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OXIDATIVE DEHYDROGENATION OF N-BUTANE OVER MIXED METAL OXIDE CATALYSTS

Rice University

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OXIDATIVE DEHYDROGENATION OF N-BUTANE
OVER MIXED METAL OXIDE CATALYSTS

by

DONALD H. CHICKERING II

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

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

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HOUSTON, TEXAS
DECEMBER, 1980
Abstract

OXIDATIVE DEHYDROGENATION OF N-BUTANE
OVER MIXED METAL OXIDE CATALYSTS

by

DONALD H. CHICKERING II

The mechanism of catalytic oxidative dehydrogenation of n-butane to n-butenes and butadiene over Ni-Sn and Mn-Li oxide catalysts has been investigated. The techniques used include kinetic modeling, stable isotopic tracers, temperature programmed desorption, x-ray diffraction, electrical conductivity, and alternate reduction-oxidation tests.

The more selective catalyst for making the dehydrogenated products was Ni-Sn, an amorphous oxide mixture containing 47% Ni, 10% Sn, 6% P, 1% K, 4% S and 32% oxygen by weight. Its BET surface area is 49 m²/g. This catalyst gave only the products n-butenes, 1,3-butadiene, water and CO₂ at temperatures up to 520°C. Over this catalyst n-butane is first converted to 1-butene which isomerizes to 2-butenes. These n-butenes may either be burned to CO₂ or be oxidatively reduced to 1,3-butadiene which may further react to CO₂.

Kinetic modeling of this reaction developed a Mars-Van Krevelen type reaction expression for both the oxidative dehydrogenation of 1-butene and deep oxidation of 1-butene and 1,3-butadiene. This model incorporates a Langmuir expression in the rate of dehydrogenation for the competitive adsorption of hydrocarbons. Parity plots indicated that agreement between predicted and measured behavior for the deep oxidation reactions and oxidative dehydrogenation of 1-butene was quite acceptable. However, the five parameter rate expressions did not predict the reaction of
n-butane with reasonable accuracy because isomerization to the 2-butenes was not included. Additional information on the rate of isomerization of the n-butenes and the rate of reaction of the 2-butenes would enable this model to be expanded to provide reasonable predictions. The activation energies for deep oxidation of 1,3-butadiene and 1-butene are 23 and 30 kcal/mole. Both the oxidative dehydrogenation of 1-butene and the reoxidation of the catalyst, by gas phase oxygen, exhibit activation energies of 45 kcal/mole.

$^{18}$O tracer studies determined that the oxygen on the Ni-Sn catalyst is easily exchanged by CO$_2$ and that the mobile oxygen amounts to 1.9 monolayers at 380°C and 3.5 monolayers at 452°C.

A redox cycle is proposed as the mechanism of oxidative dehydrogenation of n-butane over the Ni-Sn catalyst. This involves using lattice oxygen to abstract the hydrogen atoms from the hydrocarbon to form the olefin or diolefin. The metal cation is reduced during the reaction of the hydrocarbon then is reoxidized by gas phase oxygen. This mechanism accounts for a C$_4$H$_9$ species observed in the TPD experiments and is also consistent with the hydrogen-deuterium scrambling noted in the butene and butadiene products. The inhibition of the reaction rate by water is explained in this mechanism by adsorption–desorption equilibrium of water which limits the available oxygen sites.

Since the Mn-Li catalyst (7/1 molar Mn/Li ratio; 2.5 m$^2$/g) is far less selective (its major products are CO$_2$ and water) than the Ni-Sn catalyst, this material was not studied extensively. The observed product distribution was sensitive to the reactor design with a shallow broad reactor giving a peculiar selectivity hysteresis that could not be explained.
To Kim
Acknowledgements

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I. Introduction

Oxidative dehydrogenation (OXD) is a process in which hydrogen is removed from a hydrocarbon to produce an olefin or diolefin. This process differs from direct dehydrogenation by an oxidant being contained in the reactant feed. Formation of more stable compounds (e.g. H₂O) from the abstracted hydrogen shifts the equilibrium such that complete conversion is theoretically possible. The formation of these compounds also leads to an overall exothermic reaction, whereas the direct dehydrogenation is endothermic.

Several OXD reactions have been studied, with the formation of butadiene from n-butenes being the most extensively researched. Generally, mono-olefins have been found to be the most reactive in this system, although certain paraffinic hydrocarbons will also react favorably. Butane falls into the latter group and is the
subject of this study.

**General Background**

Dehydrogenation of hydrocarbons is an important reaction to the petro-chemical industry. One such dehydrogenation produces 1,3-butadiene from either butane or butene. Butadiene is an essential chemical feedstock for the production of styrene-butadiene-rubber (SBR), polybutadiene and other synthetic rubbers. SBR and polybutadiene are used in manufacturing automobile tires. The styrene needed for this and other polymers is also produced by the dehydrogenation of ethylbenzene.

**Catalytic Dehydrogenation**

At the beginning of World War II, catalytic dehydrogenation of butane and butenes was commercially implemented for the production of synthetic rubber after supplies of natural rubber were cut off.¹ Several commercial processes were developed for dehydrogenating butane and butenes. Most of the processes designed to produce butenes from butane were operated at about 600°C and near atmospheric pressure.² Catalysts used were generally a chromia-alumina preparation which were sometimes promoted by a potassium containing compound. These catalysts are not stable in the presence of steam. Operation of these processes is cyclic with the reactor being on stream for about one hour followed by regeneration with flue gas containing small
amounts of oxygen to burn off the coke deposits. This cyclic operation precipitated the use of multiple reactors to permit continuous operation. Cyclic operation was circumvented in one process by using a moving bed reactor to exchange fresh for spent catalyst. Conversions per pass for n-butane dehydrogenation are in the neighborhood of 25-40%, which, with large recycle flow, will yield about 80% butenes.

Butenes from the above process or other sources can be converted to butadiene by dehydrogenation at 600 to 700°C. This can be accomplished over a chromia-alumina catalyst, as with the n-butane processes, or over an iron oxide-chromia catalyst. The Houdry Catadiene process utilizes a chromia-alumina catalyst to produce mono or diolefins from n-butane, or butadiene from butenes. The Phillips process involves a promoted iron oxide catalyst to produce butadiene from butenes. The iron oxide catalyst normally used is known as Shell 105 and consists of about 90% Fe₂O₃ - 4% Cr₂O₃ - 6% K₂CO₃. Steam in a mole ratio steam:butenes of about 10:1 is used as a diluent in this process both to lower the partial pressure of hydrocarbon and to supply heat to the endothermic reaction. A calcium nickel phosphate catalyst is also active for this reaction. A good review of catalysts, thermodynamics and processes of catalytic dehydrogenation is provided by Kearby. Kinetics and possible reaction mechanisms, over
a chromia-alumina catalyst used for these reactions, are discussed by Carra and Forni. 3

All of the catalytic dehydrogenation reactions are endothermic (ΔH is about +32 kcal/mole) and equilibrium limited. This results in the need for a large amount of recycle flow with low per pass conversions. To accomplish this, large separators must be operated at the reactor exit to strip the small fraction of product from the stream. The recycle must also be reheated before it enters the reactor. These complications have spurred research to produce a more efficient process. One of the more interesting approaches to this problem is oxidative dehydrogenation.

**Oxidative Dehydrogenation**

Oxidative dehydrogenation is a process in which hydrocarbons are dehydrogenated in the presence of an oxidizing agent. This oxidizing agent reacts with the abstracted hydrogen to form a more stable compound. This reaction can be written as:

\[ C_4H_{10} + O_2 + C_4H_6 + 2H_2O \]

for the oxidative dehydrogenation of n-butane. Oxygen is by far the most common oxidizing agent, although it is not the only oxidant available for this reaction. The effects of adding an oxidant to the reactant stream are dramatic. The reaction becomes exothermic, having a ΔH of
about -58 kcal/mole for the production of butadiene from 
n-butane. In contrast to the direct process, equilibrium 
considerations do not limit the conversion of this reaction. 
This dramatic shift in equilibrium is a great incentive for 
commercial application since it would eliminate the need 
for costly recycle streams. Higher product concentrations 
and lower total flow rate through the reactor also decrease 
the work load on the product separation train. The exo-
thermic nature of this reaction produces benefits from 
decreased energy requirements. Most OXD processes are run 
in the temperature range of 400-500°C which, coincidentally, 
is much lower than the 600-700°C range of their direct 
counterparts. However, by-product value is usually less 
for OXD reactions.

**Butene OXD**

The most extensively investigated OXD reaction is 
that of n-butenes.

\[ \text{C}_4\text{H}_8 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} \]

This reaction proceeds readily over a variety of catalysts. 
However, when an oxidant is added to hydrocarbon reactant 
streams, reactions producing the carbon oxides also occur.

\[ \text{C}_4\text{H}_8 + 6\text{O}_2 \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O} \]

\[ \text{C}_4\text{H}_8 + 4\text{O}_2 \rightarrow 4\text{CO} + 4\text{H}_2\text{O} \]
To combat these reactions, a very selective catalyst is needed.

The catalysts used in oxidative dehydrogenation are generally unsupported metal oxides containing two or more metals. One of these is usually a transition metal. Catalysts for butene OXD can be divided into three general classifications: molybdates, phosphates and spinels. This latter group contains the ferrites, cobalites, and chromites. The Phillips Petroleum Company did most of the pioneering research and development of the phosphate catalysts while the Petro-Tex Chemical Company investigated the ferrites. A brief review of the patent literature is shown in Table 1. Skarchenko\textsuperscript{4} and Huknall\textsuperscript{5} discuss the performance of potential and commercial catalysts.

Molybdate catalysts have been exhaustively studied. The most prevalent of these catalysts is the bismuth molybdate formulation. Reaction kinetics for the oxidative dehydrogenation of 1-butene have been described by a Langmuir-Hinshelwood type expression\textsuperscript{6} with zero order dependence on oxygen and no poisoning from the diene or CO\textsubscript{2} products. Batist et al.\textsuperscript{7} proposed a mechanism which involves an oxidation-reduction cycle of the molybdenum from the +4 to the +6 valence states. Lattice oxygen participates in the dehydrogenation step of this mechanism. A variety of molybdenum catalysts have been assessed, which include cobalt-boron molybdate,\textsuperscript{8} zinc molybdate,\textsuperscript{9} and titanium molybdate.\textsuperscript{10}
<table>
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<td>Bi-Mo-O</td>
<td>2,991,320(US)</td>
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<td>Hearne &amp; Furman</td>
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<td>Co-B-Mo-O</td>
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<td>3 June 75</td>
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<td>Sn-P-O</td>
<td>3,501,548(US)</td>
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Phosphate catalysts used in this reaction seem to have good commercial applications, although little has been published outside of patent literature about their performance in kinetic or mechanistic studies. Most of the catalysts in this family contain nickel or tin, although other metal oxides such as lithium, bismuth, and iron have been used. Happel et al.\textsuperscript{11} suggest that these catalysts are comprised of amorphous solid solutions of the metal oxides.

The third class of catalysts used for this reaction includes the spinels. These catalysts have a very well defined crystal structure and, unlike the phosphates, have been studied extensively by several research groups. Detailed information on the character and kinetics of the oxidative dehydrogenation of butenes over magnesium-chromium-ferrite and zinc-chromium-ferrite have been published by Rennard and Kehl\textsuperscript{12} and Massoth and Scarpiello.\textsuperscript{13} These latter workers proposed a mechanism for this reaction over the ferrites that is very similar to that proposed by Batist et al.\textsuperscript{7} The primary difference is that an adsorbed O\textsuperscript{−} species is responsible for abstracting the first hydrogen thereby allowing the metal atom to be reduced by only one valence state before being reoxidized. In the case of iron, the metal ion changes from Fe\textsuperscript{3+} to Fe\textsuperscript{2+} during reaction with the hydrocarbon. Investigations by Cares and Hightower\textsuperscript{14} have indicated that carbon-hydrogen
bond cleavage is involved in the rate determining step over copper and cobalt ferrites. Several other ferrite systems, including magnesium$^{15}$ and manganese$^{16,17}$ ferrites, have also been investigated.

Petro-Tex and Phillips have developed commercial processes for this reaction using patented ferrite and phosphate catalysts, respectively. These processes were at one time quite profitable; however, the economics are very sensitive to fluctuating energy and product costs. This is especially true of hydrogen costs since the by-product of this reaction is valueless water and not useful hydrogen as for direct dehydrogenation. OXD reactions may become less economical in the future as hydrogen demand increases due to its use in upgrading lower quality crudes. Hydrogen demand will also increase if large scale coal liquefaction plants are built.

**Styrene**

Styrene (vinylbenzene) is the most important member of the unsaturated alkyl aromatic monomers. It is used almost exclusively in the manufacturing of plastics such as polystyrene, styrene-butadiene rubber (SBR), acrylonitrile-butadiene-styrene terpolymer (ABS) and styrene-acrylonitrile copolymer (SAN). Styrene is relatively easy to handle and polymerizes rapidly due to the aromatic ring activating the vinyl group. Production of styrene in the U.S. began in the 1930's and by 1970 approximately 5 billion lb/yr
was produced.\textsuperscript{18} All of the currently produced styrene is formed from the catalytic dehydrogenation of ethylbenzene generally over potassium doped ferric and/or chromic oxides at 580-660°C.

Oxidative dehydrogenation of ethylbenzene to styrene has been investigated because of the possible increase in theoretical yield and decrease in reaction temperatures. Although several catalysts have been investigated for this reaction,\textsuperscript{19,20,21,22,23,24} the best yields obtained are not significantly different from the current catalytic dehydrogenations. Despite the probable decrease in energy costs of the oxidative dehydrogenation reaction, the overall economics may be less favorable. This is caused by a shift in by-products from benzene, toluene, and hydrogen, to the less valuable oxides of carbon.

Catalysts for the oxidative dehydrogenation of ethylbenzene

\[
\text{\textcircled{C}}-\text{CH}_2-\text{CH}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{\textcircled{C}}-\text{CH}=\text{CH}_2 + \text{H}_2\text{O}
\]

are typified by bismuth and cobalt oxides with molybdenum.\textsuperscript{19} Metal oxides such as vanadium and antimony, tungsten with nickel, cobalt or manganese, and chromium and niobium have shown similar results.\textsuperscript{19} Joseph and co-workers\textsuperscript{20} found that high selectivity to styrene (>95%) is possible on cobalt molybdate catalysts although the conversions, and subsequently the yields, are less than 40%. Selectivity
and conversion depend strongly on the oxygen : ethylbenzene (O₂ : EB) ratio. The isothermal conversion of ethylbenzene increases slowly up to a O₂:EB ratio of about 0.3 after which there is a significant increase which levels out at about 50% conversion at 0.6 - 0.8 O₂:EB ratio. Conversely, the styrene selectivity, which starts greater than 98%, drops significantly for O₂:EB ratios greater than 0.3 and is below 85% at a ratio of 0.8. This is indicative of styrene degradation with increasing oxygen in the system. Cobalt oxide (although seemingly necessary for an active and selective catalyst) is thought to be responsible for the cracking reactions in the cobalt molybdate catalysts.

Although the reaction mechanism of ethylbenzene oxidative dehydrogenation is not well understood, it is thought to proceed through a slow step involving initial hydrogen atom abstraction. It then progresses through a rapid secondary hydrogen atom abstraction to form the olefin. The kinetics of this reaction based on initial rate data follows a Langmuir type law, in which undissociated O₂ and ethylbenzene adsorb on different sites. The rate of reaction is given by

\[ r = k \frac{aP_E}{1 + aP_E} \times \frac{bP_O}{1 + bP_O} \]

where \( k = 4.3 \times 10^{-3} \) mole hr⁻¹ g⁻¹, \( a = 1.8 \) atm⁻¹ and \( b = 39 \) atm⁻¹. \( P_O \) and \( P_E \) are the partial pressures of
oxygen and ethylbenzene, respectively. However, this rate equation fits integral reactor data over a nickel tungsten oxide catalyst up to a conversion of only about 20%. Products at this conversion are inhibiting the reaction most likely through competitive adsorption. The activation energy obtained over a temperature range of 420 to 510°C was 10.0 kcal/mole. This low activation energy was reportedly not the result of a diffusion limited reaction but rather the lowering of the true activation energy by the heat of adsorption of ethylbenzene.

Patent literature reveals a multitude of catalysts claimed to be useful in oxidative dehydrogenation of ethylbenzene to styrene. The Dow Chemical Company has several patents alluding to the use of metal phosphates and metal pyrophosphates in the formation of styrene. Of these catalysts, magnesium pyrophosphate with a surface area of 35 m²/g proved to be the most efficient. At a temperature of 527-532°C and a feed composition of 6:1:1 helium, oxygen, and ethylbenzene, respectively, the yield of styrene was about 65% at a selectivity of 92%. The only by-products of this reaction were CO and CO₂ in a ratio of about 2:3.

Several patents have noted the possible use of alternate feedstocks in the formation of styrene. Palladium oxy-hydrate (sometimes called palladium hydroxide) supported on almost any standard support (e.g. asbestos or silica-
alumina) has been used to oxidatively dehydrogenate 4-vinylcyclohexene to styrene.\textsuperscript{25} The catalyst is prepared by adding an alkali to a solution of water soluble palladium salt in water. The catalyst is placed on a suitable support and dried. With approximately a 1:1 = 4-vinylcyclohexene:oxygen ratio, the reaction proceeds at 160\textdegree C to a conversion of 86.8\% with a liquid hourly space velocity of 0.4 hr\textsuperscript{-1}. Styrene selectivity is reportedly 91.7\% by weight per pass. This yield may be high enough for the reaction to warrant considerable attention due to the probable large decrease in energy requirement with respect to the standard catalytic dehydrogenation of ethylbenzene. The lower energy requirements would be the direct result of a much lower reaction temperature (>200\textdegree C vs. ~600\textdegree C) and the exothermicity of the oxidative dehydrogenation reaction. The availability of the 4-vinylcyclohexene feed would probably be the limiting factor in the commercial feasibility of this process.

A two step process using toluene as the reactant has been claimed by Montgomery.\textsuperscript{26} The reaction of toluene in the presence of lead oxide and oxygen produced stilbene as an intermediate (stilbene is also a valuable product). Selectivities are relatively high for the aromatics (~70\% for stilbene and 23\% for benzene) with only 3.4\% selectivity to CO\textsubscript{2} at 595\textdegree C. The stilbene is then disproportionated using ethylene over a suitable catalyst such as 20\% WO\textsubscript{3}. 
and 0.75% K₂O on silica gel to yield styrene at temperatures around 500°C. This last catalyst produced a styrene selectivity of 99.1% at 73.8% conversion. The inlet mole ratio of trans-stilbene and ethylene is 1:5 and the contact time is 1.24 seconds. Improvements in yield of stilbene in the first step of the process would make it a viable alternative to using the more expensive benzene feedstock now being used.

Demand for styrene plastics is increasing at a rapid rate. With improvements, oxidative dehydrogenation reactions with both traditional and alternate feedstocks could help supply some of the future styrene.

Butane OXD

Oxidative dehydrogenation of paraffins is much more difficult that of butenes or styrene. OXD of paraffins is generally a process with low or moderate selectivity, because of an affinity for oxygen incorporation and deep oxidation. Butane OXD is no exception. This reaction is of interest because it can be used to form 1,3-butadiene from a non-petroleum source.

Stepanov et al.²⁷ investigated the oxidative dehydrogenation of n-butane over several metal oxides. These workers found that the most active metal oxides

\[ \text{Co} > \text{Mn} > \text{Cr} > \text{Cu} \]

were not the most selective. The order of selectivity was
found to be

Ni > Mo > Mg > Co.

This shows that the oxygen bond energy of the catalyst determines the activity of the deep oxidation reactions, with the lowest bond energy being the most active. NiO was determined to be considerably higher in selectivity than any other single oxide.

Several oxide mixtures containing nickel have been investigated. Mixtures of NiO and MoO$_3$ are more selective than either single oxide.$^{28,29}$ A 50% mixture of both oxides yields a three to four fold increase in selectivity over NiO. Phillips Petroleum$^{30}$ has developed a selective paraffin oxidative dehydrogenation catalyst using a mixture of nickel and phosphorous oxides. These catalysts contain 0.1 to 16.8 weight percent phosphorous and from 40 to 75 weight percent nickel. Often an alkali or alkaline earth metal is used to modify the catalyst. Reactions over these catalysts are generally carried out above 500°C.

An unusual system for catalyzing the oxidative dehydrogenation of n-butane has been described by Tomezsko$^{31}$ in which a soluble transition metal oxyanion in a metal hydroxide melt and alumina is used. This reaction was found to proceed best at 425-500°C in an up-flow reactor. Although no data were given for the butane reaction, propane selectivity was said to be 79.8% at a conversion of 20.9%
over sodium hydroxide melt with 0.1 weight percent sodium vanadate. The addition of the sodium vanadate doubled the conversion while the selectivity remained almost constant.

A modified vanadium oxide catalyst, supported on silica, is active for OXD of n-butane.32 Modifiers consist of alkali metals and sulfur compounds. Typically a catalyst may have a composition of 9% V₂O₅, 29% K₂SO₄, 12% SO₃, and 50% SiO₂ by weight, with a surface area of 40 m²/g. The reaction takes place between 450 to 650°C with an optimum butane to oxygen ratio of 1:1. Selectivities to butenes and butadiene range from 60 to 90% at conversions up to 25%. These catalysts are very active and will operate at gas hourly space velocities of 20,000 hr⁻¹.

Alternate Oxidants

Several investigators have looked into the possibility of substituting or augmenting the oxygen reactant with alternate oxidants. Skarchenko33 reviews many reactions using halogens in place of, or in addition to, oxygen in the quest of improved selectivities. These reactions reportedly proceed via an alkyl radical mechanism. Fujimoto34 also reports selectivity enhancement with the use of halogens. H₂S35,36 SO₂37,38 and COS39 have also been tested with some success as replacements for oxygen. However, these oxidants are not without their drawbacks. They are all relatively expensive, compared with oxygen, which poses recovery problems. Some of these compounds are
toxic or corrosive which also increases the handling costs. These additional expenses have prevented the commercialization of such processes.

Objectives

The purpose of this research was to determine a kinetic model for the oxidative dehydrogenation of n-butane over two mixed metal oxide catalysts. Furthermore, the reaction pathways, intermediates and a possible mechanism were hoped to be determined. We also wished to gain some insight into the nature of the catalytic site or sites. Several of these objectives were achieved; however, much additional work is needed to completely characterize this complicated and important system.
II. Experimental

Catalysts

\( \text{MnLiO}_x \)

The manganese lithium oxide (\( \text{MnLiO}_x \)) used in part of this work was unsupported \( \text{Mn}_2\text{O}_3 \) doped with lithium. This catalyst was supplied by Haldor Topsøe. An atomic ratio of 7:1 Mn to Li was analyzed in the catalyst which was highly calcined to provide a final \( \text{N}_2 \) BET surface area of approximately 2.5 \( \text{m}^2/\text{g} \). A preparation of the catalyst was also made in the lab using the same formulation as that supplied by Haldor Topsøe. This calls for adding an aqueous solution of \( \text{LiCO}_3 \) to a slurry of \( \text{MnCO}_3 \) and heating while stirring until almost dry. The resulting mixture was heated overnight in an oven at 100\(^\circ\)C, then calcined in air for two days at 600\(^\circ\)C, one day at 700\(^\circ\)C, and three hours at 800\(^\circ\)C. This preparation differed little from the catalyst supplied by Haldor Topsøe.

The catalyst was crushed to 20/40 mesh size and diluted
by similar size Vycor glass particles before introducing them into the reactor. The size and design of the reactor will be discussed later.

**Ni-Sn**

A nickel tin oxide mixture catalyst supplied by the Phillips Petroleum Company\(^{40,41,42}\) was used for the major portion of this work. Its composition was 47% Ni, 9.9% Sn, 5.9% P, 1.1% K, and 3.8% S, by weight with the remainder being oxygen. This catalyst was unsupported and possessed an \(N_2\) BET surface area of 49 m\(^2\)/g. Pore volume distribution for this catalyst is shown in Figure 1. The catalyst was crushed and sieved to 30/40 mesh then diluted by similar sized Vycor glass particles before loading into a reactor, which will be discussed later.

**Gases**

Zero Grade Helium supplied by Liquid Carbonic was used as a chromatographic carrier gas in all systems and as a dilutent in the plug flow reactor and microbalance systems. This was further purified on the plug flow reactor system and the associated chromatograph by passing the helium through a Linde molecular sieve 4A column. Oxygen used in all experiments was Liquid Carbonic 99.99% purity. Hydrocarbon feeds were used without further purification and consisted of C.P. grade (99.5% purity) n-butane, Phillips Petroleum Company Research Grade 1-butene (99.96% purity),
Figure 1. Pore Volume Distribution for Ni-Sn Catalyst. Data Courtesy of Phillips Petroleum.
cis-2-butene (99.88% purity) and 1,3-butadiene (99.85% purity). CO introduced during temperature programmed desorption experiments was C.P. grade. A mixture of oxygen, 10% by volume, in helium used in some experiments was a custom mixture made by Liquid Carbonic with zero helium and high purity oxygen.

The two isotopic tracers used in this work were \( \text{n-C}_4\text{D}_{10} \) (98.0 atom %D) acquired from Merck, Sharp, and Dohme and Alfa Products' \( \text{C}^{18}\text{O}_2 \) (99% isotopic purity). These tracers were used without dilution or further purification.

**Apparatus**

**Plug Flow Reactor System**

All kinetic data on the two catalysts were gathered using a plug flow reactor system pictured in Figure 2. Reactants were admitted through V1, V2, and V3 to their respective flow controllers, FC1 through FC3. These controllers were electronic mass flow controllers model FC-260 made by Tylan Corporation. Oxygen and n-butane controllers had a range of 0.4 to 20 SCCM, while the helium controller range was 4 to 200 SCCM. Individual controller set points were adjusted by means of one of three counting, ten turn potentiometers on the Master Control (MC). A selected controller's output could be monitored on a digital display reading directly in SCCM. A ratio mode of operation could be selected in which FC2 acted as the master and the
other two controllers would stay in a predetermined ratio to FC2. This enabled the total flow rate to be changed by adjusting one potentiometer without changing the inlet concentrations. Valves V4 through V6 prevented any gas from backing up into a controller which was not being used at the time.

The reactant stream could be either bypassed through B or passed through the reactor, R1, by actuating the three-way valve, V7. Before being passed over the catalyst, the inlet stream was bubbled through a Pyrex saturator, S1, which was filled with distilled water. The concentration of water entering the reactor was adjusted by changing the temperature of an oil bath which surrounded the saturator. Heaters H1 and H2 were operated at about 120°C to prevent any water or heavy hydrocarbons from condensing on the glass tubing.

Vycor tubing (7mm I.D. was normally used, although some experiments required a change in cross sectional area) was used in the construction of the reactor with four dimples equally spaced along its 12 cm length for thermocouple wells. A short preheater section (P) of 20/40 mesh Vycor particles about 2 cm long preceded the catalyst bed (CT1). Prior to being charged to the reactor, the catalyst was diluted with Vycor particles at a ratio of catalyst/Vycor from 1/2 to 1/10. A ratio of 1/3 was close to optimum for reducing temperature gradients while allowing adequate
catalyst to be charged to obtain desirable conversion levels. Iron-Constantan thermocouples TC1 through TC4 were used to determine the temperature gradient along the bed and were monitored by a Hewlett-Packard digital multimeter, model 3465A. The reactor was heated by means of a stainless steel core furnace with a nichrome wire element wrapped with removable asbestos cloth tape. This latter feature allowed some control over temperature gradients in the catalyst bed. A homemade PID temperature controller regulated the temperature of the reactor to within \( +0.5^\circ \text{C} \). The effluent of the reactor or bypass was directed to a sampling valve in the gas chromatograph system.

**Gas Chromatograph System**

The gas chromatograph system used in conjunction with the plug flow reactor is shown in Figure 3. This system consisted of a modified Perkin-Elmer model 3920 gas chromatograph employing a T.C. detector with three columns (C1 through C3) and a ten port valve (V10). The columns used in this experiment were tubular spirals containing the following material:

1) 2 1/2 ft. x 1/4 in. O.D. Linde Molecular Sieve 5A, 40/60 mesh,

2) 6 ft. x 1/4 in. O.D. Chromosorb 104, 60/80 mesh, and

3) 30 ft. x 3/8 in. O.D. 25% Propylene Carbonate on Chromosorb W, 60/80 mesh.
Reactor effluent passed through sample loop L (~2 cc in volume) when V10 is in the position labeled A. Analysis began with V8 and V9 turned so that carrier gas flows through column C1 and with trap T1 at liquid nitrogen temperature. V10 was then switched to position B thereby introducing the sample into the analysis system. This sample passes through the cold trap where condensables remain while the light gases continue on through the molecular sieve column. This column was held at ambient temperature and elutes O₂, CH₄, and CO₂ in order.

After the light gases have been eluted from C1 (3 1/2 minutes), valves V8 and V9 were turned to allowed flow through columns C2 and C3. At this time trap T1 was heated to flash the condensable gases it contained and allow them to pass through C2 which was thermostated at 135°C. This column's function was to delay the partially oxygenated compounds and water and permit the "normal" hydrocarbons to be separated in C2 onto C3. Column C3 was held at ambient temperature. Nine minutes into the analysis all the "normal" hydrocarbons were contained in C3 and V10 was returned to position A. This action effectively switched the positions of C2 and C3 in the flow stream allowing the water and partially oxygenated compounds to elute through the detector without being essentially irreversibly absorbed on C3.

Carrier gas flow rate was adjusted, using V11, to
Figure 3. Chromatographic System
about 60 cc/min while the reference flow rate was regulated at 15 cc/min by utilizing V12. Detector current and temperature were held at 175 ma and 150°C, respectively. A Spectra Physics Minigrator digital integrator was attached to the detector output to obtain the area of the eluting peaks. A Hewlett Packard model 7100B recorder was connected to the integrator. Elution times and relative sensitivities for a typical chromatogram are given in Table 2.

The gas chromatograph connected with the microcatalytic experiments involved a single 20’ x 3/8” column packed with 25% propylene carbonate on 60/80 mesh Chromosorb W held at 0°C. Samples were introduced into the column by first trapping the reactor effluent pulse in trap T2 which was held at liquid nitrogen temperature (Figure 4). The flow was diverted from the trap by closing stopcocks S17 and S18 and then opening S16 to \$5. While the trap was still at -195°C, stopcock S19 was opened to the vacuum and S18 opened for about 3 seconds to evacuate the helium and non-condensables. The trap was warmed with a heat gun, and S17 and S18 were turned to divert a major portion of the G.C. helium stream from the restriction X through the trap which swept out the sample.

Helium flow rates were set by adjusting the regulator to the desired pressure (usually 20-30 psig) and turning the metering valves V14 and V15 to get the proper flow rate
Table 2. Chromatographic Elution Times

<table>
<thead>
<tr>
<th>Compound</th>
<th>Elution Time (min)</th>
<th>Relative Molar Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>0.7</td>
<td>0.318</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.1</td>
<td>0.42</td>
</tr>
<tr>
<td>CO</td>
<td>2.0</td>
<td>0.494</td>
</tr>
<tr>
<td>H₂O</td>
<td>12.7</td>
<td>0.388</td>
</tr>
<tr>
<td>CO₂</td>
<td>22.5</td>
<td>0.565</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>29.2</td>
<td>1.0</td>
</tr>
<tr>
<td>1-C₄H₈</td>
<td>32.5</td>
<td>0.953</td>
</tr>
<tr>
<td>t-2-C₄H₈</td>
<td>35.8</td>
<td>1.0</td>
</tr>
<tr>
<td>C-2-C₄H₈</td>
<td>40.0</td>
<td>1.02</td>
</tr>
<tr>
<td>1,3-C₄H₆</td>
<td>45.0</td>
<td>0.941</td>
</tr>
</tbody>
</table>
Figure 4. Microcatalytic System
of sample and reference streams, respectively. Helium flow rates used during the experiments were 60 cc/min for the sample stream and 10 cc/min for the reference stream. The T.C. detector was held at 130°C with a bridge current of 110 ma. The output of the detector was connected to a Perkin-Elmer model M-2 digital integrator. A recorder (Hewlett-Packard model 7100B) was connected to the integrator to record the actual chromatogram.

**Microcatalytic System**

Isotope exchange reactions were carried out in a microcatalytic (or pulse) reactor system shown in Figure 4. Helium carrier gas was metered through the system by adjusting V16 and noting the reading on rotameter RM. The stream could be saturated with water at room temperature through S2, or if needed, a bypass could be installed at the dashed line to eliminate the saturators. During the G.C. analysis, S16 was opened to S5 to enable the flow of helium to continue over the catalyst uninterrupted.

Reactant gases were introduced through S1 to the gas buret after evacuation of the gas burette manometer, M, and associated lines. Stopcock S10 was opened to allow the gas to expand from the gas burette into the doser, Z, which had a volume of 8.0 cc. The pressure in Z was measured using manometer M and controlled by changing the level of mercury in the gas burette. After the correct pressure was attained, S10, S6 and S3 were closed to reduce the loss of reactant
gas and the lines evacuated through S8. The reactant pulse could be passed over the catalyst by closing S12 and turning S10 and S11 to divert the flow through Z.

The heater used for these experiments consisted of a transite casing filled with vermiculite and a ceramic core wound with nichrome wire. A Leeds and Northrup Electromax PID controller with a Zero Voltage Power Pack was used to regulate the heater temperature. Reactor temperature was measured with an iron-constantan thermocouple using a Hewlett-Packard digital multimeter model 3465A.

**Mass Spectrometer**

A consolidated Electrodyamics Corporation Model 21-104 mass spectrometer was used to analyze deuterium labeled hydrocarbons and $^{18}$O isotopes of CO$_2$. The spectrometer was equipped with an Analog Devices model 310K amplifier and a MKS Baratron Pressure Meter for measuring the pressure upstream of the gold foil leak leading to the analyzer section. Fragmentation patterns and sensitivity factor calibrations were done using the Baratron gauge.

Ionization voltages, kept low to minimize fragmentation, were 10 eV nominal for CO$_2$ isotopes and 5 eV nominal for n-butane, butene and 1,3-butadiene deuterium isotopes. Corrections were made for contributions of $^{13}$C. Analysis of the data will be detailed later.
TPD System

Figure 5 shows the schematic for the temperature programmed desorption (TPD) apparatus. Reactor R3, filled with an appropriate weight of catalyst, could be evacuated by opening valves V17 and V19 and then adsorbate introduced by subsequently closing V17 and opening V18. Adsorbate pressure could be measured using a Bordon-tube gauge, PG1.

Valve V20 was used to isolate the mass spectrometer's analyzer section from high pressure during pretreatments or adsorptions. A Varian 80 l/s VacIon pump was used to remove desorb gases from the system.

Reactor temperatures were achieved using a nichrome wire element heater with a stainless steel core. This heater was controlled by a homemade PID temperature controller with a linear set point programmer. This set point programmer employed a variable frequency, astable multivibrator (NE555CN). The multivibrator's output drove a digital to analog converter to generate the linear, adjustable slope, voltage ramp used as the set point.

Microbalance System

The microbalance system employed for this work was a Perkin-Elmer model TGS-2 thermogravimetric scheme, shown in Figure 6. This microbalance had a maximum sensitivity of 0.2 µg and could be evacuated down to about 1 x 10^-6 torr.
Figure 5. TPD Apparatus
Figure 6. Microbalance System
A dual pen recorder was connected to the balance control and to the first derivative computer. Catalyst was suspended in a sample pan in the interior of the platinum resistance heater, which was inside the hand-down tube. This heater was controlled and programmed by a Perkin-Elmer model UU-1 temperature program controller.

Reduction-oxidation experiments were carried out by flowing either helium or a 10% oxygen in helium mixture through metering valve V22 and stopcocks S23 and S24 into the balance head. The gas then flowed from the head down the hang-down tube, over the catalyst, and out through S26. Hydrogen could be added directly into the hang-down tube when a reducing atmosphere was needed. This direct injection by-passed the balance head to eliminate an explosive mixture in that region.

Nitrogen BET surface areas could be run on the microbalance system by simply replacing the long hang-down tube with a shorter one with no side arms. The system could be evacuated through S21 and then nitrogen introduced from the glass bulb, GB, through S22. Nitrogen pressure was measured with PG2, a Texas Instruments Precision Pressure Gauge, utilizing a quartz Bourdon-tube.

**Electroconductivity System**

Electroconductivity measurements were performed in a cell consisting of a short section of sintered glass tubing packed with catalyst inside a glass enclosure (Figure 7).
Figure 7. Electroconductivity Cell
This cell could be evacuated or held at a constant pressure of oxygen. Catalyst was powdered and slurried with water then packed in the sintered glass tube (~1 cm in length) with platinum leads attached to the ends of the catalyst tube and brought outside the cell through sealed sidearms. The resistance of the catalyst was measured using a Keithly model 191 digital multimeter with a range of up to 20 MΩ. This meter measured resistance with direct current. The heater and controller were essentially the same as those on the microcatalytic system.

X-Ray Diffraction Equipment

X-Ray power diffraction was accomplished using a Phillips model 1010 utilizing a Zr filtered Molybdenum source operated at 38 kilovolts and 18 milliamperes. X-ray film was loaded into a 57 mm radius Debye-Scherer camera which held a sample of powered catalyst in a capillary at its center. The exposed film was then developed and the resulting patterns compared against compiled standards.

Experimental Procedure

Kinetic Experiments in Flow Reactor System

Kinetic runs were initiated by adjusting the reactant gas flow rate using the master control potentiometers. The reactor was then brought up to reaction temperature and allowed to reach constant activity. During this time, the
temperature of the saturator oil bath was regulated if the water concentration desired was higher than that obtained at ambient temperature. Once the reactor temperature had fairly well lined out, temperature gradients in excess of 3°C were corrected by adding or removing asbestos cloth tape from the appropriate areas on the outside of the heater. Gradients were generally able to be reduced to less than 3°C. After the system was in a steady state and the reactor temperature gradients deemed small (usually 1 to 1 1/2 hrs. from start-up), the reactor effluent was analyzed.

During the analysis of the reaction products, which normally required 45 min. to 1 hr., the next set of reaction conditions were imposed. The simplest change to effect was that of space time (i.e. overall flow rate) or individual concentrations. This was because unless these changes were dramatic, the reactor temperature and gradients remained essentially constant, allowing the system to reach a steady state in approximately 15 min. or less. Reactor temperature could also be changed, but this required a longer time to line out and subsequently damp out temperature gradients.

Inlet concentrations of oxygen and hydrocarbon were generally held between 5 and 20% by volume, although in certain cases their concentrations were brought up to 20% and 40% by volume, respectively. Normally, inlet concentrations of 10% by volume were used in the initial run,
then, the concentration of one of the reactants was halved for the next run, then doubled. The total flow rate, hence the space time, was kept constant by adjusting the helium flow to compensate for any loss or addition of other reactants. After a complete set of runs was made, often with many repetitive inlet conditions, the total flow rate was changed and another set of inlet conditions was run. Space times were varied over an order of magnitude or more if reaction conditions and equipment limitations allowed. Four separate hydrocarbon reactants (n-butane, 1-butene, cis-butene, and 1,3-butadiene) were investigated using the above procedure. A mixture of 1-butene and 1,3-butadiene was also run.

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

Exchange of \( ^{18} \text{O} \) with the catalyst was studied in the microcatalytic system. The reactor was charged with 0.1085g of undiluted Ni-Sn catalyst. Helium carrier gas, passed through saturator S2 for only the first experiment, was adjusted to 30 cc/min and directed to flow over the catalyst through trap T2 and out through S19 to the standard taper \( \equiv \) to the standard taper \( \equiv \). U-tube traps, with a design similar to reactor R2, were placed in liquid nitrogen then attached to \( \equiv \), when necessary, to trap the pulse of exchanged \( \text{CO}_2 \). Trap T2 was held at about \(-10^\circ \text{C}\) using a salt-ice bath to trap any water before it entered the U-tube traps.
$C^{18}O_2$ was drawn into a previously evacuated doser, $Z$, through stopcocks S6 and S10. The pressure, measured by mercury manometer M, was adjusted to 120 torr by raising or lowering the level of mercury in the gas burette. The doser was isolated by turning S10; the pulse was then swept out through the heated reactor by closing S12 and manipulating S10 and S11 to divert the flow of helium through $Z$. Pulses were collected for 5 minutes to ensure that all products were swept out of the reactor into the trap. Samples collected in the U-tubes were transferred to the CEC 21-104 mass spectrometer for individual analysis. The analysis gave the relative compositions of $C^{18}O_2$, $C^{18}O^{16}O$, and $C^{16}O_2$. Analysis of these data will be treated later.

**Deuterium Exchange Experiments**

Exchange of n-C$_4$D$_{10}$ with 0.5 g of Ni-Sn catalyst, diluted by 2cc Vycor particles, was studied in the microcatalytic system in a similar way as $C^{18}O_2$ exchange. The perdeuterated n-butane was charged to the doser $Z$ at approximately 200 torr then swept over the catalyst. For these experiments the pulse was trapped in T2 at -195°C then analyzed using the gas chromatograph to separate the n-butane, butenes, and 1,3-butadiene. Each fraction was then trapped individually in a U-tube at liquid nitrogen temperature for analysis of the deuterium content using the mass spectrometer.
Carrier gas was saturated with water at room temperature and adjusted to 60 cc/min. Two carrier gas streams were used in these experiments, one being helium and the other being 10\% by volume oxygen in helium.

**Temperature Programmed Desorption Experiments**

The TPD system reactor was charged with 9 mg of Ni-Sn catalyst. The catalyst was pretreated in situ with atmospheric pressure of oxygen at 500°C for not less than 1 hour at the start of each run. The reactor was cooled to the adsorption temperature and evacuated through V17 for 15 minutes. Adsorbate gas was introduced through standard taper F8 and brought up to about 100 torr after V19 was opened to expose the catalyst. The reactor was cooled to room temperature after 15 minutes then evacuated by closing V18 and opening V17 for about 1/2 hour. Desorption was accomplished by closing V17 and opening V20 then linearly programming the reactor temperature at a rate of 10°C/min. The resulting gas phase compositions were scanned by the mass spectrometer set at 10eV nominal ionization voltage. Generally, runs were terminated below 550°C to avoid sintering of catalyst.

Heating rate, catalyst weight and pumping speed of the system had been previously adjusted to enable direct rates of desorption to be measured with known response factors of the mass spectrometer. During the TPD runs, pressure above the catalyst did not exceed $1 \times 10^{-5}$ torr
and was normally in the $1 \times 10^{-6}$ to $4 \times 10^{-6}$ torr range maximum.

**Reduction-Oxidation Experiments**

Reduction-oxidation experiments were carried out in the microbalance system with an initial weight of Ni-Sn catalyst of about 46 mg. Helium purge was set at 110 cc/min and the furnace programmed up at $10^0 \text{C/min}$ to measure the initial degassing of water. The catalyst was then reduced to the desired extent by introducing hydrogen into the upper side arm of the hang-down tube. The temperature was kept at $400^0 \text{C}$ or programmed up until the reduction rate was appreciable. Hydrogen flow was regulated to 20 cc/min by opening S25 and adjusting V23. The hydrogen was introduced into the helium purge to eliminate a possible explosive mixture if hydrogen were trapped in the head when oxygen was introduced. When the reduction was complete, the hydrogen was shut off and the helium purge continued to reduce the chance of readsorption of the water formed during the reaction.

Reoxidation was performed by first cooling the catalyst to a predetermined starting temperature (often room temperature) then switching valve V21 to allow the 10% oxygen in helium mixture to flow over the catalyst. After the initial uptake of oxygen had slowed considerably, the temperature was programmed up at $10^0 \text{C/min}$ to between $500^0 \text{C}$ and $600^0 \text{C}$. After each run, the oxygen stream was replaced by pure
helium and the system purged of oxygen. Both the weight change and its first derivative were recorded.

Reduction of the catalyst was also performed in a static system to enable the surface area to be measured in situ.

**Electroconductivity Measurements**

Electroconductivity measurements were initiated by first evacuating the cell containing the catalyst, then measuring the catalyst resistance at various temperatures. The lowest temperature at which a reliable resistance reading could be made was 350°C. Measurements were made every 50°C up to 500°C, then again at every 50°C as the temperature was lowered to 350°C.

After several cycles in vacuum, approximately 100 torr of oxygen was introduced over the catalyst. One decreasing-increasing cycle (500°C to 300°C) was run again, taking measurements at 50°C intervals.

**Treatment of Data**

**Kinetic Data**

Data gathered from the plug flow reactor system consisted of temperature, individual flow rates and areas of the peaks eluted from the gas chromatograph. The latter were corrected by the appropriate sensitivity factors and normalized to give volume fractions of the reactor.
effluent stream. Inlet concentrations were not normally measured, as the saturator was located downstream of the bypass to avoid condensation of the water. This allowed only a water-free inlet to be measured. Another reason was that the analysis required several minutes (50) and for a substantial part of that time, the reactor would have no flow through it. This upset the temperature profile along the catalyst bed causing variations in the results if the temperature gradients were not smoothed out.

Inlet concentrations were back calculated from the outlet volume fractions by making three assumptions: 1) the ratio of inlet helium to inlet oxygen was proportional to the reading of the flow controllers, 2) a mass balance held around the reactor, and 3) the volume change during reaction was negligible. The error introduced by the first assumptions were less than ±2% due to the accuracy of the electronic flow controllers. The mass balance assumption was checked out several times when not using the saturator and was always well within ±5%. Volume changes are negligible due to the low inlet concentrations of reactants and the fact that a maximum change of only 1.5 moles of product per mole of reactant is available. Back calculations were made by assigning all product stream carbon atoms to the inlet hydrocarbons using the following formula:
Inlet Hydrocarbon = \[ \sum_{i=1}^{N} f(i)NC(i)/4 \]  

where:  
N = total number of compounds present in the product stream  
f(i) = volume fraction of the \( i^{th} \) compound  
NC(i) = number of carbon atoms in the \( i^{th} \) compound.

The factor of 4 in the denominator accounts for the 4 C atoms in the inlet hydrocarbon.

Calculation of the inlet oxygen utilized a slightly different scheme than the hydrocarbon calculation due to the fact that the amount of water formed during the reaction was not yet estimated. Inlet oxygen was calculated by multiplying the volume fraction of butenes, 1,3-butadiene, CO\(_2\) and any partially oxygenated hydrocarbons by the appropriate factors and summing with the oxygen outlet volume fraction. These factors are the ratio of the stoichiometric coefficients of oxygen to hydrocarbon product such as \( \frac{1}{2} : 1 \) in the equation:

\[ n-C_4H_{10} + \frac{1}{2}O_2 \rightarrow C_4H_8 + H_2O \]  

Inlet water was calculated in the same manner but instead of adding the sum of the product hydrocarbons times the appropriate stoichiometric ratio to the water, it was subtracted, as water was a product not a reactant. Inlet helium was estimated by taking the ratio of helium to oxygen inlet flow rates and multiplying by the calculated oxygen inlet. The four relative inlets were then normalized
to give the inlet volume fractions.

Concentrations of inlet and outlet gases at reaction temperatures were expressed in terms of moles per liter by the following formula:

\[ C_i(\text{mole/l}) = f(i) \cdot \frac{1 \text{ mole}}{22.4 \text{ l}} \times \frac{273}{T + 273} \]  \hspace{1cm} (3)

where:

- \( C_i \) = concentration in mole/l of the \( i \)th compound
- \( f(i) \) = volume fraction of the \( i \)th compound
- \( T \) = reactor temperature (°C)

Conversions of oxygen and hydrocarbon were calculated by the assumption of constant volume and the equation

\[ (%) \text{ Conversion}_i = \left( \frac{C_0 - C_f}{C_0} \right)_i \times 100 \]  \hspace{1cm} (4)

where the inlet and outlet concentrations of the \( i \)th compound were \( C_0 \) and \( C_f \), respectively.

Space time \( \tau \) (or more correctly, weight time) was calculated by dividing the catalyst weight by the total inlet flow rate of gas. The total inlet flow rate was the sum of the flow rates of oxygen, hydrocarbon and helium, corrected for the flow of water from the saturator and temperature.

\[ \tau = \frac{Wt}{Q_{\text{inlet}} \cdot \frac{f(H_2O) + f(O_2) + f(HC) + f(He)}{f(O_2) + f(HC) + f(He)} \cdot \frac{T + 273}{273}} \]  \hspace{1cm} (5)
where:

\[ wt = \text{weight of catalyst} \]
\[ Q_{\text{inlet}} = \text{volumetric flow rate of oxygen + hydrocarbon + helium measured at STP} \]
\[ f(H_2O) = \text{volume fraction of water} \]
\[ f(O_2) = \text{volume fraction of oxygen} \]
\[ f(HC) = \text{volume fraction of hydrocarbon} \]
\[ f(He) = \text{volume fraction of helium} \]
\[ T = \text{reactor temperature in } ^{\circ}\text{C.} \]

The space time was calculated with units of g-sec/l.

**C^{18}O_2 Exchange Data**

Raw data from the C^{18}O_2 exchange experiments were in the form of peak heights of the mass to charge ratios (m/e) of 44, 46, and 48. These m/e values corresponded to C^{16}O_2, C^{16}O^{18}O, and C^{18}O_2, respectively. The peak amplitudes, recorded from the mass spectrometer output, were proportional to the molar concentration of each species. Calibrations showed that the sensitivity factors were equal for all of the isotopes; therefore, no corrections for sensitivity were necessary.

Mole fractions of each species were calculated by normalizing the peak heights with respect to the total of the three peak heights. From these fractions, the average number of oxygen atoms exchanged per CO_2 molecule for ith pulse (\( \phi_i \)) was calculated using the equation
\[ \phi_i = \sum_{m/e=44,\text{even}}^{48} \frac{(48-m/e)}{2} f_i(m/e) - \phi_0 \]  

(7)

where \( f_i(m/e) \) is the \( i^{th} \) pulse's mole fraction of the appropriate compound. \( \phi_0 \) is a correction factor for the impurity of the inlet \( \text{C}^{18}\text{O}_2 \). This amounted to the number of oxygen atoms per \( \text{CO}_2 \) molecule that would need to be exchanged to obtain the inlet composition from pure \( \text{C}^{18}\text{O}_2 \). The total number of oxygen atoms exchanged in pulse \( i \) (\( \sigma_i \)) is equal to the total number of \( \text{C}^{18}\text{O}_2 \) atoms in the pulse time \( \phi_i \). For an experiment with several pulses, the intercept of a plot of \( 1/\Sigma \) (where \( \Sigma = \sum_{j=1}^{i} \tau_j \)) versus \( 1/i \), where \( i = \text{pulse number} \), will yield the total available number of easily exchanged oxygen atoms on the catalyst. The corresponding number of monolayers of catalyst oxygen was calculated by dividing the number of exchangeable oxygen atoms by the number of oxygen atoms per monolayer for the appropriate weight of catalyst. The number of oxygen atoms per monolayer was calculated from the known surface area, assuming the surface was fully covered by oxygen and also assuming that an oxygen atom covers \( 10\sigma^2 \) of surface. A derivation of this procedure is given in Appendix I.

The fractions of each species for each pulse were compared to that predicted by the binomial distribution where the number of independent binomial trials equals 2. If these values were significantly different, a check was made to see if there were any bypassing of reactant around
the catalyst. To accomplish this, the ratios of the frac-
tions of $^{16}O_2$ and $^{16}O^{18}O$ were calculated for each pulse
and the $\phi_i$ values corresponding to such ratios were
estimated. From these values of $\phi_i$, the predicted frac-
tions of each species, $p_i(m/e)$, were calculated. The
measured fraction divided by the predicted fraction of $^{16}O^{18}O$
gives the non-normalized total of reactant that was avail-
able for exchange. The fraction $^{18}O_2$ bypassed ($\beta_i$) was
assessed by the equation

$$\beta_i = 1 - \frac{f_i(46)}{p_i(46)}.$$  \hspace{1cm} (8)

The mean fraction bypassed and its standard deviation were
also evaluated.

**Deuterium Exchange Data**

The data from the exchange of perdeuterated n-butane
with the catalyst were in the form of peak heights for
the mass to charge ratios of 58 to 68 for n-butane, 56 to
64 for butenes, and 54 to 60 for 1,3-butadiene. These
peak heights were first corrected for the carbon-13 contri-
bution due to the approximately 4% $^{13}C$ per hydrocarbon
molecule. This contribution shows up in the one higher m/e
peak and corrections were made according to the following:

$$PH(M/e) = MH(m/e) - 0.04 \cdot PH(m/e - 1)$$  \hspace{1cm} (9)

where $PH(m/e)$ is the corrected peak height and $MH(m/e)$ is
the measured peak height. This correction was applied
starting with the singly deuterated isotope and continuing to the perdeut erated species for each compound.

After this correction was made, the mole fractions of each isotopic species were calculated by normalization, with respect to the sum of the peak heights of all species of a compound. The average number of hydrogen atoms per hydrocarbon molecule \( \phi_i \) was estimated by Equation 10:

\[
\phi_i = \sum_{n=0}^{N} n f_i(n). \tag{10}
\]

\( N \) is the total number of positions available for hydrogen or deuterium atoms on the molecule and \( n \) is the number of hydrogen atoms in the isotope. Predicted values of mole fractions for each compound (estimated from \( \phi_i \) using the binomial distribution) were compared to the experimental values.

The conversion of n-butane was calculated for each run from the following equation

\[
\text{Butane Conv.} = \frac{F(B') + F(B'') + F(CO_2)/4}{F(B) + F(B') + F(B'') + F(CO_2)/4} \tag{11}
\]

where:

- \( F(B) \) = outlet mole fraction of n-butane,
- \( F(B') \) = outlet mole fraction of butenes,
- \( F(B'') \) = outlet mole fraction of 1,3-butadiene, and
- \( F(CO_2) \) = outlet mole fraction of CO_2.

The outlet mole fractions were calculated by correcting the
peak areas measured from the gas chromatograph and normalizing with respect to the total area.

Selectivities to CO₂ and butene + 1,3-butadiene were calculated.
III. Results

X-Ray Powder Diffraction

The film exposed during the x-ray powder diffraction experiment of the Ni-Sn catalyst showed very little detail. Two very faint lines were present at diffraction angles which could not be attributed to any major component in the catalyst. A large, slightly exposed, central circle was the most prominent feature of the developed film. This lack of an observed pattern indicated that the catalyst was primarily amorphous.

C$^{18}$O$_2$ Exchange over Ni-Sn Catalyst

Three C$^{18}$O$_2$ exchange experiments were carried to determine the mobility of oxygen in the Ni-Sn catalyst charge. The first experiment was conducted at 380°C using helium, saturated with water at room temperature, as a carrier gas. A pressure of 120 torr of C$^{18}$O$_2$ was charged to the 8cc volume for each pulse giving a pulse size of 5.12 x 10$^{-5}$
moles. This experiment produced a very interesting result in that the fraction of the incoming oxygen exchanged ($\phi_i$) remained a constant 0.54. The eight pulses passed over the catalyst exchanged an amount equivalent to 2.5 monolayers of catalyst oxygen. This unusual behavior suggests that the water was also rapidly exchanging oxygen atoms with the catalyst, thus removing any $^{18}O$ atoms remaining on the surface after exchange with $^{18}O_2$.

After noting the probable exchange of water and catalyst oxygen, subsequent experiments were run without saturating the helium carrier with water. These experiments with pure helium carrier gas were carried out at both 380$^0$C and 452$^0$C. Successive pulses at both temperatures showed the expected decrease in exchanged oxygen atoms due to the buildup of $^{18}O$ on the surface. Tables 3 and 4 present the data of the $^{18}O_2$ exchange as a function of pulse number for temperatures of 380$^0$C and 452$^0$C, respectively. To estimate the total number of catalyst oxygen atoms available for exchange, a plot of $1/\Sigma$ ($\Sigma$ is the sum of the oxygen molecules exchanged) versus $1/PN$ (where PN is the pulse number) was made and the intercept evaluated. Plots for the two temperatures are shown in Figures 8 and 9. The inverse of this intercept gives the number of catalyst oxygen atoms that would be exchanged after an infinite number of pulses, $\Sigma_\infty$; it therefore represents the total number of oxygen atoms available for exchange.
Table 3. $^{18}\text{O}_2$ Exchange Data at 380°C

<table>
<thead>
<tr>
<th>Pulse Number</th>
<th>Number of $^{18}\text{O}$ Exchanged/C$^{18}\text{O}_2$</th>
<th>Mole$^{18}\text{O}$ Exchanged/pulse</th>
<th>$\Sigma$</th>
<th>1/Pulse No.</th>
<th>1/$\Sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.167</td>
<td>$8.55 \times 10^{-6}$</td>
<td>$8.55 \times 10^{-6}$</td>
<td>1</td>
<td>$1.17 \times 10^5$</td>
</tr>
<tr>
<td>2</td>
<td>0.143</td>
<td>$7.32 \times 10^{-6}$</td>
<td>$1.59 \times 10^{-5}$</td>
<td>0.5</td>
<td>$6.29 \times 10^4$</td>
</tr>
<tr>
<td>3</td>
<td>0.126</td>
<td>$6.45 \times 10^{-6}$</td>
<td>$2.23 \times 10^{-5}$</td>
<td>0.333</td>
<td>$4.48 \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>0.123</td>
<td>$6.30 \times 10^{-6}$</td>
<td>$2.86 \times 10^{-5}$</td>
<td>0.25</td>
<td>$3.50 \times 10^4$</td>
</tr>
<tr>
<td>5</td>
<td>0.115</td>
<td>$5.89 \times 10^{-6}$</td>
<td>$3.45 \times 10^{-5}$</td>
<td>0.2</td>
<td>$2.90 \times 10^4$</td>
</tr>
<tr>
<td>6</td>
<td>0.108</td>
<td>$5.53 \times 10^{-6}$</td>
<td>$4.00 \times 10^{-5}$</td>
<td>0.167</td>
<td>$2.50 \times 10^4$</td>
</tr>
<tr>
<td>7</td>
<td>0.104</td>
<td>$5.32 \times 10^{-6}$</td>
<td>$4.54 \times 10^{-5}$</td>
<td>0.143</td>
<td>$2.20 \times 10^4$</td>
</tr>
<tr>
<td>8</td>
<td>0.108</td>
<td>$5.53 \times 10^{-6}$</td>
<td>$5.09 \times 10^{-5}$</td>
<td>0.125</td>
<td>$1.96 \times 10^4$</td>
</tr>
<tr>
<td>9</td>
<td>0.102</td>
<td>$5.22 \times 10^{-6}$</td>
<td>$5.61 \times 10^{-5}$</td>
<td>0.111</td>
<td>$1.78 \times 10^4$</td>
</tr>
<tr>
<td>10</td>
<td>0.097</td>
<td>$4.97 \times 10^{-6}$</td>
<td>$5.11 \times 10^{-5}$</td>
<td>0.1</td>
<td>$1.64 \times 10^4$</td>
</tr>
<tr>
<td>11</td>
<td>0.095</td>
<td>$4.86 \times 10^{-6}$</td>
<td>$6.59 \times 10^{-5}$</td>
<td>0.091</td>
<td>$1.52 \times 10^4$</td>
</tr>
</tbody>
</table>

0.1085 g Ni-Sn

Temperature = 380°C

Pulse Size = $5.12 \times 10^{-5}$ mole $^{18}\text{O}_2$
Table 4. $^{18}$O$_2$ Exchange Data at 452°C

<table>
<thead>
<tr>
<th>Pulse Number</th>
<th>Number of $^{18}$O exchanged/C$^{18}$O$_2$</th>
<th>Mole $^{18}$O Exchanged/pulse</th>
<th>$\Sigma$</th>
<th>1 Pulse No.</th>
<th>1 $\Sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.457</td>
<td>$2.34 \times 10^{-5}$</td>
<td>$2.34 \times 10^{-5}$</td>
<td>1</td>
<td>$4.27 \times 10^4$</td>
</tr>
<tr>
<td>2</td>
<td>0.378</td>
<td>$1.94 \times 10^{-5}$</td>
<td>$4.28 \times 10^{-5}$</td>
<td>0.5</td>
<td>$2.34 \times 10^4$</td>
</tr>
<tr>
<td>3</td>
<td>0.330</td>
<td>$1.69 \times 10^{-5}$</td>
<td>$5.96 \times 10^{-5}$</td>
<td>0.333</td>
<td>$1.68 \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>0.287</td>
<td>$1.47 \times 10^{-5}$</td>
<td>$7.43 \times 10^{-5}$</td>
<td>0.25</td>
<td>$1.35 \times 10^4$</td>
</tr>
<tr>
<td>5</td>
<td>0.264</td>
<td>$1.35 \times 10^{-5}$</td>
<td>$8.79 \times 10^{-5}$</td>
<td>0.2</td>
<td>$1.14 \times 10^4$</td>
</tr>
<tr>
<td>6</td>
<td>0.248</td>
<td>$1.27 \times 10^{-5}$</td>
<td>$1.01 \times 10^{-4}$</td>
<td>0.167</td>
<td>$9.94 \times 10^3$</td>
</tr>
<tr>
<td>7</td>
<td>0.228</td>
<td>$1.17 \times 10^{-5}$</td>
<td>$1.12 \times 10^{-4}$</td>
<td>0.143</td>
<td>$8.91 \times 10^3$</td>
</tr>
<tr>
<td>8</td>
<td>0.215</td>
<td>$1.10 \times 10^{-5}$</td>
<td>$1.23 \times 10^{-4}$</td>
<td>0.125</td>
<td>$8.11 \times 10^3$</td>
</tr>
<tr>
<td>9</td>
<td>0.201</td>
<td>$1.03 \times 10^{-5}$</td>
<td>$1.34 \times 10^{-4}$</td>
<td>0.111</td>
<td>$7.49 \times 10^3$</td>
</tr>
<tr>
<td>10</td>
<td>0.194</td>
<td>$9.93 \times 10^{-6}$</td>
<td>$1.43 \times 10^{-4}$</td>
<td>0.1</td>
<td>$6.97 \times 10^3$</td>
</tr>
<tr>
<td>11</td>
<td>0.182</td>
<td>$9.32 \times 10^{-6}$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>0.901</td>
<td>$6.55 \times 10^3$</td>
</tr>
</tbody>
</table>

0.1085 g Ni-Sn

Temperature = 452°C

Pulse Size = $5.12 \times 10^{-5}$ mole C$^{18}$O$_2$
Figure 8. $^{18}O_2$ Exchange at 380°C
Figure 9. C^{18}O_2 Exchange at 452°C
At 380°C, $\Sigma_\infty$ was calculated to be $1.64 \times 10^{-4}$ mole oxygen atoms exchangeable for the 0.1085 g of Ni-Sn catalyst in the reactor. This number of oxygen atoms is equivalent to 1.86 monolayers of catalyst oxygen atoms. Appendix I includes a sample calculation for this type of data.

Results obtained at 452°C were very similar to those at 380°C. $\Sigma_\infty$ was estimated to be $3.08 \times 10^{-4}$ moles of oxygen exchangeable for this temperature. This provides a value of 3.49 monolayers of catalyst oxygen atoms by applying the appropriate factors.

The results of these experiments show that there is indeed a large amount of oxygen mobility within the Ni-Sn catalyst (which includes not only surface oxygen, but also lattice oxygen). Assuming an exponential dependence on temperature, the activation energy for oxygen mobility is about 8.5 kcal/mole. This mobility increases with temperature as one would expect. The result of a non-infinite $\Sigma_\infty$ when using a water-free carrier stream verifies that water does exchange oxygen readily with the catalyst at these temperatures.

Comparing the mole fractions of the three isotopes with the predicted binomial distribution shows a large excess of C\textsuperscript{18}O\textsubscript{2} in the experimental results. To check if this non-equilibrium behavior was due to bypassing of reactant C\textsuperscript{18}O\textsubscript{2}, a value of $\phi_1$ was estimated from the ratio of the two
exchanged isotopes. The mole fractions predicted from this \( \phi_i \) were evaluated and the fraction bypassed (\( \beta_i \)) calculated for each pulse. The fraction bypassed was constant for each run at a given temperature. Mean values of 0.59 and 0.41 were obtained for the runs at 380 and 452\(^\circ\)C, respectively. The standard deviation for both values was about 0.012.

Reduction-Oxidation Experiments

The first thermogravimetric analysis (TGA) on the Ni-Sn catalyst was with a pure helium purge stream. The weight loss of the catalyst was very noticeable and, while programming at 10\(^\circ\)C/min up to 400\(^\circ\)C, amounted to 2.32 mg out of a 46.1 mg sample. Desorption of water is the cause of this weight loss and, assuming a cross-sectional area the same as oxygen, involves more than 3.5 monolayers of water on the catalyst. (This value was arrived at using the conversion factor evaluated for the \( \text{C}^{18}\text{O}_2 \) exchange.) Water was readily adsorbed onto the catalyst as the weight increased when the catalyst was cooled. Several cycles of heating and cooling produced a weight gain or loss of less than 0.1 mg when cooled or heated between 150\(^\circ\)C and 500\(^\circ\)C.

Reduction of the catalyst took place in about 10 to 20\% hydorgen in helium. During the first reduction, the temperature was programmed up at 5\(^\circ\)C/min. The first
indication of substantial weight loss occurred at about 365°C. The subsequent weight loss was very rapid; therefore, the temperature was held at 410°C. The rate of reduction (loss of weight) seemed to be constant for as long as the temperature was held constant. After approximately 4 mg of weight had been removed, the temperature was reduced at 10°C/min. The rate of weight loss decreased with the decreasing temperature until about 300°C, where the reduction stopped. The discrepancy between the initiating temperature and the terminating temperature of reduction is probably due to the exothermic reaction heating the catalyst above the measured temperature since the measuring thermocouple was not in direct contact with the catalyst. The total loss of weight during the reduction of the catalyst was 5.29 mg, or 9.3 monolayers of catalyst oxygen (based on 10Å²/0).

Reoxidation of the catalyst was accomplished by flowing a 10% oxygen in helium stream over the catalyst. Holding the temperature at 150°C, the weight increased very rapidly for about 2 minutes at which time it leveled off after a gain of 1.11 mg. The temperature was then programmed at 10°C/min up to 550°C. Weight gain was again apparent, but the rate was considerably slower than the initial reoxidation. When the temperature was held at 550°C, the rate of oxidation leveled off somewhat, yet was still evident for about 30 minutes. The total uptake of
oxygen was 4.44 mg, which accounted for approximately 84% of the total weight loss during reduction. The initial gain was 25% of the total weight gained and was approximately equal to 2.0 monolayers of oxygen. A plot of weight of oxygen adsorbed versus time and temperature for this run is shown in Figure 10.

Several oxidations were carried out at constant temperatures ranging from 250 to 450°C. The catalyst was pretreated to remove 3.2 mg of oxygen before every oxidation and the initial uptake of oxygen measured. This initial uptake of oxygen increased with increasing temperature. A table of initial weight gain at several temperatures is given in Table 5. No precautions were taken to standardize the time between reduction of the catalyst and the introduction of oxygen.

The amount of weight permanently lost during a reduction-oxidation cycle was reduced to less than 0.1 mg after several cycles. The total weight permanently lost during all the redox experiments was 3.7 mg or about 8.5% of the initial weight of the degassed catalyst. The surface area of the catalyst also changed from 49 m²/g on a virgin catalyst to about 43 m²/g after the experiments. A surface area measurement was also made on a catalyst reduced by 7.6%, which resulted in a slight increase up to 54 m²/g.
Figure 10. Reoxidation of Ni-Sn Catalyst
Table 5. Initial Uptake of Oxygen

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Initial Uptake of Oxygen (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.85</td>
</tr>
<tr>
<td>300</td>
<td>1.5</td>
</tr>
<tr>
<td>350</td>
<td>2.0</td>
</tr>
<tr>
<td>400</td>
<td>2.4</td>
</tr>
<tr>
<td>450</td>
<td>2.7</td>
</tr>
</tbody>
</table>

39.8 mg Ni-Sn catalyst reduced by 8%.

Deuterium Exchange Reaction Using n-C₄D₁₀

The exchange of deuterium atoms from a hydrocarbon and hydrogen atoms on the catalyst was studied using per-deuterated n-butane over 0.5g of Ni-Sn catalyst. Helium carrier gas was saturated with water at room temperature and served as the source of the hydrogen atoms. Several runs were made using the 10% oxygen in helium mixture in place of the helium. It was found that while no significant scrambling occurred in the n-butane, the products (butenes and 1,3-butadiene) exchanged hydrogens for deuterium in an almost statistical distribution. The fractions of the different deuterium containing isotopes for an experiment using the oxygen-helium carrier mixture at a temperature of 475°C are given in Table 6. The average number of hydrogen atoms exchanged per hydrocarbon molecule (φ) for this run was 1.27 for the butenes and 1.82 for 1,3-butadiene.
Table 6. Hydrogen-Deuterium Exchange Data

Fraction Deuterium Species in Hydrogen-Deuterium Exchange.

<table>
<thead>
<tr>
<th>Species</th>
<th>$d_0$</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
<th>$d_4$</th>
<th>$d_5$</th>
<th>$d_6$</th>
<th>$d_7$</th>
<th>$d_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butenes:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
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<td>0</td>
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Mass of catalyst: 0.5g · 10% O₂ in He carrier flow rate: 58 cc/min
Temp. = 475°C
Without oxygen in the carrier gas, the conversion of n-butane dropped from 2.7% in the first pulse to 1.3% in the third at a temperature of 450°C. Selectivity to the butenes and butadiene increased from 74% to 95% during the same period. Conversions using oxygen in the carrier stream stayed relatively constant as did the selectivity. These values were about 6.8% and 60 to 65% for conversion and selectivity, respectively. It can be seen that as the conversion decreased, the selectivity increased.

Temperature Programmed Desorption

Temperature programmed desorptions (TPD) were carried out on 9 mg of Ni-Sn catalyst using n-butane and carbon monoxide as adsorbates. The adsorption of CO at 25 and 250°C led to the desorption of CO and CO₂. Temperatures at the maximum peak heights (Tₘ) were 70 and 100°C for CO and CO₂, respectively. Approximately 1 x 10¹⁷ molecules CO₂/g·cat. were desorbed during the TPD run.

After the adsorption of n-butane on the surface, the TPD spectra showed the expected presence of butene (mass per charge ratio (m/e) = 56), CO, CO₂, O₂, and water. The mass spectra also revealed a m/e = 57 peak during the runs. This species was determined not to be a doubly ionized molecule or a fragment of a heavier molecule since no peaks were detected with a mass heavier than the very small amount of residual n-butane. Figures 11 and 12 give the TPD spectra of m/e = 56 and 57 after adsorption
Figure 12. TPD Spectra - Butane Adsorbed at 150°C
of n-butane at 25 and 150°C, respectively. Increased 
adsorption temperature leads to a second, higher temperature, 
butene peak. At the same time the low temperature butene 
peak shifted from $T_m$ equal to 75°C to 100°C. The m/e = 57 
peak also increased in area while broadening out toward 
higher temperature. It becomes more complex in shape 
probably containing two or more separate peaks. The 
total amount of butenes desorbed was also about $1 \times 10^{17}$ 
molecules/g · cat.

Oxygen appeared in the gas phase at temperatures above 
450°C from an oxidized catalyst. The rate of desorption 
of oxygen was still increasing at 540°C when the run was 
terminated to avoid sintering the catalyst. Water was 
desorbed during all TPD runs. Water had a very complex 
TPD spectrum containing two or more peaks after the ad-
sorption of n-butane.

**Electroconductivity**

The resistance ($\rho$) of the packed powdered catalyst 
was measured from a temperature of 350 to 500°C with the 
cell evacuated. These resistances decreased with increas-
ing temperature and were in the range of 1.5 to 65 M$\Omega$.
Figure 13 shows the dependence of the conductivity 
($\sigma = 1/\rho$) of the catalyst under vacuum, with respect to 
1/T. It can be seen that the conductivity measured during 
a stepwise decrease in temperature was larger than that
measured during a stepwise increase in temperature. After holding the temperature at 500°C for 2 hours, then at 350°C for three days, the conductivity decreased about 24% across the temperature range.

Under the influence of 100 torr of oxygen the conductivity increased dramatically. The upper curve in Figure 13 shows this dependence with respect to 1/T. The conductivity difference between the two experiments is a factor of about 2.5 at 500°C and increases to an order of magnitude at 350°C.

Ehrenberg\textsuperscript{43} gives the equation

\[ \sigma = \sigma_0 e^{\varepsilon_i / 2kT} \]  

(11)

for the conductivity of oxides where \(-\varepsilon_i\) is the electronic activation energy and \(k\) is Boltzmann's constant. This equation is valid for oxides at low temperatures which have previously been tempered at high temperature. The electronic activation energies calculated from the slope of the plots in Figure 13 give values of 1.31 and 1.83 eV for the conductivity measured in 100 torr of oxygen and vacuum, respectively. The value obtained for the activation energy under vacuum was estimated from an average slope as the curve was not linear.

**Kinetic Results Over MnLiO\(_x\) Catalyst**

Kinetic studies of \(n\)-butane oxidative dehydrogenation
Figure 13. Electroconductivity Arrhenius Plot
over the MnLiO$_x$ catalyst revealed that the catalyst was very non-selective to butenes or butadiene under normal reaction conditions. The selectivity to these C$_4$ products was usually under 10%, although the activity was very high. Under most inlet conditions, the oxygen was depleted when a temperature of about 280°C was reached.

Studies using a Vycor tube reactor with a cross-sectional area of about 1.2 cm$^2$ revealed a strange phenomenon. After reaching the point where the oxygen was depleted, changing the temperature up to about 357°C caused very little alteration in the product concentrations. However, if the temperature were taken above 360°C, the product distribution was altered significantly. CO$_2$, the major product before this change, dropped from about 90% to less than 10% in selectivity, while there was an increase in the amounts of butenes and 1,3-butadiene. Large amounts of partially oxygenated products were also detected with acetaldehyde comprising the bulk. This phenomenon was sensitive to inlet concentrations as the n-butane and oxygen concentrations could not deviate by more than about ±10 mole % from 40 mole % and 20 mole %, respectively for this change in the reactor effluent to occur. A hysteresis in the curve of butene selectivity with respect to temperature was also observed as shown in Figure 14. After reaching a temperature of 360°C and initiating the change, the temperature could be changed from past 400°C
down to about 325°C while still existing in the higher selectivity mode. The selectivity decreased rapidly as the temperature was lowered below 340°C. If the temperature dropped below 300°C, the catalyst required heating up to 360°C again to initiate the change in selectivity. This hysteresis was easily reproduced.

Experiments run with the catalyst in a smaller diameter reactor (cross-sectional area of 0.2 cm²) resulted in no high selectivity mode up to the highest temperature reached (450°C). Inlet concentrations and space times were changed drastically with little effect on the reactor effluent. The selectivity to CO₂ remained about 90% and little partially oxygenated products were observed. The flow in both the large and small cross-sectional area reactors was within the laminar regime (see Appendix III).

Kinetic Results over Ni-Sn Catalyst

The oxidative dehydrogenation of n-butane is obviously a complex reaction; therefore, it was studied by breaking it into several sections. The first of these sections was the burning of 1,3-butadiene to CO₂. This study was undertaken in the 7mm Vycor plug flow reactor where the reaction takes place at approximately constant pressure and negligible volume change. The reaction proceeded smoothly at temperatures between 325°C and 400°C. Above 400°C, the formation of CO became appreciable with higher 1,3-butadiene
inlet concentrations. Figures 15 and 16 show CO₂ concentrations versus space time at about 370°C with varying oxygen and 1,3-butadiene concentrations, respectively. These data were taken at conversions of less than 10% of either reactant. If power law kinetics were adopted, the rate of formation of CO₂ would have the form

\[ r_{CO₂} = k C_{O₂}^n C_{C₄H₆}^m. \] (12)

The order of reaction for either of the reactants could be estimated from the slope of a plot of the natural logarithm of \( r_{CO₂} \) with respect to the natural logarithm of the concentration of the compound under investigation while holding the other reactant constant. Using the data from Figures 15 and 16, Figure 17, curve a, shows that reaction order for oxygen is close to 1, but demonstrates a very slight deviation from a linear slope at the higher concentrations of oxygen. This deviation becomes greater as the temperature increases. The deviation from a linear plot is much more prominent in the case of 1,3-butadiene, shown as curve b of Figure 17. The power law kinetic model was discarded because of these deviations.

Several reaction models were investigated with no success. These included competitive and non-competitive adsorption for Langmuir-Hinshelwood kinetics. The first model to be explored with any success was one developed by Mars and Van Krevelen\(^{44}\) for the partial oxidation of certain
Figure 15. CO$_2$ Concentration vs. Space Time
Figure 16. CO$_2$ Concentration vs. Space Time
Figure 17. Effect of Reactant Concentration on the Rate of CO$_2$ Formation
aromatic compounds. This model assumes a redox type of system with the catalyst being reduced by the hydrocarbon and subsequently being oxidized by gas phase oxygen. The rates of these processes are assumed to be proportional to the respective gas phase concentrations. The reaction rate of the hydrocarbon is assumed to be proportional to the number of available oxygen atoms on the catalyst. The oxygen coverage of the catalyst, \( \theta \), is proportional to the number of these available oxygen atoms. Re-oxidation of the catalyst is supposed to be proportional to the fraction of the available surface not covered by oxygen. The rates of reaction of hydrocarbon and oxygen can be expressed by the following relations:

\[
\begin{align*}
    r_1 &= k_1P_{C_4H_6}\theta \\
    r_{O_2} &= k_{O_2}P_{O_2}(1 - \theta).
\end{align*}
\]  
(13)  
(14)

Once the system has come to steady state, the rate of oxidation and reduction of the catalyst must be equal. This can be expressed as

\[
r_{O_2} = \beta_1r_1
\]  
(15)

where \( \beta_1 \) is the ratio of the stoichiometric coefficients of oxygen to hydrocarbon. These relations can be used along with the plug flow design equation to yield an expression for the space time which is given by
\[ \tau = \frac{1}{k_1} \ln \left( \frac{P_{C_4H_6}}{P_{C_4H_6,f}} \right) + \frac{1}{k_{O_2}} \ln \left( \frac{P_{O_2}}{P_{O_2,f}} \right) . \]  

(16)

The initial and final pressures of reactants are denoted by the subscripts 0 and f, respectively. A complete derivation of all the Mars-Van Krevelen type models used in this work is given in Appendix II.

This model was fit to the data obtained from the plug flow reactor at 325, 373, and 400°C using a bivariate linear regression routine on a Commodore Pet model 16N microcomputer. The reaction constants resulting from this analysis were found to have an Arrhenius form with the following values:

\[ k_1 = 1.86 \times 10^4 e^{-\frac{23 \text{kcal/mole}}{RT}} \frac{1}{g \cdot \text{sec}} \]  

(17)

\[ k_{O_2} = 1.7 \times 10^{12} e^{-\frac{45 \text{kcal/mole}}{RT}} \frac{1}{g \cdot \text{sec}} . \]  

(18)

The units of these rate constants are liters of total inlet gas at reaction conditions per gram of catalyst per second. To obtain the more standard units of sec\(^{-1}\), the rate constants must be multiplied by the density of the catalyst which is of the order of 1 g/cm\(^3\). A parity plot of predicted versus actual CO\(_2\) concentration for this model is shown in Figure 18.

The second section of the OXD system studied was the reaction of 1-butene to form 1,3-butadiene and CO\(_2\). A
Figure 18. Predicted vs. Actual CO₂ Concentration

Temperature

Actual CO₂ (mole/1 x 10⁵)

Predicted CO₂ (mole/1 x 10⁵)
model incorporating the burning of 1,3-butadiene previously studied plus the reaction rates of 1-butene in the form of

\[ r_2 = k_2 P_C_4H_8^\theta \]  \hspace{1cm} (19)

\[ r_3 = k_3 P_C_4H_8^\theta \]  \hspace{1cm} (20)

for OXD and deep oxidation, respectively, was developed. At steady state, Equation 15 is replaced by

\[ r_{O_2} = \beta_1 r_1 + \beta_2 r_2 + \beta_3 r_3 \]  \hspace{1cm} (21)

to account for the additional reactions. The resulting reaction rate expressions were not integratable by standard means since they were coupled nonlinear equations. Therefore, an approximation was made to the plug flow design equation to allow an iterative approach to the integral. Assuming the reactant concentrations are constant over a very small distance along the catalyst bed, the change in pressure of a compound is equal to the reaction rate at these conditions times \( \Delta \tau \), a small increment of space time. Using this relation to estimate the inlet concentrations for the next incremental distance, or space time, the outlet concentrations can be estimated by iterating from the reactor inlet to any specified space time. Fifty increments were normally used in this calculation, although values from twenty to two
hundred gave approximately the same values.

Using the previously calculated rate constant values for the burning of 1,3-butadiene and the reoxidation of the catalyst, this model gave a predicted value of 1,3-butadiene concentration which was considerably higher than experimentally obtained at higher conversions. The predicted values of 1,3-butadiene concentrations using this model were also high at low conversion of 1-butene when a mixture of approximately 42% 1,3-butadiene and 58% 1-butene were used as the hydrocarbon feed. Therefore, a model was developed assuming that deep oxidation and oxidative dehydrogenation occur on different sites and that there is product poisoning on the OXD site. A model assuming a single site with 1,3-butadiene poisoning could not be made to fit the data. Using a Langmuir-Hinshelwood expression for the concentration of the adsorbed 1-butene species, the following rate expression was developed to replace Equation 19:

$$r_{\text{DEHY.}} = \frac{k_2 P_{\text{C}_4\text{H}_8}}{1 + K_1 P_{\text{C}_4\text{H}_8} + K_2 P_{\text{C}_4\text{H}_6}} \theta.$$ \hspace{1cm} (22)

It was determined that $K_1 P_{\text{C}_4\text{H}_8} << 1$ for all the pressures of butene encountered; therefore, Equation 22 reduces to

$$r_{\text{DEHY.}} = k_2 \frac{P_{\text{C}_4\text{H}_8}}{1 + K_2 P_{\text{C}_4\text{H}_6}} \theta.$$ \hspace{1cm} (23)
Using the iterative approach described previously, the values for the rate constants and the equilibrium constant were found to be

\[
k_2 = 4.0 \times 10^{12} e^{\frac{-45 \text{kcal/mole}}{RT}} \frac{1}{g \cdot \text{sec}} \quad (24)
\]

\[
k_3 = 1.5 \times 10^{6} e^{\frac{-30 \text{kcal/mole}}{RT}} \frac{1}{g \cdot \text{sec}} \quad (25)
\]

\[
K = 2 \times 10^{4} e^{\frac{+5 \text{kcal/mole}}{RT}} . \quad (26)
\]

Parity plots of the predicted versus actual concentration for 1,3-butadiene and CO$_2$ are shown in Figures 19 and 20. The temperature range studied was 375 to 425°C. Inlet 1-butene concentrations varied from $6 \times 10^{-5}$ to $8 \times 10^{-4}$ mole/l and several runs were made with 1-butene+1,3-butadiene mixture. Isomerization of the 1-butene to cis-2-butene and trans-2-butene occurred although their concentrations were always less than 10% of the 1-butene concentration.

The reaction of cis-2-butene was somewhat slower than that of 1-butene. Pre-exponential factors smaller by factors of 1.5 and 3 for burning and OXD, respectively, were needed to describe the reaction rate. These values were arrived at by using the model described for the reaction of 1-butene. The overall reaction of n-butane to form butenes, 1,3-butadiene and CO$_2$ was studied over a temperature range of 420 to 510°C. Typical product
Figure 19. Predicted vs. Actual 1,3-Butadiene Concentration
Figure 20. Predicted vs. Actual CO\textsubscript{2} Concentration
concentration dependence on space time is shown in Figure 21 for the reaction of n-butane with oxygen over the Ni-Sn catalyst. It was possible to get a selectivity to butenes and butadiene of 80% at 20% conversion of the n-butane. The distribution of the butene isomers with varying space time at 510°C is displayed in Figure 22. The butenes are generally not in equilibrium. At very low conversions, 1-butene is the only product observed; therefore, it is thought to be the primary product with the 2-butenes, 1,3-butadiene and CO₂ apparently being secondary products.

A modified Mars-Van Krevelen model was derived using the Langmuir adsorption redox relationship, used in the 1-butene model, as a basis. The addition of the term \( \beta q r_4 \) to Equation 21 and the rate relation for the formation of 1-butene

\[
r_4 = k_4 \frac{p_{C_4H_{10}}}{1 + K_2 p_{C_4H_6}}
\]

completes the modification. No rate expression was added for the formation of CO₂ since it does not seem to be formed directly from n-butane. The iterative technique previously discussed was used in an attempt to fit the data with the addition of only the rate constant \( k_4 \) as a parameter. The data were not successfully described by this model as shown in Figure 23. Values of \( 2 \times 10^{11} \) \( \frac{\ell}{g \cdot \sec} \) and 45 kcal/mole for the pre-exponential and the
Figure 21. Typical n-Butane OXD Product Distribution
Figure 23. Predicted vs. Actual 1-Butene Concentration
activation energy were used to generate this plot. General trends were followed by the model yet the parity plot resulted in a distinctly non-linear curve. This model assumes equal reactivity of the n-butene isomers, however, when run at 399°C with a space time of about 270 g · sec/l, 17.5% of 1-butene was converted while only 13% of an equal concentration of cis-2-butene was reacted. The selectivity to 1,3-butadiene was 60% for 1-butene, which was 4% higher than that yielded by cis-2-butene. The addition of water to the reactant stream slowed the rate of both the OXD and deep oxidation reactions. The effect was zero order with concentrations of water obtained by saturation at room temperature or higher. Equipment limitations did not allow for saturation of the reactant stream at below room temperature.

The effect of the exothermic reaction on the temperature of the catalyst was calculated in two ways. The first is the adiabatic temperature rise which gives an indication of the highest temperature attainable if all the heat released were absorbed by the gas. This temperature was 530°C for 20% conversion of n-butane to selectivities of 40,30, and 30% for CO₂, butenes and butadiene, respectively. If it is assumed under the same reaction conditions that there is enough heat transferred from the gas through the reactor wall to the outside to obtain isothermal conditions, then there needs to be only about a 4°C
temperature difference between the reaction gas mixture and the outside of the reactor wall. This assumes a heat transfer coefficient of 15 BTU/hr \cdot \text{ft}^2 \cdot \text{C} for the gas-solid interface and a thermal conductivity of 10 BTU/hr \cdot \text{ft}^2 \cdot \text{C} for the Vycor wall. Appendix IV contains the calculations of these values.

Diffusion control was deemed to be negligible since the modified spherical Thiele modulus calculated for a reaction carried out at high temperature was much less than 1. Calculation of this value is shown in Appendix V.
IV. Discussion

Reactions over Manganese Oxide Catalyst

Under most conditions, the reaction of n-butane and oxygen over the MnLiO$_x$ catalyst produced CO$_2$ as the major product. This is not surprising since manganese oxides are strong oxidizers. The activity of the catalyst was so high that perhaps the reaction would have proceeded with a better selectivity to butenes if it were run at a space time much shorter than the present flow reactor system allowed. The only interesting item noted during the investigation of this catalyst was the phenomenon occurring at high temperatures. This was well above the temperature where all the inlet oxygen (which was the limiting reactant) was depleted at the shortest space time available. Therefore, it is not known how much of the actual catalyst bed participated in the reactions. This mode of reaction is most likely caused by external diffusion effects since it only occurred in the reactor with the lower superficial velocity. According to Trimm,
Corrie, and Lam, the formation of the partially oxygenated compounds observed in the products may have caused the initiation of homogeneous gas phase reactions, thus producing the larger amounts of butenes.

The rate of OXD and burning of n-butane were affected somewhat by the concentrations of oxygen and n-butane. However, the low amounts of butenes formed caused difficulty in analyzing the OXD reaction. Since OXD is the principle reaction under investigation, study of this catalyst was discontinued in favor of the Ni-Sn catalyst.

Reactions Over Ni-Sn Catalyst

Kinetic Model

Oxidative dehydrogenation of n-butane and butenes proceeded smoothly and with good selectivity to the olefin and diolefin products. The reaction of 1,3-butadiene to form CO$_2$ in the presence of oxygen can be satisfactorily modeled using a Mars-Van Krevelen type reaction scheme. This kinetic model predicts an activation energy of 45 kcal/mole for the oxidation of the catalyst surface which is in close agreement with the value of the bond energy of oxygen on NiO given by Sazanov et al. They determined that the oxygen bond energy increased from about 20 kcal/mole to just above 40 kcal/mole when 8% of the monolayer was removed from the catalyst surface. Stone also observed a value of 43 kcal/mole for heat of adsorption of oxygen.
on an outgassed NiO surface. The predicted CO$_2$ concentrations were sensitive to the choice of activation energies of both the C$_4$H$_6$ reaction and the reoxidation of the catalyst. Therefore, their values should be within $\pm 2$ kcal/mole. The scatter in the data, shown in Figure 18, can be attributed to differences between the measured and actual reaction temperatures. This discrepancy can cause large errors due to the large activation energies.

OXD of 1-butene requires not only a Mars-Van Krevelen redox model, but also an adsorption model to describe the reaction rates. This scheme indicates that the two reactions, OXD and burning, occur on different sites since only the OXD reaction is hindered by 1,3-butadiene. No further reaction of 1,3-butadiene is believed to occur on the OXD sites. This does not contradict the assumptions made in the development of the Mars-Van Krevelen model. In the model, it is assumed that the rate of reaction of the hydrocarbon is proportional to the amount adsorbed on, or the amount coming down on the surface from the gas phase. In this case, the amount of adsorption of hydrocarbon on the OXD sites is not only proportional to its gas phase concentration, but is also dependent on the product concentration.

The oxygen involved in both reactions seems to be the same since only one reaction rate constant was needed to describe the data. The activation energies provided by
this model are not as well defined as those in the previous model because of the addition of several parameters. Errors in these activation energies are on the order of \( \pm 5 \) kcal/mole. The Gibbs free energy for the equilibrium constant can range from as low as 2 kcal/mole up to 10 kcal/mole and still yield acceptable results. However, a value of 5 kcal/mole gave the best overall effect.

The dehydrogenation of n-butane could not be adequately described using the 1-butene model modified by a reaction term for the formation of butenes from n-butane. This occurred even though it was determined that the OXD of n-butane was either the only primary reaction or that the burning of n-butane was very much slower than the dehydrogenation. The failure of this model can be traced to the fact that the butene isomers react at different rates. Although 1-butene is the primary product in the OXD of n-butene, it subsequently undergoes isomerization to the 2-butenes which, under most conditions, exist at fairly high concentrations. The model could have been changed to include these differences in rates; however, this was not done for two major reasons. First, the study of the rates of isomerization under these conditions would be very complex and involved due to the OXD and burning reactions proceeding simultaneously. Secondly, with such a large number of parameters involved, it would be very difficult to sort out the contributions of each component by simply curve-fitting the data.
Characterization of Catalyst Oxygen

Exchange experiments with C\textsuperscript{18}O\textsubscript{2} at temperatures above 350\textdegree C indicate that the oxygen on the Ni-Sn catalyst surface is quite mobile and easily exchanged. The results of these experiments attest to the fact that this mobile surface is not limited to a single monolayer, but can also involve several monolayers of oxygen.

Winter\textsuperscript{48} noted that at 225\textdegree C, NiO exchanged very little oxygen with the surface. The exchange amounted to less than 5\% of a monolayer on a catalyst with about 7 m\textsuperscript{2}/g surface area. A mechanism involving the formation of a carbonate species to explain the method of oxygen exchange was suggested by Winter. The values obtained for the amounts of mobile oxygen in these experiments are valid despite the large fraction of the inlet C\textsuperscript{18}O\textsubscript{2} bypassed. This results because the intercept of the plot is not a function of the number of inlet oxygen atoms. Bypassing may occur from two major sources, the first being channeling of reactant through the catalyst bed. Channeling is not unexpected as it is sometimes difficult to obtain uniform flow through such a small catalyst bed. The second source of bypassing is chromatographic effect. The high concentrations involved in pulse experiments may cause the surface sites to be completely covered by only a small amount of inlet CO\textsubscript{2}. If the rate of adsorption-desorption is not high enough, some of the CO\textsubscript{2}
molecules will pass by the sites before they can be adsorbed. If this effect is pronounced, an appreciable number of reactant molecules can elute from the reactor, having never been adsorbed. Higher temperatures tend to lower this effect since the rates of adsorption and desorption are increased. This is indeed the case as the fraction bypassed dropped from 0.59 to 0.41 when the temperature was raised from 380 to 452°C.

The exchange of catalyst oxygen with those of gas phase water was evident when the exchange of C¹⁸O₂ was carried out with a carrier gas saturated with water. This has also been pointed out by Novakova and Jiru and Winters. The ¹⁸O atoms left on the surface of the catalyst by the C¹⁸O₂ were removed by the water, producing a non-exchanged surface. This allowed the same number of ¹⁸O atoms from the C¹⁸O₂ to be exchanged during each pulse. In effect, the water produced an infinite amount of exchangeable oxygen in the system.

The exchange of catalyst oxygen for that in the water could be explained by a mechanism similar to the following:

\[
\begin{align*}
&\text{H}_2\text{O}(g) \\
&\downarrow \\
&\text{H}_2\text{O} + \text{H} \\
&18\text{O}(s) \rightleftharpoons 18\text{O}(s) \\
&0(s) \rightleftharpoons 0(s)
\end{align*}
\]
This mechanism was also aluded to by Wragg, Ashmore, and Hockley.\textsuperscript{51}

Marak et al.\textsuperscript{52} proposed that the reduction of the catalyst leads to the formation of Ni\textsuperscript{0} species which are then reoxidized according to:

\[ \frac{1}{2} O_2 + Ni^0 \rightarrow Ni^{2+}O^2^- \]

These workers observed a small amount of oxygen uptake when the catalyst was exposed to air at room temperature. This uptake only caused oxidation of the Ni\textsuperscript{0} on the surface and not in the bulk; however, the bulk could be reoxidized by heating to 550\textdegree C in the presence of oxygen. During a temperature programmed run, Marak et al.\textsuperscript{52} observed that reoxidation of the bulk was initiated at a temperature slightly above 200\textdegree C. These results were consistent with those obtained during this work, although the initial temperature was restricted to a lower limit of 150\textdegree C because of the weight gain due to water adsorption. It was observed that the initial weight gained by the catalyst during reoxidation increased as the temperature was increased from 250\textdegree C to 450\textdegree C. This is possibly due to the increased oxygen mobility at higher temperatures which allows the oxygen to partially diffuse from the surface into the bulk.

The oxygen mobility in this catalyst is not unexpected, as lattice oxygen mobility seems to be a common factor
for this type of oxide catalyst.\textsuperscript{53} NiO is also a p-type semi-conductor which is deficient in Ni atoms\textsuperscript{54} and therefore, may cause a higher oxygen mobility than a stoichiometric oxide. The Ni-Sn catalyst was investigated to determine if its electrical conductivity properties were similar to NiO. It is apparent that, since the charge transfer leading to conduction is between Ni\textsuperscript{2+} and Ni\textsuperscript{3+} generated by excess oxygen, adsorbing oxygen on the catalyst should increase the amount of Ni\textsuperscript{3+} present and hence the conductivity. This was indeed observed with the Ni-Sn catalyst. Measurement of the conductivity at low oxygen pressure also leads to the characterization of the catalyst as NiO, as the conductivity measured while decreasing the temperature was higher than that measured while increasing the temperature. This hysteresis behavior was also noted by Choe and Yo\textsuperscript{55} in their investigation of nickel oxide.

**Mechanism**

Butane OXD apparently proceeds in consecutive reactions over the Ni-Sn catalyst, with 1-butene being the first product in this chain. This product undergoes isomerization to the 2-butenes which, perhaps, can react further although at a slower rate. Experiments involving isotopic tracers must be performed before this point can be elucidated. The final step in the dehydrogenation chain
is the formation of 1,3-butadiene. CO₂ is formed from 1,3-butadiene, 1-butene, and probably the 2-butenes. The formation of CO₂ does not seem to proceed directly from n-butane. This reaction scheme is displayed in Figure 24.

![Figure 24. Reaction Pathway](image)

The mechanism for the OXD reactions is, by all indications, a redox cycle. Batist et al.⁷ proposed such a mechanism for the oxidative dehydrogenation of 1-butene over molybdenum-containing catalysts. Using their mechanism as a basis and modifying it to accept a Ni⁺² metal atom, a mechanism was developed for the OXD of n-butane. The use of Ni for the cation of this mechanism is not exclusive. Sn can also be used as the metal atom since it can exist in valence states of +2 and +4, therefore allowing the acceptance of the two electrons. Ni is thought to be the cation involved for two reasons: 1) NiO is known to be a selective catalyst for this reaction,²⁷ and 2) Ni⁰ was
observed during OXD of n-butane over a similar catalyst.\textsuperscript{52} This speculative mechanism is shown in Figure 25. The adsorption of the hydrocarbon is thought to take place on a coordination site (□). The lines drawn between atoms in Figure 25 do not necessarily denote the traditional chemical bond. The redox cycle begins with the adsorption of butane which then loses a hydrogen atom to a neighboring oxygen atom. It is believed that this is a lattice oxygen because of information gathered by Marak et al.\textsuperscript{52} and Keulks et al.\textsuperscript{56} Evidence is available indicating that an adsorbed O\textsuperscript{−} species is responsible for the hydrogen abstraction on ferrite catalysts.\textsuperscript{57} This is also suggested for reactions on molybdenum oxide\textsuperscript{58} and magnesium oxide\textsuperscript{59} when using NO to produce the desired oxygen on the surface. However, in light of such a high activation energy for oxidation (~45 kcal/mole), it is unlikely that this is the case in the present study.

The charged species formed by the abstraction of the hydrogen can then transfer its charge to the Ni atom. This charge may not be confined to the immediate Ni atom, but may be transferred to neighboring metal atoms in a similar manner to that which causes conductivity in the solid. The uncharged hydrocarbon molecule is then able to desorb under certain conditions to produce the C\textsubscript{4}H\textsubscript{9} species observed in the TPD experiments. This species is also likely to cause complete oxidation in the gas phase.
Figure 25. Proposed Mechanism
Sn$^{+4}$/Sn$^{+2}$ could also be involved as cation.
The adsorbed $C_4H_9$ species is then thought to lose another hydrogen to a lattice oxygen. The resulting system is quite probably very unstable, with three negative charges in close proximity. This may cause rapid reverse reaction, accounting for the H-D exchange found in the olefin product. This exchange would occur because of the large concentration of highly mobile hydroxyl groups on the surface from adsorbed water. The $C_4H_8^-$ species transfers an electron to the nickel, creating the olefin product which then desorbs. After the hydrogen of one $OH^-$ group transfers to a second hydroxyl group, water can desorb. This process is reversible, as observed during the $C^{18}O_2$ exchange experiments, and may account for the inhibition of the rate of dehydrogenation by water. This is due to partial coverage of the lattice oxygen by hydrogen, making them unavailable for hydrogen abstraction.

The final step in the redox cycle is the reaction of gas phase oxygen with an anion vacancy (■) to replace that desorbed in the water. This oxygen is incorporated into the lattice and oxidizes the nickel atom back to its original $Ni^{2+}$ state. The reaction of butenes most likely proceeds via the same mechanism. However, the $C_4H_7$ species will probably not be desorbed because of the strong $\pi$ allylic bond which can form.$^7$
V. Summary

The oxidative dehydrogenation of n-butane is a viable route for the production of 1,3-butadiene from non-crude sources. Such a process is highly dependent on the selectivity of the catalyst used in the system. Two possible catalysts for n-butane OXD were examined in this study.

The first catalyst, MnLiO\textsubscript{x}, showed very poor selectivity with very high activity under normal conditions. A high selectivity mode existed when the reaction was carried out at high inlet concentrations of butane and oxygen while running in a large cross-sectional reactor. This mode of operation was accompanied by the formation of partially oxygenated products which may have induced gas phase reactions. This phenomenon was not encountered when employing a reactor with 1/6 of the cross-sectional area; therefore, it is thought that the high selectivity mode was initiated by external diffusion effects due to flow in the laminar regime.
N-Butane OXD over a Ni-Sn catalyst proceeded quite readily, although its activity was considerably less than that of the MnLi0.7x catalyst. On the other hand, selectivities to butenes and butadienes over this catalyst were high, easily reaching 80% at 20% conversion of n-butane. The kinetics of the reactions over this catalyst were best described by a Mars-Van Krevelen type model. The kinetics of the overall reaction were not completely discerned, as the effects of the isomerization to and reaction of the 2-butenes were not distinguished. The activation energy of oxygen reaction (45 kcal/mole) in the kinetic model agrees with several values obtained by other workers for the bond energy of oxygen on NiO.

It was established that the reaction proceeds through a 1-butene intermediate which then isomerizes to the 2-butenes, dehydrogenates to butadiene or burns to CO₂. A mechanism involving lattice oxygen was proposed for the oxidative dehydrogenation of both n-butane and 1-butene. The hydrocarbon proceeds to transfer two electrons to the Ni²⁺ reducing it to the metallic Ni⁰ state. Gas phase oxygen then reoxidizes the nickel to reform the Ni²⁺ species and replaces the O²⁻ lattice oxygen.
Appendix I.

Oxygen Exchange Between $^{18}\text{O}_2$ and Ni-Sn Surface

Exchange of $\text{O}_2$ atoms from a CO$_2$ molecule with those on the catalyst surface can be modeled by the following reactions:\textsuperscript{60}

\[
\begin{align*}
\text{CO}_2 & \quad \text{Surface} \\
1) & \quad {}^{18}\text{O} \rightarrow {}^{16}\text{O} \\
2) & \quad {}^{16}\text{O} \rightarrow {}^{18}\text{O} \\
3) & \quad {}^{16}\text{O} \rightarrow {}^{16}\text{O} \\
4) & \quad {}^{18}\text{O} \rightarrow {}^{18}\text{O}
\end{align*}
\]

The extent of the oxygen involvement in this derivation is not limited to one monolayer. Assuming the exchange is isothermal and in equilibrium, reactions 1 and 2 must be equal. This can be expressed by:

\[
r^{18}\text{O} = r^{16}\text{O} \tag{28}
\]

with the rates being those experienced by the CO$_2$. Reactions 3 and 4 yield no net change.

The following terms will be used in this derivation:

\begin{align*}
N &= \text{Total number of exchanges} \\
F &= \text{fraction of surface which is } {}^{18}\text{O} \\
\theta &= \text{no. of } {}^{18}\text{O} \text{ atoms per CO}_2 \text{ molecule} \\
(2-\theta) &= \text{no. of } {}^{16}\text{O} \text{ atoms per CO}_2 \text{ molecule}
\end{align*}
\[ n = \text{no. of } \text{CO}_2 \text{ atoms per pulse} \]
\[ 18O_s = \text{no. of } 18O \text{ atoms on surface} \]
\[ 18O_g = \text{no. of } 18O \text{ atoms in gas phase} \]
\[ \Sigma_{\infty} = \text{total number of available oxygen on surface} \]

The rates of oxygen exchange for the CO\(_2\) molecules are equal to

\[ r^{16}O = N(2-\theta)F \quad (29) \]
\[ r^{18}O = N\theta(1-F) \quad (30) \]

Equating these rates yields:

\[ (2-\theta)F = \theta(1-F) \quad (31) \]

which leads to:

\[ \theta = 2F. \quad (32) \]

The number of \(^{18}O\) atoms per pulse is equal to

\[ 18O_g = n\theta \quad (33) \]

and the fraction of the surface that is \(^{18}O\) is given by:

\[ F = \frac{18O_s}{\Sigma_{\infty}}. \quad (34) \]

Combining Equations 32 through 24 gives the expression:

\[ n\theta = 2n \frac{18O_s}{\Sigma_{\infty}} = 18O_g. \quad (35) \]
For each new pulse which is added, 2n O atoms are injected into the system. A material balance around the system gives:

\[ \frac{18O_j}{S} + \frac{18O_j}{G} = 2n + \frac{18O_{j-1}}{S} \]  

(36)

where \( j \) is the pulse number. Assuming Equation 35 is valid for each pulse and substituting it into Equation 36, produces

\[ \frac{18O_j}{S} + 2n \frac{18O_j}{S}/\Xi_\infty = 2n + \frac{18O_{j-1}}{S} \]  

(37)

After much algebraic manipulation, this equation can be rearranged to give

\[ \frac{18O_j}{S} = \frac{\alpha \Xi_\infty + \frac{18O_{j-1}}{S}}{\alpha + 1} \]  

(38)

where:

\[ \alpha = 2n/\Xi_\infty. \]  

(39)

Define the amount of \( ^{18}O \) initially on the surface as:

\[ \frac{18O_0}{S} = S\alpha \Xi_\infty = S2n. \]  

(40)

The amount of \( ^{18}O \) on the surface after each new pulse is:

\[ \frac{18O_1}{S} = \frac{\alpha \Xi_\infty (1+S)}{1 + \alpha} \]  

(41)

\[ \frac{18O_2}{S} = \frac{\alpha \Xi_\infty [(1+\alpha) + 1 + S]}{(1+\alpha)^2} \]  

(42)
\[
18_0 \frac{3}{S} = \frac{\alpha \Sigma_\infty [(1+\alpha)^2 + (1+\alpha) + 1 + S]}{(1+\alpha)^3}
\] (43)

By induction it can be shown that

\[
18_0 \frac{3}{S}^j = \frac{\alpha \Sigma_\infty}{(1+\alpha)^j} [S + \sum_{i=1}^{j-1} (1+\alpha)^i].
\] (44)

The term \[\sum_{i=0}^{j-1} (1+\alpha)^i\] represents the sum of the \(n\) terms of a geometric progression of common ratio \(r = (1+\alpha)\) with the first term \(a_1 = 1\) and the \(n^{th}\) term \(a_n = (1+\alpha)^{j-1}\).

For such a geometric progression, the sum of the \(n\) terms is given by

\[
S_n = a_1 \frac{1-r^n}{1-r} = 1 - \frac{(1+\alpha)^j}{1 - (1+\alpha)}
\] (45)

therefore,

\[
18_0 \frac{3}{S}^j = \frac{\alpha \Sigma_\infty}{(1+\alpha)^j} [S + \frac{1 - (1+\alpha)^j}{1 - (1+\alpha)}].
\] (46)

Defining \(\Sigma\) as the cumulative number of \(18_0\) atoms given to the surface, the following expressions can be generated

\[
\Sigma = 18_0 \frac{3}{S}^j - 18_0 \frac{3}{S}^0
\] (47)

\[
\Sigma = \frac{\alpha \Sigma_\infty}{(1+\alpha)^j} [S + \frac{1 - (1+\alpha)^j}{1 - (1+\alpha)}] - Sa\Sigma_\infty.
\] (48)

The latter equation can be rearranged to give:

\[
\Sigma = \frac{\alpha \Sigma_\infty}{(1+\alpha)^j} [(Sa-1)(1 - (1+\alpha))].
\] (49)
The reciprocal of this expression yields:

\[
\frac{1}{\Sigma} = \frac{1}{\Sigma_\infty} \left[ \frac{1}{(1-S\alpha)} - \frac{1}{(1(Sa)(1-(1+S\alpha)^j)} \right].
\] (50)

Expanding \((1+S\alpha)^j\) into a Taylor series and neglecting all terms above 1st order generates:

\[
\frac{1}{\Sigma} = \frac{1}{\Sigma_\infty} \left[ \frac{1}{(1-S\alpha)} - \frac{1}{(1-S\alpha)(j\ln(1+S\alpha))} \right].
\] (51)

A plot of \(1/\Sigma\) versus \(1/j\) will produce the following information:

\[
\text{slope} = \frac{1}{(1-S\alpha) n(1+S\alpha)} \frac{1}{\Sigma_\infty}
\] (52)

\[
\text{intercept} = \frac{1}{\Sigma_\infty} \left[ \frac{1}{1-S\alpha} \right].
\] (53)

When starting with a clean surface, the value of \(S = 0\), therefore:

\[
\text{slope} = \frac{1}{\Sigma_\infty} \left[ \frac{1}{j\ln(1+S\alpha)} \right].
\] (54)

\[
\text{intercept} = \frac{1}{\Sigma_\infty}.
\] (55)

**Calculations**

The number of oxygen atoms per catalyst monolayer can be estimated from the \(N_2\) BET surface area of the catalyst divided by the area per oxygen atom. Assuming \(10^{0.2}\) per oxygen, this yields
\[
\frac{\text{O atoms}}{\text{monolayer}} = \frac{49 \text{ m}^2}{\text{g} \cdot \text{cat-monolayer}} \times \frac{10^2 \text{ A}^2}{\text{m}^2} \times \frac{1 \text{ atom O}}{10 \text{ A}^2}
\]

\[
\frac{\text{O atoms}}{\text{monolayer}} = 4.9 \times 10^{20} \frac{\text{atom O}}{\text{monolayer-g \cdot cat}}
\]

This can also be expressed as \( 8.14 \times 10^{-4} \) mole O/monolayer-g \cdot cat.

The number of moles of oxygen atoms in a monolayer of catalyst charge is:

\[
\frac{\text{moles O}}{\text{monolayer}} = 8.14 \times 10^{-4} \frac{\text{mole O}}{\text{monolayer-g \cdot cat}} \times 0.1085 \text{ g \cdot cat}
\]

\[
\frac{\text{moles O}}{\text{monolayer}} = 8.83 \times 10^{-5} \text{ mole O/monolayer}.
\]

Using the intercept of the plot \( 1/\Sigma \) versus \( 1/j \) equal to \( 6.09 \times 10^3/\text{mole O} \) gives the amount of available oxygens

\[
\Sigma_\infty = 1 \text{ mole O} / 6.09 \times 10^3 = 1.64 \times 10^{-4} \text{ moles O}.
\]

To obtain the number of corresponding monolayers, \( \Sigma_\infty \) is multiplied by

\[
\# \text{ monolayers} = 1.64 \times 10^{-4} \text{ moles O} \times \frac{1 \text{ monolayer}}{8.83 \times 10^{-5} \text{ mole O}}
\]

\[
\# \text{ monolayers} = 1.86.
\]
Appendix II.

Derivation of Mars-Van Krevelen Kinetics

The kinetic models discussed below all use a model developed by Mars and Van Krevelen$^{44}$ as a basis. This model was developed to explain the kinetics of the partial oxidation of aromatic compounds. A redox cycle is used in which the hydrocarbon reacts with the catalyst to reduce the surface. Gas phase oxygen then reoxidizes the catalyst to close the cycle. To develop this model, the following assumptions need to be made:

1) the reaction of the hydrocarbon is proportional to the amount of hydrocarbon adsorbed on the surface or the amount striking the surface from the gas phase,

2) the reaction of the hydrocarbon is proportional to the coverage of oxygen on the catalyst,

3) the reoxidation reaction is proportional to the fraction of the surface not covered by oxygen, and

4) equilibrium is established between the reduction and oxidation of the catalyst.

Butadiene Burning Kinetics

The burning of butadiene:

\[ C_4H_6 + 5.5O_2 + 4CO_2 + 3H_2O \]

yields only one reduction and one oxidation step for the catalyst. The rates of these processes can be expressed as:

\[ r_1 = k_1 P_{C_4H_6}^\theta \]

(56)
and
\[ r_{O_2} = k_{O_2} P_{O_2} (1 - \theta) \quad (57) \]
for the reaction of the hydrocarbon and oxygen, respectively. The fractional coverage of oxygen is given by \( \theta \). At steady state the rate of these reactions are proportional to each other, differing by only the ratio of the stoichiometric coefficients. This is expressed as:
\[ r_{O_2} = \beta_1 r_1 \quad (58) \]
where \( \beta_1 \) is the ratio of the oxygen to hydrocarbon coefficients (for this case 5.5). Substituting Equation 56 and 57 into this equilibrium relationship yields:
\[ k_{O_2} P_{O_2} (1 - \theta) = \beta_1 k_1 P_{C_4H_6} \theta \quad (59) \]
which can be solved for \( \theta \):
\[ \theta = \frac{k_{O_2} P_{O_2}}{\beta_1 k_1 P_{C_4H_6} + k_{O_2} P_{O_2}} \quad (60) \]
Inserting this result back into Equation 56 gives an expression for the rate of reaction of hydrocarbon which is:
\[ r_1 = \frac{k_1 P_{C_4H_6} k_{O_2} P_{O_2}}{\beta_1 k_1 P_{C_4H_6} + k_{O_2} P_{O_2}} \quad (61) \]
This relationship can be integrated in the plug flow reactor design equation to give the space time (\( \tau \)) as a function of inlet and outlet concentrations of oxygen and hydrocarbon.
\[ \tau = \frac{1}{k_1} \ln \left( \frac{P_{\text{C}_4\text{H}_6,0}}{P_{\text{C}_4\text{H}_6,f}} \right) + \frac{1}{k_{O_2}} \ln \left( \frac{P_{O_2,0}}{P_{O_2,f}} \right) \]  
\[ (62) \]

The subscripts \( o \) and \( f \) refer to the initial and final pressures of the respective compounds. This equation can be expressed in terms of oxygen conversion \( (x) \) by:

\[ \tau = -\frac{1}{k_1} \ln [1 - \left( \frac{P_{O_2,0}}{P_{\text{C}_4\text{H}_6,0}} \right)^{\frac{x}{\beta_1}}} - \frac{1}{k_{O_2}} \ln [1-x]. \]  
\[ (63) \]

### 1-Butene OXD

The model derived for the reaction of 1-butene with oxygen:

\[ \text{C}_4\text{H}_8 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} \]

\[ \text{C}_4\text{H}_8 + 6 \text{O}_2 \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O} \]

\[ \text{C}_4\text{H}_6 + 5.5 \text{O}_2 \rightarrow 4\text{CO}_2 + 3\text{H}_2\text{O} \]

uses the previously discussed 1,3-butadiene model with the addition of two equations. The first is to account for the formation of 1,3-butadiene from 1-butene and can be expressed as:

\[ r_2 = k_2 P_{\text{C}_4\text{H}_8}^\theta. \]  
\[ (64) \]

The second expression is the rate of burning of the 1-butene which is given by:

\[ r_3 = k_3 P_{\text{C}_4\text{H}_8}^\theta. \]  
\[ (65) \]
To account for the additional reactions, Equation 58 must be modified to yield:

$$r_0 = \beta_1 r_1 + \beta_2 r_2 + \beta_3 r_3$$  \hspace{1cm} (66)

The respective rate equations can again be substituted into the equilibrium expression, Equation 66, and solved for $\theta$ to give:

$$\theta = \frac{k_{02}^{o} P_{02}}{k_{1}^{o} C_{4}H_{6} + k_{2}^{o} C_{4}H_{8} + k_{3}^{o} C_{4}H_{6} + k_{02}^{o} P_{02}}.$$  \hspace{1cm} (67)

As before, this result can be inserted into the individual rate equations which produces rate expressions similar to Equation 61 although the denominator contains terms for all the reactions instead of just the burning of 1,3-butadiene.

This model can be modified to account for the effect of 1,3-butadiene on the amount of 1-butene adsorbed on the surface. A Langmuir type expression which assumes competitive adsorption of the hydrocarbons on the OXD site can be incorporated into the rate equation giving the rate of reaction of 1-butene to form 1,3-butadiene equal to:

$$r_2 = k_2 \left[ \frac{P_{C_{4}H_{8}}}{1 + k_{1}^{o} P_{C_{4}H_{8}} + k_{2}^{o} P_{C_{4}H_{6}}} \right] \theta$$  \hspace{1cm} (68)
where \( K_1 \) and \( K_2 \) are equilibrium constants of adsorption-desorption. \( K_1 \) was determined to be very small; therefore, the expression reduces to:

\[
r_2 = k_2 \left( \frac{P_{C_4H_8}}{1 + K_2 P_{C_4H_6}} \right)^\theta.
\]  

(69)

It can be seen that this expression is the same as Equation 64 with the terms \( P_{C_4H_8}/1 + K_2 P_{C_4H_6} \) in place of the pressure of 1-butene. This leads to the following rate expressions:

\[
r_1 = \frac{k_1 P_{C_4H_6} k_0 P_{O_2}}{\beta_1 k_1 P_{C_4H_6} + \beta_2 k_2 \left( \frac{P_{C_4H_8}}{1 + K_2 P_{C_4H_6}} \right) + \beta_3 k_3 P_{C_4H_8} + k_0 P_{O_2}}
\]  

(70)

\[
r_2 = \frac{k_2 \left( \frac{P_{C_4H_8}}{K + K_2 P_{C_4H_6}} \right) k_0 P_{O_2}}{\beta_1 k_1 P_{C_4H_6} + \beta_2 k_2 \left( \frac{P_{C_4H_8}}{1 + K_2 P_{C_4H_6}} \right) + \beta_3 k_3 P_{C_4H_8} + k_0 P_{O_2}}
\]  

(71)

\[
r_3 = \frac{k_3 P_{C_4H_8} k_0 P_{O_2}}{\beta_1 k_1 P_{C_4H_6} + \beta_2 k_2 \left( \frac{P_{C_4H_8}}{1 + K_2 P_{C_4H_6}} \right) + \beta_3 k_3 P_{C_4H_8} + k_0 P_{O_2}}
\]  

(72)
n-Butane OXD

The reaction of n-butane and oxygen can be modeled by adding only a term for the formation of 1-butene:

$$C_4H_{10} + \frac{1}{2} O_2 \rightarrow C_4H_8 + H_2O.$$ 

No terms were needed for the formation of CO$_2$ or 1,3-butadiene since they were determined to be secondary products.

The reaction rate of n-butane is given by:

$$r_4 = k_4 \frac{P_{C_4H_{10}}}{1 + \frac{P_{C_4H_6}}{K_2}}$$

including the product poisoning term. An expression for $\theta$ can be derived by using the steady state equation:

$$r_O = \beta_1 r_1 + \beta_2 r_2 + \beta_3 r_3 + \beta_4 r_4$$

which yields

$$\theta = \frac{k_0 P_{O_2}}{\beta_1 k_1 P_{C_4H_6} + \beta_2 k_2 \alpha_1 + \beta_3 k_3 P_{C_4H_8} + \beta_4 k_4 \alpha_2 + k_0 P_{O_2}}$$

where:

$$\alpha_1 = \frac{P_{C_4H_8}}{1 + K_2 P_{C_4H_6}}$$

$$\alpha_2 = \frac{P_{C_4H_{10}}}{1 + K_2 P_{C_4H_6}}.$$
This expression can be transformed into the rate equations, as before, by multiplying by the appropriate factors shown in Equations 56, 65, 68, and 73.
Appendix III.

Estimation of Flow Regime in Reactor Bed

The estimation of the flow regime in a packed bed makes use of the modified Reynolds Number \( \text{Re'} \) given by:

\[
\text{Re'} = \frac{D_p G}{\mu}
\]  

(78)

where:
\( D_p \) = particle diameter
\( G \) = mass flow rate per unit cross sectional area
\( \mu \) = viscosity of the gas.

Assuming inlet concentrations of 40% butane, 20% oxygen, and 40% helium, the arithmetic mean molecular weight is equal to:

\[ \text{M.W.} = 31.2 \text{ g / mole.} \]

A linear extrapolation of known viscosities\(^1\) yields the following values at 360\(^\circ\)C:

\[ 
\mu_B = 159 \mu p \\
\mu_{\text{He}} = 327 \mu p \\
\mu_{O_2} = 353 \mu p.
\]

A mean value of 265 \( \mu p \) for the mixture was calculated. The viscosity of butane was obtained by assuming its value was the same as butene.

The diameter of the particles can be estimated knowing that 20/40 mesh sieves have a mean opening of 0.063 cm. The
highest flow rate attainable with this inlet composition is 50 SCCM due to equipment limitations. The maximum molar flow rate is:

\[ \dot{N} = 50 \frac{\text{cc}}{\text{min}} \times \frac{\text{mole}}{22,400 \text{ cc}} = 2.2 \times 10^{-3} \text{ mole/min.} \]

the mass flow rate is then equal to:

\[ \dot{M} = 2.2 \times 10^{-3} \frac{\text{mole}}{\text{min}} \times \frac{31.2 \text{ g}}{\text{mole}} \times \frac{1 \text{ min}}{60 \text{ sec}} \]

\[ \dot{M} = 1.1 \times 10^{-3} \text{ g/sec.} \]

To obtain a value for \( G \) this must be divided by the cross sectional area of the reactor. For the two reactors this yields:

\[ G_1 = 1.1 \times 10^{-3} \text{g/sec} \times \frac{1}{1.2 \text{ cm}^2} = 9.2 \times 10^{-4} \frac{\text{g}}{\text{sec} \cdot \text{cm}^2} \]

\[ G_2 = 1.1 \times 10^{-3} \text{g/sec} \times \frac{1}{0.2 \text{ cm}^2} = 5.5 \times 10^{-3} \frac{\text{g}}{\text{sec} \cdot \text{cm}^2} \]

Substituting into Equation 78 gives a modified Reynolds Number of:

\[ \text{Re}_1' = 0.063 \text{ cm} \times 9.2 \times 10^{-4} \frac{\text{g}}{\text{sec} \cdot \text{cm}^2} / 2.65 \times 10^{-4} \frac{\text{g}}{\text{sec} \cdot \text{cm}^2} \]

\[ \text{Re}_1' = 0.22 \]

and

\[ \text{Re}_2' = 0.063 \text{ cm} \times 5.5 \times 10^{-3} \frac{\text{g}}{\text{sec} \cdot \text{cm}^2} / 2.65 \times 10^{-4} \frac{\text{g}}{\text{sec} \cdot \text{cm}^2} \]

\[ \text{Re}_2' = 1.31 \]
Both these values are well below the transition region which begins at a Re' of about 10. Therefore, the flow in both of the reactors is laminar.
Appendix IV.

**Calculation of Heat Effects**

The method of calculating the heat of reaction and heat capacities were those described by Smith and Van Ness.\(^6\) Individual heats of reaction at 450°C were -27.8 kcal/mole, -58.2 kcal/mole and -634.6 kcal/mole for the reaction of n-butane to form 1-butene, 1,3-butadiene and CO\(_2\), respectively.

**Calculation of the Adiabatic Temperature Rise**

The adiabatic temperature rise is the temperature difference of the inlet and outlet gas if all the heat released during the reaction were absorbed by the product stream. In this calculation, it is assumed that the reaction takes place at 450°C then the products increase in temperature. Assume the following reaction conditions:

Inlet concentrations: 70% He  
10% Butane  
10% CO\(_2\)  
10% H\(_2\)O  

Total Flow Rate = 25 SCCM = 1.1 x 10\(^{-3}\) mole/min

Selectives: 40% CO\(_2\)  
30% 1-Butene  
30% 1,3-Butadiene  

The overall heat of reaction is:
\[ \Delta H_T = 0.4 \times (-634.6) + 0.3 \times (-27.8) + 0.3 \times (-58.2) \frac{\text{kcal}}{\text{mole-Butane}} \]

\[ \Delta H_T = 279.6 \text{ kcal/mole-Butane} \]

Using a basis of 100 moles of inlet gas, the total heat released is:

\[ Q = 279.6 \frac{\text{kcal}}{\text{mole-Butane}} \times 0.2 \times 10 \text{ moles Butane} \]

\[ Q = 559.2 \text{ kcal} \]

An estimated outlet mole distribution for 100 moles inlet using the stoichiometric equations is given in Table 7. From these values the heat capacity of the outlet gas is estimated to be:

\[ C_p = 542 + 7.38 \times 10^{-1} T - 2.14 \times 10^{-4} T^2 \frac{\text{cal}}{\text{K}}. \]

From the equation

\[ Q = \int_{T_1}^{T_2} C_p dt \quad (79) \]

the dependence of the heat absorbed with temperature can be found:

\[ Q = 542[T-723] + \frac{7.38 \times 10^{-1}}{2}[T^2-723^2] - \frac{2.14 \times 10^{-4}}{3}[T^3-723^3] \text{cal}. \]

This can be solved by trial and error for the amount of heat released during the reaction \( Q_T = 559.2 \text{ kcal} \). The final temperature reached for these conditions is 979°C which yields an adiabatic temperature rise of:

\[ \Delta T_{\text{ADB}} = 979 - 450^\circ\text{C} = 529^\circ\text{C}. \]
Table 7. Estimated Outlet Mole Distribution

<table>
<thead>
<tr>
<th>Compound</th>
<th>Moles in Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>70</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>8</td>
</tr>
<tr>
<td>1-C₄H₈</td>
<td>0.6</td>
</tr>
<tr>
<td>1,3-C₄H₆</td>
<td>0.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.2</td>
</tr>
<tr>
<td>O₂</td>
<td>3.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>15.8</td>
</tr>
</tbody>
</table>

102.1

Calculation of Heat Transfer

The calculation of the temperature difference between the reacting gas and the outside of the reactor wall needed for isothermal conditions can be effected by noting the heat transferred out of the system. Using the same conditions as those for the adiabatic temperature rise calculations, the heat needed to be transferred per 100 moles of inlet gas is 559.2 kcal. The time for 100 moles of gas to pass through the system is:

\[ t = \frac{100 \text{ moles} \times 1.1 \times 10^{-3}/\text{min} \times \frac{\text{hr}}{60 \text{ min}}}{\text{hr}} \]

\[ t = 1515 \text{ hr}. \]

The amount of heat transferred per hour is:

\[ q = \frac{559.2 \text{ kcal}}{1515 \text{ hr}} \times \frac{\text{Btu}}{0.252 \text{ kcal}} = 1.46 \text{ Btu/hr}. \]
Assume a heat transfer coefficient for the reactant gas stream to the Vycor wall of \(15 \frac{\text{BTU}}{\text{hr} \cdot \text{ft}^2 \cdot \text{oC}}\) and a thermal conductivity of \(10 \frac{\text{BTU}}{\text{hr} \cdot \text{ft} \cdot \text{oC}}\) for the Vycor glass. The amount of heat transferred to the wall must equal the heat transferred through the wall. The heat transferred to the reactor wall is:

\[
q = h_i A_i (T_1 - T_2)
\]  
(80)

and through the wall is:

\[
q = \frac{k A_{\text{ln}} (T_2 - T_3)}{\Delta r}
\]  
(81)

where:
- \(h_i\) = inside heat transfer coefficient
- \(A_i\) = inside area
- \(A_{\text{ln}}\) = log mean area
- \(\Delta r\) = difference between the inside and outside radius
- \(k\) = thermal conductivity
- \(T_1\) = reactant gas temperature
- \(T_2\) = inside wall temperature
- \(T_3\) = outside wall temperature.

The log mean area is calculated by:

\[
A_{\text{ln}} = \frac{2\pi (r_o - r_i) L}{\text{ln}(r_o/r_i)}
\]  
(82)

where:
- \(r_o\) = outside radius
\( r_i = \text{inside radius} \)
\( L = \text{length of wall}. \)

The values for the various parameters are:
\( r_i = 0.7 \text{ cm} \)
\( r_o = 0.8 \text{ cm} \)
\( L = 5.0 \text{ cm} \)
\( A_{2m} = 23.53 \text{ cm}^2 = 2.53 \times 10^{-2} \text{ft}^2 \)
\( A_i = 2.37 \times 10^{-2} \text{ft}^2 \)

From Equations 80 and 81, the temperature differences can be calculated:

\[
T_1 - T_2 = \frac{q}{h_i A_i} \tag{82}
\]
\[
T_2 - T_3 = \frac{q}{k A_{2m}} \tag{83}
\]

Employing the above values in these equations gives the values:

\( T_1 - T_2 = 4.2^\circ C \)

and

\( T_2 - T_3 = 0.02^\circ C. \)

It can be seen that there is essentially no temperature gradient across the reactor wall. The temperature difference between the actual reaction temperature and that which is measured should not exceed about \( 4^\circ C. \)
Appendix V.

Calculation of Modified Spherical Thiele Modulus

In the evaluation of diffusion control in a catalyzed reaction, the parameter \( \bar{\theta}_S \) can provide some insight. This parameter is defined as:\(^6^5\)

\[
\bar{\theta}_S = \frac{R^2}{D_{\text{eff}}} \left( - \frac{1}{V_{\text{cat}}} \frac{dn}{dt} \right) \frac{1}{C_s}
\]

where:

\( R = \) particle radius

\( D_{\text{eff}} = \) effective diffusivity

\( V_{\text{cat}} = \) volume of catalyst

\( \frac{dn}{dt} = \) rate of reaction

\( C_s = \) surface concentration.

Assume the reactant (butane) inlet concentration is \( 1 \times 10^{-3} \) mole/\( \ell \) and the reaction proceeds to 20% conversion. This could be accomplished at higher temperatures with a total flow rate of 0.2 \( \ell/\text{min} \). The rate of reaction is equal to:

\[
\frac{dn}{dt} = \frac{0.2 \times 10^{-3} \text{ mole}}{\ell \cdot \text{gas}} \times \frac{0.2 \ell \cdot \text{gas}}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ sec}}
\]

\[
\frac{dn}{dt} = 6.7 \times 10^{-7} \text{ mole/sec}
\]

Using a mean value for the opening of 30/40 mesh sieves,\(^6^0\) the radius of the particle is 0.0254 cm. The average concentration is \( 9 \times 10^{-7} \) mole/cm\(^3\) and \( D_{\text{eff}} \) is assumed to be \( 1 \times 10^{-2} \) cm\(^2\)/sec. The volume of the standard 0.7g catalyst bed is approximately 0.6 cc. Assuming a 40% void fraction,
the catalyst volume is 0.36 cc. Applying these values to Equation 84 yields:

$$\bar{\phi}_s = \frac{(0.0254 \text{ cm})^2}{1 \times 10^{-2} \frac{\text{cm}^2}{\text{sec}}} \left[ \frac{6.7 \times 10^{-7} \text{mole/sec}}{0.36} \right] \frac{1}{9 \times 10^{-7} \frac{\text{mole}}{\text{cc}}}$$

$$\bar{\phi}_s = 0.13.$$  

Since this value is much less than unity, it can be assumed no diffusion control exists.
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