16}\text{O} \\
2) & \quad ^{16}\text{O} \leftrightarrow ^{18}\text{O} \\
3) & \quad ^{16}\text{O} \leftrightarrow ^{16}\text{O} \\
4) & \quad ^{18}\text{O} \leftrightarrow ^{18}\text{O}
\end{align*}
\]

The following terms are used in this derivation:

\[
\begin{align*}
R & = \text{total exchange reaction rates} \\
f & = \text{fraction of } ^{18}\text{O on catalyst surface} \\
\theta & = \text{fraction of } ^{18}\text{O in gas phase} \\
n & = \text{no. of CO}_2 \text{ molecules per pulse} \\
\Sigma_{\infty} & = \text{total exchangeable oxygen on the catalyst surface (atoms)} \\
\Sigma_j & = \text{amount of exchanged oxygen after } j\text{th pulse (atoms)}
\end{align*}
\]

The rates of oxygen exchange for the CO_2 molecules may be expressed as

\[
\begin{align*}
r_1 & = R\theta(1-f) \quad (A-1) \\
r_2 & = R(1-\theta)f. \quad (A-2)
\end{align*}
\]

1) Equilibrium exchange

Assuming the exchange is isothermal and reaches equilibrium in each pulse,
the rates of reactions 1 and 2 must be equal, since the reactions 3 and 4 yield
no net change. This can be expressed by

$$r_1 = r_2$$  \hspace{1cm} (A-3)

or

$$R\theta(1-f) = R(1-\theta)f$$  \hspace{1cm} (A-4)

which leads to

$$\theta = f.$$  \hspace{1cm} (A-5)

Since the amount of oxygen injected into the system is $2n$ for each new pulse,
a material balance around the system gives

$$\Sigma_{j-1} + 2n = \Sigma_j + 2n\theta_j$$  \hspace{1cm} (A-6)

where $j$ is the pulse number. If the oxygen species are equally active for the
exchange reaction, the fraction of $^{18}$O on the catalyst surface after the $j$th
pulse ($f$) can be expressed by

$$f_j = \Sigma_j/\Sigma_{\infty}.$$  \hspace{1cm} (A-7)

Combining equations 5 through 7 gives

$$(1 + a) f_j - f_{j-1} - \alpha = 0$$  \hspace{1cm} (A-8)

where

$$\alpha = 2n/\Sigma_{\infty}.$$  

With some mathematical manipulations, this becomes

$$f_j - 1 = \{1/(1 + a\})\{f_{j-1} - 1\}$$  \hspace{1cm} (A-9)

$$= \{1/(1 + a\})^j (f_0 - 1)$$  \hspace{1cm} (A-10)

If there were no $^{18}$O on the catalyst surface initially, or if $f_0 = 0$, then

$$f_j = 1 - 1/(1 + a\})^j.$$  \hspace{1cm} (A-11)

The term $(1 + a\})^j$ can be expanded into a Taylor series, and when $a << 1,$
neglecting all terms above 1st order, (A-11) may be rewritten as
\[ \frac{1}{\Sigma_j} = \frac{1}{\Sigma_\infty} - \left\{ \frac{1}{\Sigma_\infty a} \right\} (1/j). \]  \hfill (A-12)

Thus, \( \Sigma_\infty \) can be calculated from a linear plot of \( 1/\Sigma_j \) vs. \( 1/j \).

2) Non-equilibrium exchange

When the exchange reaction is not fast enough to reach equilibrium, the rates of reactions 1 and 2 are not equal. In such a case, the net exchange rate can be expressed by

\[ r = r_1 - r_2. \] \hfill (A-13)

Combining equations 1, 2, and 13 gives

\[ r = R (\theta - f) \] \hfill (A-14)

which from the \( ^{18}O \) material balance yields

\[ \Sigma_j = \Sigma_{j-1} + R \int (\theta - f) \, dt \bigg|_j. \] \hfill (A-15)

If we assume that \( \theta \) and \( f \) are constant throughout the reactor (CSTR assumption) and that for the \( j^{th} \) pulse both \( \theta_j \) and \( f_j \) attain values which are the average between the inlet and outlet values, they then become

\[ \theta_j = \frac{1}{2} (1 + \theta_j) \] \hfill (A-16)

and

\[ f_j = \frac{1}{2} (f_{j-1} + f_j). \] \hfill (A-17)

Combining equations 15 through 17 gives the equation

\[ f_j - f_{j-1} = a (1 + \theta_j) - a (f_j + f_{j-1}) \] \hfill (A-18)

where, \( a = R \tau/(2 \Sigma_\infty) \) and \( \tau \) is the residence time for each pulse.

From equations 6 and 18 we have

\[ (a + \beta + a\beta) f_j = (a + \beta - a\beta) f_{j-1} + 2a\beta \] \hfill (A-19)

where, \( \beta = 2n/\Sigma_\infty \).

Rearranging equation 19 gives
(\alpha + \beta + a\beta) (f_j - 1) = (\alpha + \beta - a\beta) (f_{j-1} - 1). \quad (A-20)

Thus,

f_j = \{(\alpha + \beta - a\beta)/(\alpha + \beta + a\beta)\}^j (f_o - 1) + 1. \quad (A-21)

When \( f_o = 0 \),

\[ f_1 = \frac{2a\beta}{(\alpha + \beta + a\beta)} \quad (A-22) \]

and

\[ f_j = 1 - (1 - f_1)^j. \quad (A-23) \]

Finally,

\[ \Sigma_j = \Sigma_\infty \{ 1 - (1 - f_1)^j \}. \quad (A-24) \]

As before, this equation can be linearized by Taylor series expansion to become

\[ 1/\Sigma_j = 1/\Sigma_\infty + (1/\Sigma_1) (1/j). \quad (A-25) \]

Thus, a linear plot of 1/\( \Sigma_j \) and 1/j will give

Intercept = 1/\( \Sigma_\infty \) \quad (A-26)

Slope = 1/\( \Sigma_1 \). \quad (A-27)
REFERENCES


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