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STUDIES ON THE SELECTIVE OXIDATION ACTIVITY OF IRON-TELLURIUM-OXIDE CATALYSTS

The Louisiana State University and Agricultural and Mechanical Col. Ph.D. 1983

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STUDIES ON THE SELECTIVE OXIDATION ACTIVITY OF FE-TE-O CATALYSTS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemical Engineering

by

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ABSTRACT

The selective oxidation of 1-butene to 1,3-butadiene and propylene to acrolein are important industrial processes. One of the critical factors which determines the feasibility of these processes is selectivity.

Since iron oxide has shown potential as a component of a selective mixed oxide catalyst, and tellurium has been used as a promoter for selective oxidation catalysts, this study focusing on the development and investigation of an iron-tellurium mixed oxide catalyst for the selective oxidation of propylene and 1-butene has been undertaken. The study includes kinetic and mechanistic investigations, and simultaneous activity/selectivity and spectroscopic measurements for iron-tellurium catalysts have been developed. The purpose of this work is to characterize the role of tellurium in iron-tellurium mixed oxide selective oxidation catalysts, and to gain insight into other tellurium containing catalysts.

Catalysts containing only iron and tellurium have been prepared and the active phase identified by X-ray powder diffraction as Fe₂TeO₆. The catalysts show very good yields for the oxidation of 1-butene to butadiene and propylene to acrolein. The reaction orders and activation energies for the oxidation of propylene and 1-butene to both selective and extensive oxidation products have been determined. Selective oxidations of propylene and 1-butene are both first- and zero-order in hydrocarbon and oxygen partial pressures, and with activation energies of 35 and 33 kcal/mole, respectively. Extensive oxidation of propylene and 1-butene are first-order and half-order, respectively, in both
hydrocarbon and oxygen partial pressures, and with activation energies of 41 and 29 kcal/mole, respectively. Pulse experiments have shown that the catalyst has different sites for the oxidation and isomerization reactions. However, the active sites for the selective and extensive oxidation reactions appear to be identical at first and rate-determining step. From Mössbauer and IR spectroscopies we infer that iron does not undergo oxidation state shifts during the selective oxidation process. Tellurium (VI) is thought to be the active species while iron simply provides a suitable environment for tellurium (VI) to exist.
I. INTRODUCTION

In the petrochemical industries, plastics, man-made fibers and synthetic rubbers are three major fields of manufacture. In 1982, about thirty-eight billion pounds of these three products were produced [1], which corresponded to 25 percent of the total amount of twenty-nine organics in the top fifty chemicals. Besides those which are made directly from upstream products, such as polyethylene, polypropylene and others, raw materials for these three fields can be obtained by certain kinds of reactions which convert upstream products to products that are needed for further treatment. Catalytic oxidation, dehydrogenation, and ammoxidation are examples of these kinds of reactions.

D.J. Hucknall [2] has pointed out that homogeneous oxidations have received a great deal of attention in terms of developing these as industrial processes. Unfortunately, homogeneous gas-phase oxidations are generally nonselective. Therefore, heterogeneous catalytic processes have the majority of the market for quite a long time. At present, heterogeneous processes play very important roles in the petrochemical industry. Most of the petrochemical processes need to utilize heterogeneous catalysts in order to make the desired products, increase selectivities, or save energy by means of reducing the reaction temperature.

The need for organic chemicals for rubber processing were predicted to rise 3 to 7% (127,000 to 132,000 metric tons) in 1983 [3]. 1,3-Butadiene is used mainly for the manufacture of styrene-butadiene rubber and polybutadiene rubbers, which corresponds to 56 and 19% respectively,
of the total volume of synthetic rubbers. 1,3-Butadiene may be produced by steam cracking, dehydrogenation and selective oxidation processes.

1,3-Butadiene produced from steam cracking is not a primary product. It is a by-product, or a so-called co-product, of the ethylene steam cracking process. According to Chemical Market Associates, Inc. [4] its yields from steam cracking processes were 2.5, 7.2, 13.5, and 26.2 percent of ethylene production from the feedstocks ethane, propane, light naphtha and gas oil, respectively. The amount of ethylene made from steam cracking of light feedstocks was predicted to increase from 71% to about 74% in 1982. Thus, steam cracking processes produced about 2.3 billion pounds of 1,3-butadiene in 1982, 200 million pounds less than the 2.5 billion pounds produced in 1981. This is because of the low production of ethylene, and a switch to cheap natural gas feedstocks due to gas deregulation. The United States has needed to import 1,3-butadiene from Canada and Europe for years. I.L. Levowitz, olefins vice-present at Exxon Chemical Americas, said that the current low production rate of ethylene is due to two simple facts: weak demand and significant over capacity of equipment [4]. But, the demand for 1,3-butadiene has been predicted to increase by the stimulation of even the slightest uptick in the economy or the auto business. Nevertheless, this demand still cannot increase ethylene cracking rates or induce ethylene producers to switch to heavier feedstocks. Thus, the production of 1,3-butadiene by steam cracking processes will not meet the demand. So, Petro-Tex Chemical Corporation, the largest direct producer of 1,3-butadiene [4], expects that the direct 1,3-butadiene processes can exist for quite a long time even though it is an energy-intensive process.
The dehydrogenation process to produce 1,3-butadiene was commercialized in the United States at the beginning of World War II as a substitute source for rubber [5]. From a thermodynamic point of view, Sterrett and McIlvried [6] pointed out that the equilibrium conversions for the dehydrogenation process were 35% at 930°F and 71% at 1100°F at a pressure of 0.1 atm, while that for selective oxidation is essentially 100% over a wide range of temperatures and pressures. Commercially, the former process was operated at 40 to 50% conversion with 70 to 90% selectivity while the latter was run at at least 70% conversion with selectivity greater than 90% per pass. The dehydrogenation process requires catalyst regeneration from every few minutes to a few days. Selective oxidation processes enjoy on-stream times on the order of several months since the oxygen reactant tends to keep the catalyst clean.

In 1978, 75% of the United States primary 1,3-butadiene capacity was reportedly based on the Petro-Tex selective oxidation technology [7] by using manganese iron spinel or magnesium chromium ferrite as a catalyst [5]. Welch et al. [7] reported that 90 to 95% selectivity at 70 to 80% conversion was obtained with the selective oxidation of n-butene, for inlet temperature ranges of 610 to 665°F.

Although acrolein does not have as big a market as other important industrial petrochemicals, it is the intermediate for manufacturing acrylic acid and acrylic esters which have production volumes of about 700 million pounds per year. Acrolein is also used in the production of glycerin, polyurethane and polyester resins, and pharmaceuticals. It also can be used as an additive to improve the water resistance of some paper coatings.
A wide variety of catalysts have been described that are active and selective for production of acrolein. In the Shell process, about 85% yield is obtained at about 20% conversion [5]. With cuprous oxide (Cu$_2$O), the reaction conditions are 350°C, 200 kPa. The O$_2$/propylene ratio must be carefully controlled or the catalyst may be oxidized to cupric oxide (CuO) which reduces selectivity.

Because of the importance of acrolein and 1,3-butadiene in the petrochemical industry, considerably research work on the catalytic selective oxidation associated with these materials has been done. In spite of the structural differences between them, the selective oxidation of propylene and n-butene may usually be performed with the same catalysts. Therefore, it is convenient to use these reaction systems to study heterogeneous catalysts for selective oxidation.
II. PREVIOUS WORK ON ALLYLIC OXIDATION CATALYSTS

Fifty-three catalyst formulations have been listed by Hucknall [2] as commercial catalysts for the selective oxidation of propylene to acrolein and thirty-eight for the selective oxidation of butene/butane mixtures to 1,3-butadiene. Most of them can be classified into categories by means of major components of the catalysts. Each of these categories are considered in greater detail.

A. Bismuth Molybdates:

Bismuth molybdate catalysts have been patented by Callahan et al. [8] for the oxidation of propylene to acrolein (known as the SOHIO process), and Heavne and Furman [9] for the oxidation of 1-butene to 1,3-butadiene. Adams and co-workers [10,11,12] have reported that bismuth molybdates are very active and selective for the production of dienes and unsaturated aldehydes as true selective oxidation catalysts (not dehydrogenation followed by oxidation of hydrogen). Although the selectivities of hydrocarbons heavier than C\textsubscript{4}'s decreased as high conversions were achieved due to product inhibition, those of C\textsubscript{3} and C\textsubscript{4} olefins stayed at relatively high levels even though the conversion reached 80 to 90\% in the range of 450 to 500°C. Above these temperatures, the catalysts began to lose activity due to structural collapse. The reasons for the high selectivity were explained by the stabilities of the products and low rate of direct oxidation to CO\textsubscript{2}. For example, the rate of oxidation of 1,3-butadiene was 1/20 of the rate of 1-butene to 1,3-butadiene; which was also twenty times faster than the direct oxidation of 1-butene to CO\textsubscript{2}. 

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Schuit et al. [13] found that bismuth molybdates only possessed superior activities and selectivities for olefin oxidation within the Bi/Mo atomic ratio of 2/3 to 2/1. Generally, they could be prepared by the solid phase reaction of oxides, or by the co-precipitation or slurry reaction of ammonium salts, nitrates, and oxides, followed by calcination at temperatures around 500°C. The highest activity observed by Schuit et al. [14] was from a catalyst of composition Bi$_2$O$_3$·MoO$_3$($\gamma$), which came from the slurry reaction of BiO(OH)·H$_2$O and H$_2$MoO$_4$ followed by calcination at 500°C for two hours. Generally, Bi$_2$O$_3$·MoO$_3$($\gamma$) (Koechlinite modification) and Bi$_2$O$_3$·2MoO$_3$($\beta$) (Erman modification) have higher activities than Bi$_2$O$_3$·3MoO$_3$($\alpha$) [14].

Adams [12] observed that the reaction rate for the selective oxidation of olefins was first-order in olefins and zero-order in oxygen at low conversion levels. Large values of the equilibrium adsorption constant were observed as the reactants were changed to hydrocarbons heavier than C$_4$'s. Schuit et al. [15,16] stressed that the strong 1,3-butadiene inhibition on the oxidation of 1-butene caused a failure to observe a 1-butene concentration dependence in some instances. A Langmuir-Hinselwood type rate equation was derived based upon first-order, single site adsorption model. In the absence of product inhibition, such as during a pulse reaction, the rate equation could be simplified to first-order with respect to olefins with an activation energy of 11 kcal/mole. The corresponding activation energy for the inhibition reaction was 36 kcal/mole.

Although the consumption rate of gas phase oxygen was faster than that of propylene, oxygen did not react with adsorbed propylene [17]. Almost all of the selective and non-selective products came from the
lattice oxygen including the deep sub-level lattice oxygen. Gas phase oxygen served only to rapidly reoxidize the reduced catalyst. The adsorbed oxygen diffused through a great number of layers and reached equilibrium with the oxygen ions of the bulk. Peacock et al. [18] had quantitatively substituted the lattice oxygen, which had been converted to products, by gaseous oxygen. Therefore, no oxygen partial pressure dependency would be expected. However, this can not explain the fact that reaction rates did depend on the partial pressure of oxygen for olefins heavier than C_4's.

Recently, Keulks et al. [19,20,21] investigated the kinetics of propylene oxidation over \(\alpha\)-, \(\beta\)- and \(\gamma\)-bismuth molybdates over a wide temperature range. The reaction orders for both propylene and oxygen changed in different temperature ranges. By using the relationship between the rates of catalyst reoxidation and reduction, and a material balance for oxygen in the catalyst under steady-state reaction conditions, coupled rate equations based on catalyst reduction and reoxidation were found. Generally, in the reduction-limited (high temperature) region, the reaction rate was first-order in propylene and zero-order in oxygen. In the reoxidation-limited (low temperature) region, the reaction rate showed a partially positive order in oxygen and zero-order in propylene.

The Arrhenius plots Keulks et al. [19,20,21] obtained for \(\gamma\)-bismuth molybdates consisted of two intersecting lines which represented high values of activation energy in the low-temperature range and low values in the high-temperature range. Temperature programmed reoxidation yielded two well-defined temperature ranges of reoxidation and showed that complete reoxidation was possible only at high temperatures.
Low-temperature reoxidation was found to be a result of the oxidation of \( \text{Mo}^{4+} \) to \( \text{Mo}^{6+} \) and \( \text{Bi}^{0} \) to \( \text{Bi}^{n+} \), where \( 0 < n < 3 \). The high-temperature reoxidation region corresponded to the direct oxidation of bismuth by gas phase oxidation, i.e., complete oxidation of \( \text{Bi}^{n+} \) to \( \text{Bi}^{3+} \). The activation energy for reoxidation at temperatures below 400°C, 45.8 kcal/mole, is very close to that for acrolein formation below 419°C, 43 kcal/mole. This implied that the rate-limiting step for propylene oxidation below 400°C could be related to the reoxidation process of the catalyst. The theoretical reaction orders and rate constants calculated from the empirical rate equation based on power law kinetics of the redox cycle indicated a close relationship between the observed propylene oxidation kinetics and the general kinetic features of a redox reaction. The low-temperature activation energies, 40-53 kcal/mole, were significantly higher than those reported previously, 35 kcal/mole, which were the result of assuming first order kinetics over the entire temperature range.

It is widely accepted that the abstraction of the allylic hydrogen, i.e., dissociative chemisorption of propylene and 1-butene to form a symmetrical \( \pi \)-allylic intermediate, is the first, slowest, and rate-determining step in the selective oxidation sequence [11,12,13,22]. The position of this abstraction was shown to be the allylic hydrogen by carbon-14 tagged propylene [22] and 3,3,3-d\(_3\)-propylene [8]. After this step, two mechanisms, redox and peroxide (or hydroperoxide), have been used to describe these reactions (see Figure II-1). The redox mechanism included a second hydrogen abstraction from a terminal carbon atom followed by the incorporation of a lattice oxide ion. The catalyst was used as an oxidizing agent and was reoxidized by gas phase oxygen. The
peroxide mechanism involved oxygen substitution (either gas-phase or adsorbed) onto an allylic intermediate to form peroxide or hydroperoxide and subsequently, decomposition into products and water through surface reaction [23].

The peroxide mechanism would give equal opportunity for oxygen to incorporate on either end of the allyl intermediate and since oxygen incorporation is slow, it would show no isotope effect for CH₃−CH=CD₂. But the redox mechanism would show an isotope effect due to different bond strengths of C-D and C-H since removal of the vinylic hydrogen would limit the rate. Forissier et al. [24] showed that only bismuth molybdates had an isotope discrimination effect (defined as CD₂=CH-CHO/CH₂=CH-CDO = K_h/K_d) which was interpreted as the abstraction of the second hydrogen prior to the introduction of oxygen.

Through studying deuterated propylene oxidation over α-, β- and γ-bismuth molybdates, Keulks et al. [21,25] concluded that acrolein was formed exclusively via the redox mechanism and carbon dioxide was produced from consecutive oxidation of acrolein and involved only lattice oxygen.

Adams [12] suggested that the second hydrogen abstraction from the intermediate yielded a conjugated diene and that oxygen substitution
formed an unsaturated aldehyde. In his scheme (Figure II-2), there was no distinction between lattice and adsorbed oxygen. The difference between the incorporation of oxygen at each end of the allyl

\[
\begin{align*}
\text{O}_2 & \rightarrow 2\text{O}_{\text{ads}} \\
\text{C} \equiv \text{C} & \quad + \text{O}_{\text{ads}} \rightarrow \text{C} \equiv \text{C} \equiv \text{C} \quad + \text{O}_{\text{Hads}} \\
\text{C} \equiv \text{C} \equiv \text{C} & \quad + \text{O}_{\text{ads}} \rightarrow \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \quad + \text{O}_{\text{Hads}} \\
(\text{C} \equiv \text{C} \equiv \text{C}) & \quad + 20\text{O}_{\text{ads}} \rightarrow \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CHO} \quad + \text{O}_{\text{Hads}} \\
20\text{O}_{\text{Hads}} & \rightarrow \text{H}_2\text{O} \quad + \text{O}_{\text{ads}}
\end{align*}
\]

Figure II-2  Reaction scheme from Adams [12]

intermediate was developed by Adams and Jennings [11] and Voge et al. [26] (Figure II-3). They explained that isomerization would give equal chances for oxygen substitution on both terminal carbons. This was confirmed by Sachtler and De Boer [22] by photochemically splitting acrolein produced from \(^{14}\text{C}\) tagged propylene.

\[
\begin{align*}
\text{CH}_2 & \equiv \text{CH} \equiv \text{CH}_3 \\
\text{CH}_2 & \equiv \text{CH} \equiv \text{CH}_2 \\
\text{CH}_2 & \equiv \text{CH} \equiv \text{CH}_2
\end{align*}
\]

Figure II-3  Incorporation of oxygen in an allylic intermediate from Adams and Jennings [11] and Voge et al. [26]
Batist and co-workers [13,27] first proposed a reaction scheme involving the role of the solid state (Figure II-4). The reverse of the abstraction of the first hydrogen from 1-butene was considered to be the source of cis- and trans-2-butene. The high selectivity of the bismuth molybdate could be explained if Bi$^{3+}$(H$_2$O) dissociated its water ligand faster than Mo$^{6+}$ and Mo$^{4+}$ and therefore, lower hydroxyl group coverage resulted.

\[
\begin{align*}
C_4H_8 + \square + O^{2-} & \rightarrow C_4H_7^- + OH^- \\
Mo^{6+} + C_4H_7^- & \rightarrow [\text{Mo}--C_4H_7]^{5+} \\
[\text{Mo}--C_4H_7]^{5+} + O^{2-} & \rightarrow Mo^{4+} + \square + OH^- + C_4H_6 \\
2OH^- & \rightarrow O^{2-} + \square + H_2O \\
o_2 + 2\square + 2Mo^{4+} & \rightarrow 2O^{2-} + 2Mo^{6+}
\end{align*}
\]

where: \(\square\) is anion vacancy and \([\text{Mo}--C_4H_7]\) is \(\pi\)-complex of Mo$^{6+}$ and allyl carbanion

Figure II-4 Mechanism of selective oxidation of 1-butene over bismuth molybdates by Batist et al. [13,27]

The structure of bismuth molybdate is widely accepted as platelike, consisting of layers of \((\text{MoO}_2)_n\)\(^{2+}\), (octahedral or square pyramid), and \((\text{Bi}_2\text{O}_2)_n\)\(^{2+}\) interconnected by \(O^{2-}\) layers [14,28]. IR spectroscopy [29] indicated that MoO$_3$ was on the surface of Bi$_2$O$_3$·MoO$_3$ and showed that in the formation of adsorbed species on the surface, double-bonded oxygen of Mo=O was involved in propylene oxidation by losing its metal oxygen double bond character at 990 cm$^{-1}$. Matsuura and Schuit [28,30] proposed a mechanism which involved two different sites in bismuth molybdates. A-sites were single-site Langmuir isotherm adsorption sites for 1,3-butadiene in a slow but strong adsorption (heat of adsorption, 19 kcal/mole) and were probably active surface oxygen anions (Oa). B-sites
were dual-site Langmuir isotherm adsorption sites for 1-butene and also 1,3-butadiene in fast and weak adsorption (heat of adsorption, 10-12 kcal/mole). These sites were surface oxygen anions (Ob). Selective oxidation over these binary oxides occurred on a cluster of one Oa (A-site) and two or four Ob (B-sites).

The mechanism Matsuura and Schuit proposed (Figure II-5) included the adsorption of 1-butene on a B-site (Ob$_1^{2-}$) by δ- or π-allyl adsorption, the allyl then moving over to an A-site (V$_{Bi}$) for oxidation where the allyl donated its second hydrogen atom and finally, the reaction product was released after a subsequent transfer to another B-site (Ob$_2^{2-}$). Thus, A-sites were oxygen anions connected to Bi$^{3+}$ cations and B-sites were anion vacancies next to Mo$^{6+}$ cations. Reoxidation of a reduced sample starts at the A-site and, at high

For butene:

\[
\begin{align*}
C_4H_8 + Mo^{6+} + 2Ob^{2-} & \rightarrow [C_4H_7Ob_1]^- + (Ob_1H)^- + Mo^{4+} \\
[C_4H_7Ob_1]^- + V_{Bi} + Mo^{4+} & \rightarrow Mo^{6+} + [C_4H_7]^-Bi + Ob_1^{2-} \\
[C_4H_7]^-Bi + Ob_2^{2-} & \rightarrow [C_4H_6]^{2-}Bi + (Ob_2H)^- \\
[C_4H_6]^{2-}Bi & \rightarrow Bi^+ + C_4H_6 \\
(Ob_1H)^- + (Ob_2H)^- + Oa^{2-} & \rightarrow H_2O + Va + Ob_1^{2-} + Ob_2^{2-}
\end{align*}
\]

For propylene:

\[
\begin{align*}
[C_3H_5]^-Bi + Ob_1^{2-} \text{ or } Ob_2^{2-} & \rightarrow [C_3H_4]^{2-}Bi + (Ob_1H)^- \text{ or } (Ob_2H)^- \\
[C_3H_4]^{2-}Bi + 2Bi^{3+} + Oa^{2-} & \rightarrow C_3H_4O + Va + 2Bi^+
\end{align*}
\]

where: Ob$_1^{2-}$ and Ob$_2^{2-}$ are oxygen ions belonging to B-site number 1 and 2, respectively. Va is vacancy left after removal of Oa.

Figure II-5 Two site mechanism of selective oxidation of 1-butene & propylene over bismuth molybdates [28,30]
temperatures of reduction, an internal rearrangement in the catalyst led to a transfer of $O^{2-}$ from MoO$_2$ layers to Bi$_2$O$_2$ layers. The A-sites were always on the edges of the Bi$_2$O$_2$ layers. The low value of heat of adsorption of $H_2O$ on the reduced A-sites elucidated the absence of an inhibition by water in the selective oxidation of 1-butene. $O_2$ was adsorbed on vacant B-sites.

Studies on $^{18}O$ labeled catalysts reduced by hydrogen [31] revealed that the oxygen of Bi$_2$O$_2$ layers was incorporated into acrolein and supplied through the MoO$_2$ layer from gas phase oxygen. Presumably the anion vacancy formed by the reduction caused the transfer of oxygen atoms between MoO$_2$ and Bi$_2$O$_2$ layers.

Obviously, bismuth molybdates are well-characterized catalysts for selective oxidation of 1-butene and propylene. Well-developed mechanisms can be used for comparison with other systems. In spite of their high activity and selectivity, the commercialized bismuth molybdate catalysts almost always have some kind of additive to enhance their performance [2]. We will consider these additives later.

B. Antimony Containing Allylic Oxidation Catalysts

Sala and Trifiro [32] found that the mixed iron or tin antimony oxides had higher activity and selectivity over the mixed oxides of antimony with Co, Ni, Mn, Zn, U, Ce, and Cd. The active oxidation sites of the mixed antimony oxides were attributed to Sb$^{5+}$ only. The reduced antimony ion was reoxidized by two methods:

1) adsorbed oxygen species transferred to antimony through peroxidic bridges.
2) reoxidation by the second metal ion which would in turn be reoxidized by gaseous oxygen.

Belousov and Gershingorina [33] concluded that the second cation simply served as a stabilizer for the oxidation state of the antimony.

The mixed iron antimony oxide catalysts for oxidation of 1-butene possessed reaction orders of 0.5 in both oxygen and 1-butene and an activation energy of 14.5 kcal/mole [34]. Boreskov et al. [35] discovered that the fully oxidized catalyst had very poor selectivity to 1,3-butadiene. However, the partially reduced catalyst showed decreased activity and increased selectivity with a selectivity maximum at 40% of the oxygen layer removed from the surface. The oxidations of 1-butene and 1,3-butadiene to the carbon oxides over an Fe-Sb-O catalyst were first-order in hydrocarbons and half-order in oxygen [36]. The activation energy for the formation of carbon dioxide was reported around 20 kcal/mole for various Fe-Sb-O catalysts.

Trimm and Gabbay [37] studied the oxidation of n-butene over a mixed tin antimony oxide catalyst with a Sn/Sb atomic ratio of 1/4. They found that the reaction orders to 1,3-butadiene were around 1/2, both in n-butenes and oxygen, while those to CO₂ were approximately first-order in both n-butenes and oxygen. The activation energies for the oxidation of 1-butene to 1,3-butadiene and carbon dioxide were 17 and 24 kcal/mole, respectively. No 1,3-butadiene inhibition was observed on this catalyst. Sn⁴⁺ was proposed as the active site in tin antimony oxides.

A mixed uranium antimony oxide catalyst for the oxidation of 1-butene, studied by Simons et al. [38], showed first-order behavior in 1-butene and zero-order in oxygen. The activation energy was
22 kcal/mole from continuous-flow measurements and 8 kcal/mole from pulse reactions; however, the reaction was determined to be restricted only to the surface in contrast to the bismuth molybdate catalysts which show multi-layer oxygen participation. The uranium antimony oxide catalyst did not catalyze the double-bond isomerization of the butenes. A slight reduction of this catalyst resulted in an irreversible decomposition of the structure. Simons et al. [38] suggested that the neighboring U\(^{5+}\)=O and Sb\(^{5+}\)=O groups in the USB\(_3\)=O\(_{10}\) catalyst could behave the same as two Sb\(^{5+}\)=O groups.

In summary, the active site on several mixed antimony oxides was attributed to Sb\(^{5+}\) only [32] while that of the tin antimony oxide was Sn\(^{4+}\) [37]. The second metal in these mixed oxides was supposed to reoxidize the reduced active site via electron transfer.

C. Iron Containing Allylic Oxidation Catalysts

Among the pure oxides of the first row transition metals, Fe\(_2\)=O\(_3\) showed the highest surface area and the greatest yield of 1,3-butadiene from the oxidation of 1-butene (data of scandium was not available) [39] but it became poisoned very quickly [40]. The conversion of 1-butene to 1,3-butadiene over Fe\(_2\)=O\(_3\) was 50%, while that for the highest of the others was only 22%. Yoneda et al. [41] found that the activity of the spinel structural \(\gamma\)-Fe\(_2\)=O\(_3\) was higher than that of \(\alpha\)-Fe\(_2\)=O\(_3\) and Fe\(_3\)=O\(_4\) probably due to the fact that it readily accepted and donated oxygen. Based on the redox mechanism, only a mixed oxide with a reducible cation capable of a reduction-reoxidation cycle could be a good catalyst. It is possible that there exists a mixed oxide catalyst in the first row transition metals similar to bismuth molybdates in the second row transition metals. The most likely candidate is mixed iron oxide.
Various ferrite spinel structures are a very good starting point for comparing the catalytic properties of mixed iron oxides. A normal spinel has the divalent cations in the tetrahedral sites and trivalent cations in octahedral sites, \([A^{2+}][B^{3+}]_0\). Inverse spinels have divalent cations in octahedral sites and distribute half of the trivalent cations into tetrahedral sites and the other half into octahedral sites, \([B^{3+}][A^{2+}B^{3+}]_0\). In mixed or random spinels, di- and tri-valent cations distribute in both tetrahedral and octahedral sites. The higher activity of \(\gamma\)-Fe\(_2\)O\(_3\) than \(\alpha\)-Fe\(_2\)O\(_3\) was explained by Kung et al. [42] as the participation of the cation vacancy sites of spinel structure, which was electron rich and made the surrounding oxygen ions more basic. The activity of \(\alpha\)-Fe\(_2\)O\(_3\) was due to the transformation of the reduced form between \(\alpha\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) to \(\gamma\)-Fe\(_2\)O\(_3\) by rapid migration of lattice oxygen to the surface at high temperatures. A non-ferrite spinel structure mixed oxide, zinc aluminum oxide, was found to be inactive in the selective oxidation of 1-butene to 1,3-butadiene [43]. Neither Zn\(^{2+}\) nor Al\(^{3+}\) is easily reducible. So, the spinel structure is not a sufficient criterion for a selective oxidation catalyst.

Cobalt ferrites and copper ferrites were active but not selective catalysts for the oxidation of 1-butene [43]. Product poisoning was very extensive even at low conversion levels. The reaction rate was somewhat greater than zero-order in oxygen, less than first-order in 1-butene and inverse order in 1,3-butadiene. Because of a temperature surge and product poisoning during the reaction, Hightower and Cares [43] found that it was difficult to measure kinetics accurately. The fact that the activity of copper ferrites was ten times that for cobalt ferrite was justified by the greater reducibility of the copper ion.
compared to the cobalt ion. Mössbauer spectra indicated that the
catalysts changed from a random spinel in the oxidized state to an
inverse spinel in the reduced state [44]. The steady states of these
catalysts were very nearly the fully oxidized states.

Kehl and Rennard [45,46] described a general method for the
production of a magnesium-chromium ferrite and zinc-chromium ferrite.
Magnesium- and zinc-chromium ferrites were spinel structures with Cr$^{3+}$
replacing Fe$^{3+}$ in octahedral sites. The introduction of chromium into
the zinc ferrite, ZnFe$_2$O$_4$, has no effect on the high selectivity of
ZnFe$_2$O$_4$ to 1,3-butadiene, but increases the activity [47]. Based on the
high activity of FeCrO$_3$ and the disappearance of the Cr$_{1/2}$Fe$_{2-1/2}$O$_3$ phase in
the used zinc-chromium ferrite, the authors suggested that the higher
activity of the chromium containing zinc ferrite was not due to the
incorporation of Cr$^{3+}$ into the spinel structure but to the presence of a
Cr$_{1/2}$Fe$_{2-1/2}$O$_3$ phase. The same situation, increasing activity, occurred with
chromium incorporated into MgFe$_2$O$_4$ though it was not so dramatic as with
ZnCrFeO$_4$. Kung et al. [42] showed that in the binary Cr and Zn ferrites
both additives enhance the activity to selective oxidation at high
temperatures, because of an increase in the number of cation vacancies.
The addition of Zn promoted the formation of cation vacancies in the
spinel structure and the presence of Cr$^{6+}$ induced the formation of
cation vacancies. Both additives increased the resistance to reduction
in the near-surface region and hence, reduced the production of CO$_2$ at
high temperatures.

The rate of formation of 1,3-butadiene over these catalysts was
found to be zero-order in both oxygen and 1-butene. With an absence of
gas phase oxygen, the formation of 1,3-butadiene ceased when adsorbed
oxygen was consumed and the reduction of the catalyst surface had been achieved. The reduction of Fe$^{3+}$ to Fe$^{2+}$ (as shown by Mössbauer spectroscopy) could only proceed to the extent that a monolayer of lattice oxygen was removed. The incorporation of chromium into the mixed ferrite catalyst was able to inhibit the bulk reduction of the catalysts (shown as the increase in activity). The so-called Rennard-Massoth mechanism and its surface reactions [47,48] were proposed as in Figures II-6 and II-7. The zero-order dependence of 1-butene was consistent with their mechanism, which showed a non-competitive adsorption of 1-butene and oxygen on two different adsorption sites; an anion vacancy adjacent to an Fe$^{3+}$ ion and a lattice oxygen site adjacent to Fe$^{2+}$.

\[ \square + C_4H_8 + Fe^{3+} + O_k^- \rightarrow [C_4H_7\cdot Fe]^{3+} + OH^- \]
\[ [C_4H_7\cdot Fe]^{3+} + O_j^{2-} \rightarrow C_4H_6 + Fe^{2+} + OH^- \]
\[ 2OH^- \rightarrow H_2O + O_j^{2-} + \square \]
\[ Fe^{2+} + \frac{1}{2}O_2 \rightarrow Fe^{3+} + O_k^- \]

where: \( \square \) is an anion vacancy adjacent to an Fe$^{3+}$ ion; \( O_k^- \) is an adsorbed oxygen radical ion; \( O_j^{2-} \) is a lattice oxygen; and \([C_4H_7\cdot Fe]^{3+}\) is a complex of Fe$^{3+}$ & an allylic radical

Figure II-6 Rennard-Massoth mechanism [47]
Magnesium ferrite was effective for the selective oxidation of hydrocarbons containing four to seven carbon atoms [49]. A spinel magnesium ferrite with 90% MgFe$_2$O$_4$, 5% α-Fe$_2$O$_3$ and 5% MgO was investigated by Gibson and Hightower [50,51]. The high selectivity and activity of the fresh catalyst decreased drastically as it was used. Because some reactants were left when the synthesis of the catalyst was completed, α-Fe$_2$O$_3$ disappeared by reaction with the excess MgO to form magnesium ferrite via Fe$_2$O$_3$ + MgO → MgFe$_2$O$_4$ during the catalytic reaction.

The reaction rate was zero-order in oxygen and near first-order in 1-butene under low 1-butene concentrations. Several layers of lattice oxygen might participate in the reaction as evidenced by Gibson and Hightower [51,52]. The extensive oxidation product, CO$_2$, was formed both from the oxidation of 1-butene and 1,3-butadiene with gas phase oxygen and adsorbed oxygen, but not with lattice oxygen. Isotope studies showed almost no H/D exchange during the oxidation of a mixture of 1-butene and perdeuterated 1-butene. This result implied that all reactions proceed through an intramolecular pathway involving only one 1-butene molecule.
The Rennard-Massoth mechanism was used to explain the zero-order dependence in oxygen by assuming rapid adsorption of oxygen maintaining the surface essentially covered with the \( \text{O}^- \) species. Isomerization and the majority of the deep oxidation were suggested to be due to the undesired adsorption of 1-butene on a reduced ion (\( \text{Fe}^{2+} \)) site. Deactivation was proposed to be due to an increased population of \( \text{Fe}^{2+} \) sites at the expense of \( \text{Fe}^{3+} \) sites.

Kung et al. [52] demonstrated that temperature-programmed desorption (TPD) could be used to characterize selective oxidation catalysts. The TPD profile of cis-2-butene over \( \text{Fe}_2\text{O}_3 \) consisted of two well-defined regions. The low temperature region showed desorption of \( \text{C}_4 \) hydrocarbons only and the high temperature region showed desorption of \( \text{CO}_2 \) and water. The two regions implied that different products were formed on two different sites, a selective oxidation site and an extensive oxidation (combustion) site. Zinc ferrite showed similar types of TPD curves [53] to that of \( \text{Fe}_2\text{O}_3 \). But, zinc ferrite showed a larger desorption peak in the low temperature region and almost no desorption in the high temperature region. The positions (temperatures) of the peak maxima were determined by the rate constants of the rate-limiting step leading to the observed peak. Since the two catalysts had similar selective oxidation peak positions, the activities of the selective oxidation sites on these two catalysts were similar. The higher density (peak height) of the selective oxidation sites and lower density of combustion sites on \( \text{ZnFe}_2\text{O}_4 \) was consistent with the observation that \( \text{ZnFe}_2\text{O}_4 \) has higher selectivity and activity, as shown in Table II-1. Furthermore, as the temperature increased the combustion sites of \( \text{Fe}_2\text{O}_3 \) increased more rapidly than that of \( \text{ZnFe}_2\text{O}_4 \); the
difference in selectivities of these two catalysts were more apparent at higher temperatures.

Table II-1 Summary of site densities and selectivities [52,53]

<table>
<thead>
<tr>
<th></th>
<th>site density</th>
<th>selective to butadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>combustion 10(^{17})/m(^2)</td>
</tr>
<tr>
<td>ZnFe(_2)O(_4)</td>
<td>2.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>1.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Matsuura and Schuit proposed a two site adsorption model which was applied to the iron oxides series (\(\alpha\)-Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), Fe\(_4\)Bi\(_2\)O\(_7\), FeSbO\(_4\), FeAsO\(_4\) and FePO\(_4\)) [54]. Generally, the selective catalysts, such as FeSbO\(_4\) and FeAsO\(_4\), showed weak and reversible adsorption of 1-butene; non-selective ones (\(\alpha\)-Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\) and Fe\(_4\)Bi\(_2\)O\(_9\)) had strong adsorption and a non-active catalyst (FePO\(_4\)) revealed very weak adsorption of 1-butene. Two types of sites, A and B were proposed. B-sites were connected with bulk octahedral Fe\(^{3+}\) which was active in oxidation, and A-sites only showed their adsorption ability when next to one or more B-sites. The latter argument was supported by the fact that Sb\(_2\)O\(_4\) did not adsorb 1,3-butadiene strongly while Sb behaved as an A-site in FeSbO\(_4\). The authors further proposed the active site clusters of selective catalysts to be an alternate arrangement of A and B sites, which presumably were segregated by inactive sites of reduced A-sites and non-selective clusters of blocks of B-sites. The reaction mechanism over FeSbO\(_4\) started with butene adsorbed dissociately on Fe\(^{3+}\) (B) site, then the allyl moved to a vacancy next to the oxide on Sb\(^{5+}\) (A) site and
donated two electrons, and finally migrated to the second Fe$^{3+}$ (B) site with loss of the second hydrogen atom. In this mechanism, mobility of the adsorbed species was emphasized.

Iron oxide was found most active for the selective oxidation of olefins among the pure oxides of the first row transition metals. However, mixed iron oxides were found to be suffering either from low selectivity or thermal instability. Phenomenological explanations were used for different systems.

D. Tellurium Containing Allylic Oxidation Catalysts

Presently, tellurium is used as an additive to many commercial mixed oxide catalysts [2]. Several attempts have been made to elucidate the role it plays in selective oxidation processes. A series of non-selective or poorly selective mixed molybdates, CaMoO$_4$, CdMoO$_4$, Fe$_2$(MoO$_4$)$_3$ and MnMoO$_4$, showed moderate selectivities to 1,3-butadiene in the oxidation of 1-butene at low partial pressures of oxygen [55]. However, Forzatti et al. [56] have studied the effects of the addition of various amounts of Te to essentially the same series of oxides (Co instead of Ca). They found that Te acted as a promoter of activity up to certain levels (~1%) by means of promotion of the formation of new active and selective oxidation sites, and as a moderator of the activity above this level by the effect of destruction of extensive oxidation sites. But, the addition of Te to MnMoO$_4$ at high Te levels only served as a poisoning agent, along with no change in the IR and Raman spectra and the formation of a new compound, α-Te$_2$MoO$_7$, at 8% Te. The decrease in the yield of isomers was explained by postulating that Te destroyed surface acid sites which were responsible for the production of isomers.
The addition of Te shifted IR bands of metal-oxygen double bonds to a lower energy by reducing bond strength. Weaker metal-oxygen bonds would have more oxygen anion vacancies, higher activity and lower selectivity [22]. Forzatti et al. speculated that the new selective oxidation sites could be Te$^{6+}$ sites which were stabilized over 300°C and/or Mo=O groups at the surface whose bond strength was modified by neighboring tellurium. They also proposed that Te$^{6+}$ might fill ordered octahedral vacancies interstitially or substitute for Mo$^{6+}$ in the crystal lattice.

Investigating isomerization and extensive (deep) oxidation of 1-butene in the presence of steam over tellurium modified molybdate catalysts, Forzatti et al. [57] concluded that the Brönsted and Lewis acid sites were interconvertable via changing the temperature or the amount of steam. The Brönsted sites were responsible for isomerization and became more populous at low temperature or high steam pressure. Lewis acid sites were responsible for deep oxidation and were populous whenever Brönsted sites were not populous. The Te doped selective catalysts increased the rate of formation of CO$_2$, but no appreciable change was detected in the yield of isomers due to increasing the temperature. The effect of steam addition on isomerization over Te doped catalysts was greater than the effect on undoped and poorly selective catalysts. The reason for the above facts as postulated by Forzatti et al. [57] was that the Brönsted sites of undoped and poorly selective molybdate catalysts no longer exist in Te doped selective catalysts; i.e., Te destroyed the surface Brönsted sites present in pure molybdates. The increase in the selectivity to 1,3-butadiene in the Te-promoted molybdates was due to the decrease in surface acidity.
Forzatti et al. [58] reported that the reactions of 1-butene to 1,3-butadiene and propylene to acrolein over the Te-promoted Cd-, Co-, Mn- and Zn-molybdates were highly selective even to high conversion levels. IR and Ramam spectroscopies indicated the presence of cis-MoO$_2$ groups with high Mo=0 double bond character. According to the redox mechanism, two hydrogens need to be removed from the olefin in consecutive steps. The authors speculated that cis-MoO$_2$ groups with high Mo=0 bond character might provide two continuous sites for the removal of hydrogen atoms. On the other hand, the higher resonant frequencies of Mo=0 bonds than in pure molybdates indicated a shortening of the bond lengths. The increase of Mo=0 bond strength might be related to a reduction in the numbers of oxygen anion vacancies and a reduction in activity while increasing the selectivity [22]. Therefore, it appears that optimal Te levels can be established from measurements of Mo=0 bond strengths.

Although Te was present as Te$^{4+}$ in the bulk, the authors speculated that Te$^{6+}$ could still occur in the structure of the tellurium molybdates partially substituted for Mo$^{6+}$. As Kozlowski [59] reported, CoTeMo$_6$ was found as a stable product in the annealing of Co$_4$TeMo$_3$O$_{16}$, which corresponded to the decomposition of a Te$^{6+}$ compound to a Te$^{4+}$ one. X-ray diffraction patterns by Forzatti et al. [58] indicated that the positions of metals, Te and Mo, and O atoms in the structures were similar. In these selective ternary tellurium molybdates, the role of the third cation (Cd, Co, Mn, Zn) was not understood.

Sloczynski and Kozlowski [60] constructed two new cobalt molybdotellurates, CoTeMo$_6$ and Co$_4$TeMo$_3$O$_{16}$, by co-precipitation and solid state reactions of Co and Mo salts and TeO$_2$ or H$_2$TeO$_4$. The
authors reported that Co₄TeMoO₁₆ and CoMoO₄ had the same structure except that every fourth Co⁶⁺ was replaced by Te⁶⁺. This partially substituted compound has the Wolframite type structure. In the case of CdTeMoO₄, Forzatti and Tieghi [61] reported that it exhibited a plate-like structure analogous to the Scheelite CdMoO₄ structure. In another paper [62], they disclosed that, from the X-ray diffraction patterns, the structures of MnTeMoO₆, CoTeMoO₆, and ZnTeMoO₄ were most likely isotypic.

The oxidations of 1-butene and propylene over Te rich Cd- and Mn-molybdates (up to Metal/Te/Mo ratio of 1/1/1) were also investigated by Forzatti et al. [63] and Forzatti and Trifiro [64]. Addition of Te to a Cd-molybdate increased the rate of formation of 1,3-butadiene at low Te levels (maximum at Te=3.8%) but decreased the rate at high Te levels. However, the rates for CO₂, CO and isomers dropped more rapidly than that for 1,3-butadiene. So CdTeMoO₆ was particularly suitable for production of 1,3-butadiene though the activity was lowered. The effect of addition of Te over Cd- and Mn-molybdates only showed positive effects at low Te levels in the oxidation of propylene. Besides the previously proposed explanation, the authors further accounted for the high selectivity to the possible redox mechanism Mo⁴⁺ + Te⁶⁺ → Mo⁶⁺ + Te⁴⁺, which by-passed the formation of Mo⁵⁺ state. The Mo⁵⁺-O₂ species for the deep oxidation processes can no longer be formed in this mechanism. They explained the existence of Te⁶⁺ substituted Wolframite MnTe⁶⁺Mo₁₋₁₆ by the comparable sizes of Te⁶⁺ and Mo⁶⁺ ions, whereas Te⁴⁺ is much larger. The dopant might enter the lattice interstitially in the case of Scheelite CdMoO₄ structure.

Only one direct spectroscopic study of the valence state of Te in cobalt-tellurium-molybdates was published by Firsova et al. [65]. Two
Te valence states, 4+ and 6+, were found in Co-Mo-Te and Co-Mo-Te-Fe mixed oxides by Mössbauer spectroscopy. The Te^{6+}/Te^{4+} ratio decreased upon reduction of the catalyst with propylene. This ratio can be restored to its original value by heating in O_2 at the same temperature. Obviously, Te participated in a redox cycle and Te^{6+} acted as an active center in the oxidation process. Firsova et al. [65] have proposed a mechanism for the oxidation of propylene with tellurium as in Figure II-8.

Recently, Forzatti and Villa [66] studied an Fe_2(MoO_4)_3 catalyst doped with low levels of Te for the oxidation of propylene to acrolein. They reported that Te became mobile and could easily be lost when present in high quantities. This probably is related to the poisoning effect of Te at high levels. The great improvement of selectivity in the Te doped catalyst indicated that Te tends to concentrate at the catalyst surface to form Te^{6+}-O-M-Te^{4+} or Te^{6+}-O-Te^{4+} with an oxidation state of Te higher than IV. A two-electron-transfer redox mechanism was reconfirmed by this work.
Te can be regarded as a selectivity promoter and activity moderator (or even as a poisoner) to the ternary molybdates. It works both on low and high doping levels, though the results vary with Te loading. The effects were attributed to the modification of Mo=O by the addition of Te or the presence of Te$^{6+}$ in the ternary mixed oxides.

Because tellurium has been used as an additive for various commercial catalysts in selective oxidation reactions, understanding the role which Te plays in these reactions would provide information on the design of improved catalysts. Iron tellurium mixed oxides may provide a convenient system to study the catalytic character and behavior of tellurium in a selective oxidation catalyst. The objectives of this research work have therefore been to synthesis iron tellurium mixed oxides which have reasonably good activity and selectivity and to characterize their catalytic properties so that the behavior of tellurium in these catalysts may be evaluated.
III. EXPERIMENTAL APPARATUS AND PROCEDURES

Many types of experimental procedures have been performed in order to evaluate the catalytic behavior of iron tellurium mixed oxides. Catalyst preparation, catalytic reactions, isotopic tracer experiments and spectroscopic analyses have been performed. This chapter contains a discussion of the equipment and procedures.

A. Equipment

The experimental equipment employed in this research work can be separated into two categories. The reactor system was used to study the kinetics of the selective catalytic oxidation process and several spectroscopic instruments were used to characterize the catalytic properties. These are described below.

1. Reactor System

An all Pyrex, batch recirculation reactor system was constructed for this research work (Figure III-1). The system components can be separated into evacuation, storage, adsorption and reaction sections.

The system is evacuated by a Sargent-Welch 1400 Duo-Seal, two-stage vacuum pump, which can obtain a vacuum of $10^{-4}$ torr. In case high vacuum is needed, there is also a diffusion pump with a liquid nitrogen trap which can be used in series with the mechanical pump to evacuate the system to $10^{-6}$ to $10^{-7}$ torr. The pressure gauge and ionization gauge are products of Cooke Vacuum Products.

The system has six 5-liter flasks for storage of reactants. Each flask has a condensation trap attached, which can be used for single stage distillation of reactants to remove impurities.
The batch recirculation reactor consists of recirculation, mixing, and reaction sections. The majority of the system volume resides in two mixing flasks, one 500 ml and the other 300 ml. The smaller one can be by-passed in order to reduce the volume of the system. Usually only the 500 ml flask is used which results in a total system volume of about 700 ml with interconnecting tubing, the reactor, and the pump. For the 1-butene oxidation reaction, an ice-water trap was used to keep the partial pressure of water constant and to prevent condensation of water on the check valves. But the trap was not used in case of propylene oxidation because of the high solubility of acrolein in water and the low reaction rate which produces a smaller amount of water than the 1-butene oxidation.

The whole system was connected with ¼" glass tubing. A U-tube upstream of the reactor was used to trap propylene or 1-butene with liquid nitrogen when making a mixture of reactants.

A diaphragm pressure transducer with digital readout, produced by the MKS Instruments, Inc., was used to monitor the amount of gas put into the system. The transducer had a useful range of 0 to 1000 mmHg. The reactants were mixed and recirculated by a magnetically operated pump, which has a 7/8" diameter Teflon-coated iron plunger and four check valves. The pump was controlled by an electronic device, which has oscillating frequencies of 63 to 94 cycles per minute. Generally, the pump was operated at a frequency of 75 cycles per minute so that the gas circulation rate was about 300 ml/min against a normal pressure drop across the catalyst bed, and the mixing rate was about one half a system volume per minute.
The reactor was made of 10 mm O.D. glass tube and was connected to a stop-cock by two pieces of 6 mm O.D. glass tubing on each end. Through a pair of ground glass joints, the reactor was connected to the recirculation system. A concentric thermocouple well made by a 4 mm O.D. glass tube was immersed from the top into the reactor. The total volume of reactor was about 16 ml.

The catalyst was placed in the section of 10 mm O.D. glass tube with Pyrex wool on each end of catalyst bed. About 2.5 g of 3 mm glass beads were used to "dilute" the catalyst so as to increase the thermal stability of the catalyst bed. The section containing the catalyst was heated by a concentric electric heater controlled by a PID controller, a product of Omega Engineering, Inc. An iron-constantan thermocouple was used as a temperature sensor. The temperature control system was calibrated at 0°C and 100°C. The mixed reactants were pumped by the magnetically operated pump through the inlet 6 mm O.D. glass tubing to the bottom of the reactor, then upward through the catalyst bed. The inlet path had a length of 20 cm immersed in the heater which provided for preheating of the reactants.

With the same reactor used in recirculation reaction, a pulse reaction could be carried out by adding a source of purge gas in front of the reactor and a trap on the effluent side. Helium, used as carrier gas, was monitored by a rotameter, a product of Brooks Instrument Company, Inc. The calibration curve is shown in Figure III-2.

The volume of the pulse chamber was measured by mercury as 2.28 ml. From the volume and the pressure the amount of each pulse could be calculated.
Figure III-2  Rotameter calibration curve
A liquid nitrogen trap was used to trap all the reactants and products except oxygen and helium downstream of the reactor when the system was used in the pulse mode. Oxygen and helium were evacuated from the trap after condensation of the pulse, then the trap was removed from the reaction system and contents injected into GC for analysis.

2. Catalyst Characterization Equipment

a. Adsorption Apparatus

A 50 ml gas buret with a pressure indicator provided the basic P-V measurement devices necessary for volumetric adsorption measurements. A double-O-ring sealed plunger driven up and down in the gas buret by a small motor allowed for volume changes. A diaphragm pressure transducer with digital readout was used as the pressure indicator. The transducer had a useful range of 0 to 1000 mmHg. Interconnecting tubing used in the adsorption apparatus was capillary tubing in order to keep the dead-volume small. The system was connected to the same vacuum system used with the reactor system.

The apparatus doubles as a system for producing mixtures of known composition for chromatographic standards.

b. Analytical Facilities

1) Gas Chromatograph and Integrator

A Gow-Mac 550P gas chromatograph with a thermal conductivity detector was used to analyze the reaction products. A Valco gas sampling valve was connected to the reaction system through a 1/16" S.S. tube and a three-way stopcock. This sampling system had a total volume of about 4 ml, which was less than 1% of the volume of the reaction system. Helium carrier gas flow rates were set at 30 ml/min.
A 1/8" x 20' S.S. tube packed with 65% Chromosorb PAW 80/100 mesh, 28.3% Bis-(2-ethoxy-ethyl) adipate, 4.7% Squalene and 2% Carbowax 1540, followed by a 1/8" x 20" S.S. tubing packed with Porasil C 80/100 mesh coated with 1% Reoplex-400 (polyester), was used to analyze the reactants and products of the 1-butene oxidation process. The column used for analysis of products from the propylene oxidation was a 1/8" x 2 m S.S. tubing packed with sylanized Porapak Q 80/100 mesh.

GC output was monitored by an HP-3390A integrator which performed standard chromatographic area analysis and calculations. External standards were used for calibration purposes. Standard mixtures for external standards were prepared by expanding known amounts of gas into an evacuated flask. The parameters of the GC and integrator are listed in Table III-1. Typical gas chromatograms for the analyses of the propylene and 1-butene reaction are shown in Figures III-3 and III-4, respectively.

Several runs were also checked for carbon monoxide concentrations on a Carle 111 H chromatograph set up to separate the components of air and carbon monoxide. No carbon monoxide was found.

2) GC/MS

A Finnigan 1020 GC/MS was used to analyze the reaction products of isotopic tracer experiments. The system is completely controlled and monitored by a Nova 4C computer. The same separation column and GC parameters, as described above, were used to separate the reaction mixture of propylene oxidation except the flow rate of carrier gas was reduced to 25 ml/min. A Valco gas sampling valve was used to inject samples which were expanded into a glass vial from the reactor. Most of
Table III-1  Gas chromatograph and integrator parameters

<table>
<thead>
<tr>
<th>parameters</th>
<th>propylene oxidation</th>
<th>1-butene oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector Temp.</td>
<td>150°C</td>
<td>150°C</td>
</tr>
<tr>
<td>Detector Current</td>
<td>150 mA</td>
<td>150 mA</td>
</tr>
<tr>
<td>Attenuation</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Carrier Gas, He</td>
<td>30 ml/min.</td>
<td>30 ml/min.</td>
</tr>
<tr>
<td>Initial Temp.</td>
<td>95°C</td>
<td>75°C isothermal</td>
</tr>
<tr>
<td>Initial Time</td>
<td>1 min.</td>
<td>-</td>
</tr>
<tr>
<td>Ramp Rate</td>
<td>30°C/min.</td>
<td>-</td>
</tr>
<tr>
<td>Final Temp.</td>
<td>170°C</td>
<td>-</td>
</tr>
<tr>
<td>Final Time</td>
<td>5 min.</td>
<td>-</td>
</tr>
<tr>
<td>Attenuation</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Threshold</td>
<td>-1 ~+0</td>
<td>-1 ~+0</td>
</tr>
<tr>
<td>Area Reject</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Integrator

<table>
<thead>
<tr>
<th>Component</th>
<th>Response 1/(Amount/Area)</th>
<th>Relative Molar Response [67]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>0.741 - 0.811</td>
<td>40 (0.833)†</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>1</td>
<td>48 (1)</td>
</tr>
<tr>
<td>propylene</td>
<td>1.290</td>
<td>63 (1.312)</td>
</tr>
<tr>
<td>1-butene</td>
<td>1.593 - 1.674</td>
<td>81 (1.688)</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>1.579 - 1.677</td>
<td>85 (1.771)</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>1.490 - 1.581</td>
<td>80 (1.667)</td>
</tr>
<tr>
<td>acrolein</td>
<td>1.039</td>
<td>-</td>
</tr>
</tbody>
</table>

† Normalized to $CO_2 = 1$
RUN # 215  ID 13.3.4-500  APR/01/83  15:31:58

<table>
<thead>
<tr>
<th>RT</th>
<th>AREA TYPE</th>
<th>CAL#</th>
<th>AMOUNT</th>
<th>COMPOUND</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>409770</td>
<td>IR</td>
<td>73.632</td>
<td>OXYGEN</td>
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<tr>
<td>0.79</td>
<td>33613</td>
<td>2</td>
<td>4.472</td>
<td>CO₂</td>
</tr>
<tr>
<td>2.82</td>
<td>470400</td>
<td>3</td>
<td>48.507</td>
<td>PROPYLENE</td>
</tr>
<tr>
<td>6.38</td>
<td>17323</td>
<td>4</td>
<td>3.643</td>
<td>ACROLEIN</td>
</tr>
</tbody>
</table>

TOTAL AREA= 931110
MUL FACTOR= 1.0000E+00

Figure III-3 Typical gas chromatogram for the propylene reaction.
<table>
<thead>
<tr>
<th>RT</th>
<th>AREA</th>
<th>TYPE</th>
<th>CAL#/</th>
<th>AMOUNT</th>
<th>COMPOUND</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.09</td>
<td>410290</td>
<td>D PB</td>
<td>1R</td>
<td>69.187</td>
<td>OXYGEN</td>
</tr>
<tr>
<td>3.23</td>
<td>195880</td>
<td></td>
<td>2</td>
<td>26.820</td>
<td>CO₂</td>
</tr>
<tr>
<td>9.49</td>
<td>1044700</td>
<td></td>
<td>3</td>
<td>90.440</td>
<td>1-BUTENE</td>
</tr>
<tr>
<td>11.17</td>
<td>17814</td>
<td></td>
<td>4</td>
<td>1.568</td>
<td>t-2-BUTENE</td>
</tr>
<tr>
<td>12.39</td>
<td>19472</td>
<td></td>
<td>5</td>
<td>1.714</td>
<td>C-2-BUTENE</td>
</tr>
<tr>
<td>13.19</td>
<td>28501</td>
<td></td>
<td>6</td>
<td>2.641</td>
<td>BUTADIENE</td>
</tr>
</tbody>
</table>

TOTAL AREA= 1716600
MUL FACTOR= 1.0000E+00

Figure III-4 Typical gas chromatogram for the 1-butene reaction.
the carrier gas was evacuated from the effluent by a jet separator interface between the GC and MS. The fragmentation voltage was reduced to 17 volts to minimize fragmentation.

3) X-Ray Powder Diffractometer

All the X-ray powder diffraction patterns were kindly provided by Exxon Research and Development Laboratories, Baton Rouge, Louisiana. The X-ray diffractometer is a Scintag, Inc. automated powder diffraction system. The system has fixed slits and a germanium crystal energy dispersive detector operated to remove the Cu Kβ radiation. Patterns were obtained from 2° to 90° with 0.03° steps counting at each step for 0.50 second. The system is completely automated with Scintag software and includes complete libraries and library search routines.

4) Mössbauer Spectrometer

The Mössbauer spectrometer was Nuclear Data 2400 with ASA-K3 velocity transducer. The γ-ray source was a 50 mci 57Co source in rhodium host lattice from Spire Corporation, Bedfold, Maine. The data reduction was carried out by a conventional least-square Lorentzian line shape program and the parameters of the Mössbauer spectra were evaluated with a Mössbauer parameter fitting program.

5) Infra-red Spectrometer

A Perkin-Elmer 283 Infrared Spectrophotometer with a range of 4000 cm\(^{-1}\) to 200 cm\(^{-1}\) was used to record IR spectra. Because of the low transparancy of our catalysts, the reference beam of the IR spectrometer was strongly attenuated. The IR spectrophotometer was calibrated with a Perkin-Elmer 0.05 mm thick polystyrene calibration film.

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B. Raw Materials

Raw materials used in this work are listed in Table III-2. It includes information about manufacturers, specifications and lot numbers where available.

All hydrocarbons including acrolein used for reactions were purified by using a freeze-pump-thaw procedure twice for both the light and heavy ends before storing in the 5-liter flasks. The hydrocarbons were purified again just before reaction. Oxygen was purified by evacuating while condensed in liquid nitrogen. Helium, nitrogen, carbon dioxide and oxygen-18 were used without any purification. Perdeuterated propylene had been purified once by a freeze-pump-thaw process before being used.

C. Procedures

1. Manufacture of Catalysts

Several methods, including co-precipitation and solid state reaction from various materials, were used to make catalysts for the selective oxidation of propylene and 1-butene. High temperature annealing processes in the range 600-700°C resulted in completely melted catalysts which solidified on cooling. These materials had essentially no surface area, and therefore were not catalytically active. Other solid reactions at lower temperatures were also performed, but with no good catalyst candidates. Roughly 50 catalysts of varying compositions and different preparation techniques were screened for catalytic activity.

Based on selectivity, activity and life-time of these catalysts, two were chosen for more thorough study of the catalytic properties for
<table>
<thead>
<tr>
<th>Item</th>
<th>Chemicals</th>
<th>Manufacturer</th>
<th>Spec.</th>
<th>Lot #</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chromosorb PAW</td>
<td>TEKLAB</td>
<td>80/100 mesh</td>
<td>CP-20009</td>
</tr>
<tr>
<td>2</td>
<td>Bis-(2-ethoxy-ethyl)-adipate</td>
<td>Supelco</td>
<td></td>
<td>AIA</td>
</tr>
<tr>
<td>3</td>
<td>Squalane S-2700</td>
<td>TEKLAB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Carbowax 1540</td>
<td>TEKLAB</td>
<td></td>
<td>C-1800</td>
</tr>
<tr>
<td>5</td>
<td>Porasil C</td>
<td>TEKLAB</td>
<td>80/100 mesh</td>
<td>349</td>
</tr>
<tr>
<td>6</td>
<td>Reoplex-400 (polyester)</td>
<td>Supelco</td>
<td></td>
<td>2-1093</td>
</tr>
<tr>
<td>7</td>
<td>(CH₃)₃SiCl</td>
<td>Aldrich</td>
<td>b.p. 57°C</td>
<td>KE-5217</td>
</tr>
<tr>
<td>8</td>
<td>KBr</td>
<td>K&amp;K Laboratories, Inc.</td>
<td>for IR</td>
<td>63890X</td>
</tr>
<tr>
<td>9</td>
<td>Iron powder</td>
<td>Mallinckrodt</td>
<td>100 mesh</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Tellurium powder</td>
<td>Alfa</td>
<td></td>
<td>120579</td>
</tr>
<tr>
<td>11</td>
<td>FeO</td>
<td>Alfa</td>
<td></td>
<td>071481</td>
</tr>
<tr>
<td>12</td>
<td>FeCl₂·4H₂O</td>
<td>Matheson Coleman &amp; Bell (MCB)</td>
<td>&gt;98%</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>H₂TeO₄·2H₂O</td>
<td>Alfa</td>
<td>99.5%</td>
<td>091879</td>
</tr>
<tr>
<td>14</td>
<td>TeO₂</td>
<td>Alfa</td>
<td>comm. gr.</td>
<td>110679</td>
</tr>
<tr>
<td>15</td>
<td>Fe₂O₃</td>
<td>Fisher</td>
<td>&gt;99.8%</td>
<td>742859</td>
</tr>
<tr>
<td>16</td>
<td>Acrolein</td>
<td>Chem. Service</td>
<td>97%</td>
<td>6-161</td>
</tr>
<tr>
<td>17</td>
<td>Propylene</td>
<td>Matheson</td>
<td>C.P.</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1-Butene</td>
<td>Phillips</td>
<td>&gt;99.9%</td>
<td>1595</td>
</tr>
<tr>
<td>19</td>
<td>trans-2-Butene</td>
<td>Phillips</td>
<td>research grade</td>
<td>1604</td>
</tr>
<tr>
<td>20</td>
<td>1,3-Butadiene</td>
<td>MG Scientific Gases</td>
<td>&gt;99.67%</td>
<td></td>
</tr>
</tbody>
</table>

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Table III-2  Raw materials (continued)

<table>
<thead>
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<th>Item</th>
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<th>Spec.</th>
<th>Lot #</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Oxygen</td>
<td>MG Scientific Gases</td>
<td>extra dry</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Nitrogen</td>
<td>Lincoln Big Three Company</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Helium</td>
<td>AirCo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>CO₂</td>
<td>Matheson</td>
<td>bone dry</td>
<td>DOT E-8074</td>
</tr>
<tr>
<td>25</td>
<td>Perdeuterated Propylene</td>
<td>Isotope Labeling Corp.</td>
<td>98% D pure</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Oxygen-18</td>
<td>Monsanto Research</td>
<td>95-99% isotopic purity</td>
<td></td>
</tr>
</tbody>
</table>
the oxidation of propylene and 1-butene. The preparation of these catalysts are described below.

a. Acrolein Catalyst

86 g FeCl$_2$·4H$_2$O (.4325 mole) was dissolved in 40 ml HCl and 1000 ml distilled water and filtered. The filtrate was neutralized by 230 ml NH$_4$OH, forming a black precipitate. The precipitate was then washed with 400 ml distilled water and dried at 100°C for 160 minutes. The resulting black solid weighed 40 g. 12.5 g of this black solid was ground with 24.8 g TeO$_2$ (.1554 mole) then calcined at 760°F under air for 10 hours. The Fe/Te ratio was about 1/1. The total weight loss during calcination was about 1.5 g. The dark brown calcined solid was then ball milled, pelletized, ground, and sieved to different particle sizes. The surface area of the particles was measured as 11 m$^2$/g. One g of these particles mixed with glass beads was put into a reactor, evacuated at 100°C for 4 hours, activated by a mixture of about 120 torr oxygen and 800 torr helium at 500°C for more than 10 hours, and then was ready for the propylene oxidation reaction. We shall refer to this material as catalyst a. It had a surface area about 3 m$^2$/g and almost no activity for 1-butene oxidation.

b. Butadiene Catalyst

53 g FeCl$_2$·4H$_2$O (.2666 mole) was dissolved in 18.5 ml HCl and 600 ml distilled water and filtered. The filtrate was neutralized by 95 ml NH$_4$OH resulting in a black precipitate. After filtering, this black precipitate was washed with 170 ml distilled water and dried at 123°C for 11 hours. The dried solid, which weighed 17.6 g, was mixed with
15.0 g TeO₂ (0.0940 mole) and calcined at 750°F under air for 26 hours. The Fe/Te ratio was about 2/1. The total weight loss during calcination was about 0.45 g. In this case, about 1.6 g of black crystals with particle sizes 20 to 40 mesh range were formed during calcination. The powder was ball milled, pelletized, ground, and sieved to different sizes. The surface area of the particles was 13 m²/g. One gram of this particle mixed with glass beads was put into a reactor, evacuated at 100°C for 4 hours, activated by a mixture of about 120 torr oxygen and 800 torr helium at 350°C for more than 10 hours, and then was ready for the reaction of 1-butene oxidation. We shall refer to this material as catalyst β. The activation process had no effect on the surface area. When it was used for the oxidation of propylene, the selectivity to acrolein was very low.

2. Surface Area Measurement

Before the surface area was measured, the catalyst was weighed and degassed at a temperature of about 100°C for four to six hours. The volume of the adsorption system was measured by PV expansion of helium using the ideal gas law. While measuring the volume of the system, the catalyst was held at liquid nitrogen temperatures as during the adsorption process.

Nitrogen was used for physisorption at liquid nitrogen temperature. A known amount of nitrogen was put into the system, then, by changing the pressure and volume of system, the amount of nitrogen that had been adsorbed by the catalyst could be calculated by subtracting the amount of nitrogen in the vapor phase from the initial amount put into the system.
The temperature of the system (other than the catalyst containing
tube) was assumed to be in equilibrium with the ambient temperature
which was read from a thermometer. The vapor pressure, \( P_0 \), of
adsorbate, \( \text{N}_2 \), was measured directly from the vapor pressure of
adsorbate in equilibrium with its own liquid.

The Brunauer-Emmett-Teller equation was used to determine the
surface area. A typical plot of \( P/(V_{\text{ads}}(P_0-P)) \) vs. \( P/P_0 \) is shown as
Figure III-5. The average size of an adsorbed \( \text{N}_2 \) molecule was taken to
be \( 16.2 \text{ Å}^2 \) [68].

3. Catalytic Reactions

Before any catalyst was used for a catalytic reaction, it was
pretreated following a standard procedure. The catalyst was purged at
the activation temperature with a helium flow rate of about 10 ml/min.
for 30 minutes. Then, the reactor was by-passed, still containing
helium, and the rest of the system was evacuated. The system was then
ready for a catalytic reaction.

Before propylene or 1-butene was put into the system, a freeze-
pump-thaw purification was performed. A measured amount of purified
propylene or 1-butene was put into the system and trapped in the U-tube
portion with liquid nitrogen. Then, a measured amount of oxygen was
introduced in the system to produce the desired oxygen/hydrocarbon ratio
in the reaction mixture. Helium was then added to make the total
pressure 800 to 950 torr so as to minimize atmospheric contamination and
to improve heat transfer characteristics in the reactor. The reactants
were then mixed thoroughly. A GC analysis was used to check the initial
mixture. Once the oxygen/hydrocarbon ratio was within an acceptable
Figure III-5 Typical surface area measurement
range, catalytic reactions were started by switching the reactor into the stream. An ice-water trap was put in series with the reactor in the recirculation loop for 1-butene oxidation.

During 1½ hours of propylene oxidation or 2½ hours for 1-butene oxidation, eight samples were analyzed using the on-line GC. Before each sample was taken, a volume equal to one sample-loop was thrown away to avoid contamination caused by the previous sample. The conversion of reactants during the whole period was less than 25%.

After the run was complete, the catalyst was purged with 10 ml/min helium for 30 minutes and it was then ready for the next reactivation and catalytic reaction cycle.

4. Pulse Reactions

Catalyst β was purged with helium at a steady flow rate and heated to 340°C before the pulse reaction was started. A pulse size of reactant was placed in the pulse chamber then purged with helium through the catalyst. A liquid nitrogen trap placed at the effluent of the reactor trapped the products. In case a large pulse size was needed, several smaller pulses could be trapped in the U-tube portion upstream of the reactor and then released by heating the U-tube quickly. After a pulse had been introduced into the system, the helium flow was maintained for 30 minutes to make sure that all the reactant had passed through the catalyst and reached the liquid nitrogen trap.

At the end of the purging period, the reactor was by-passed and the trap, which was still immersed in liquid nitrogen, was evacuated. All of the helium and oxygen in the trap were removed by this procedure. Then, the trap was removed, thawed and a GC analysis performed.
5. Isotopic Tracer Experiments

a. Oxygen-18 Exchange Reactions

To complete a reduction and re-oxidation cycle of the catalyst in the recirculation reactor, 1 g of catalyst \(\alpha\) was reduced by about 33 torr pure propylene to about 8\% conversion of propylene and then re-oxidized by 10 torr of oxygen. Before any oxygen-18 was introduced, the catalyst was reduced and reoxidized twice by oxygen-16. Then, the catalyst was reduced and oxygen-18 was used for the reoxidation cycle. At the end of each catalytic reaction, (about an hour after reduction started), all products were trapped by liquid nitrogen. The trapped sample was expanded into an evacuated sample vial and taken to the GC/MS for analysis of the oxygen-18 content in carbon dioxide and acrolein.

In order to check for oxygen-16/oxygen-18 scrambling by the catalyst, an equal amount of oxygen-16 and oxygen-18 were mixed with propylene and helium and reacted over catalyst \(\alpha\) at 500°C in the recirculation reactor. Three gaseous samples were drawn from the recirculation system for GC/MS analyses at 0, 11 and 47 minutes after the start of the reaction. The ratio of oxygen-16 and oxygen-18 was checked to determine the extent of 0-16/0-18 scrambling.

b. Deuterated Propylene Oxidation

Isotope effects were examined by comparing the reaction rates of perdeuterated propylene and non-deuterated propylene. All the reaction conditions were identical to the regular propylene oxidation process except that 98\% isotopic purity perdeuterated propylene was used.
6. Spectroscopic Analyses
   a. X-Ray Powder Diffraction Pattern

   The samples used for X-ray powder diffraction patterns were simply catalyst α and catalyst β in their completely oxidized conditions without any protection from atmospheric contamination. The patterns of the unactivated catalysts α and β were also taken and showed less crystalline structure than activated catalysts, but no clear compounds different from the activated materials were detected.

   b. Mössbauer Spectroscopy

   The reduced catalyst α used for the Mössbauer spectrum was prepared by reduction of catalyst α with 500 torr propylene at 500°C for 2½ hours in the recirculation reactor. The reactor containing the reduced catalyst was closed and the catalyst was transferred into a 3/4" diameter plastic cell under an argon atmosphere via a glove-box. The catalyst was held vertically in the plastic cell by a thin layer of paraffin. The tightly closed plastic cell was also wrapped with paraffin and teflon tape before determination of the Mössbauer spectrum. The sample was transferred to the spectrometer, then data was accumulated from this specimen. The Mössbauer spectra of oxidized samples of catalyst α and β were also taken but without the protection from atmospheric contamination.

   c. Infra-red Spectroscopy

   Samples for IR spectroscopy were prepared in a KBr host wafer. Catalysts which were reduced, and therefore susceptible to oxidation in the air were sealed in a reactor and transferred in an argon glovebox.
In the glovebox, the samples were mixed with KBr powder, placed in the pressing die, then sealed in a ziplock plastic bag. The bag containing the catalyst and die was then removed and the wafer was pressed in a hydraulic press. The wafer was then removed and the IR spectrum was taken immediately.

To observe the effect of different degrees of catalyst reduction, several 0.0050 g samples of the activated acrolein catalyst were put in 6 mm ID x 10 cm glass tubes and evacuated, then different amounts of propylene were admitted and the tubes sealed. Five samples containing 0, 25, 50, 75 and 470 torr of propylene were prepared then heated at 940-960°F in a muffle furnace for 10 hours. The samples were then analyzed using the IR spectrometer following the KBr pellet method described previously.
IV. RESULTS

A. Kinetic Measurements

1. Standard Conditions

A standard condition was established for blank, reproducibility, and mass-transfer limitation test runs. These same conditions were used, with slight modifications, in the kinetic studies. The procedure involved the use of the recirculation reactor system described in Section III.C.3. (Catalytic Reaction). For the propylene reaction, standard conditions included partial pressures of propylene and oxygen in the ranges 90 to 100 and 110 to 120 torr, respectively. Helium was then added to bring the system to atmospheric pressure. The temperature was 500°C except in the experiments performed to determine the temperature dependence. In the reaction of 1-butene, the initial mixture had 110 to 120 torr and 120 to 130 torr partial pressures of 1-butene and oxygen, respectively. Helium was also used to bring the total pressure of the system up to atmospheric pressure. The temperature for non-temperature dependence experiments was fixed at 340°C.

2. Blank Runs

In order to assure that the catalytic properties were based on the iron tellurium mixed oxide only, some blank runs were carried out under the standard conditions. For the acrolein reaction, a blank run with glass wool was obtained. After an 1½ hour period, only 0.2 torr carbon dioxide and no acrolein was produced. Another reaction under standard
conditions with a TeO$_2$ bed for 1½ hours produced only 0.7 torr carbon dioxide and no acrolein.

Similar standard experiments with 1-butene yielded 0.4 torr of carbon dioxide and 0.01 torr of 1,3-butadiene with glass wool in two hours. No carbon dioxide, 1,3-butadiene or isomers were produced over TeO$_2$. Thus, no corrections for homogeneous reactions were made due to the insignificance of the products in the blank runs.

3. Reproducibility Test Reactions

Figure IV-1 provides evidence that propylene oxidation over catalyst $\alpha$ at 500°C was very reproducible. The relative errors of the initial rates of each component are within 1%.

Figure IV-2 presents two different runs of 1-butene oxidation using catalyst $\beta$ under standard conditions. The initial rates in these two runs had relative errors within 4%, 5%, 4%, 14% for oxygen, 1-butene, carbon dioxide and 1,3-butadiene, respectively.

Many factors can influence the reproducibility of experiments of this type. Slight differences in the initial mixture, catalyst weight, and catalyst homogeneity can contribute to signification differences. These results indicate that methods and procedures have been defined well enough to collect data with confidence.

4. Internal Mass Transfer Limitation Test Reactions

Figure IV-3 compares the partial pressures of each component versus time in two runs of the selective oxidation of propylene catalyzed by two different sizes of the catalyst $\alpha$, 60/80 and 20/40 mesh. The relative errors of the initial rates of propylene and acrolein between
Figure IV-1 Reproducibility test runs for the selective oxidation of propylene by catalyst α.
Figure IV-2 Reproducibility test runs for the selective oxidation of 1-butene by catalyst $\beta$. Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure IV-3  Comparison of the selective oxidation of propylene by catalyst α with different particle sizes.
these two runs were smaller than could be measured. However, because of a slightly higher partial pressure of oxygen in the run over catalyst α with smaller particle size, the relative errors in the initial rates of oxygen and carbon dioxide were 8% and 12.9%, respectively. Due to the independence in oxygen partial pressure of the reaction rate to acrolein, as will be demonstrated later, the different oxygen partial pressures had no effect on the acrolein production rate. We conclude that the particle size of catalyst α had no effect on the oxidation reaction of propylene under these conditions and therefore internal mass transfer limitation are negligible.

In two runs on the oxidation of 1-butene at 350°C over catalyst β with different particle sizes, 20/40 and 60/80 mesh, the relative errors for the initial rates of 1-butene, oxygen, carbon dioxide and 1,3-butadiene were 3.2%, 23%, 18% and 8.2%, respectively (Figure IV-4). The higher carbon dioxide production rate was probably due to the higher partial pressures of 2-butenes in the run with smaller size (60/80 mesh) catalyst β. The pore volume of the 20/40 mesh catalyst β was 0.022 cm³/g with less than 0.1% of the pore volume and surface area belonged to the pores with radii less than 35 Å. It is not appreciately porous, so diffusion resistance are unlikely in any event. As in the case for the 1-butene reaction, internal mass transfer limitation are negligible.

5. Kinetics

a. Oxidation of Propylene

A simple reaction network for propylene oxidation may be written:

\[ \text{CH}_2 = \text{CH} - \text{CH}_3 + \text{O}_2 \xrightarrow{k_1} \text{CH}_2 = \text{CH} - \text{CHO} + \text{H}_2\text{O} \quad (\text{IV.1}) \]

\[ \text{CH}_2 = \text{CH} - \text{CH}_3 + 9/2 \text{O}_2 \xrightarrow{k_2} 3\text{CO}_2 + 3\text{H}_2\text{O} \quad (\text{IV.2}) \]
Figure IV-4 Comparison of the selective oxidation of 1-butene by catalyst β with different particle sizes.
\[ \text{CH}_2 = \text{CH} - \text{CHO} + \frac{7}{2} \text{O}_2 \rightarrow 3\text{CO}_2 + 2\text{H}_2\text{O} \]  \hspace{1cm} (IV.3)

If we base a model on irreversible power law kinetics, we can write the reaction rates as:

\[ \frac{\text{d}P\text{}_{\text{ACR}}}{\text{d}t} = k_1 P_{\text{C}_3}^a P_{\text{O}_2}^b - k_3 P_{\text{ACR}}^c P_{\text{O}_2}^d \]  \hspace{1cm} (IV.4)

\[ \frac{\text{d}P\text{}_{\text{CO}_2}}{\text{d}t} = 3k_2 P_{\text{C}_3}^c P_{\text{O}_2}^f + 3 k_3 P_{\text{ACR}}^c P_{\text{O}_2}^d \]  \hspace{1cm} (IV.5)

\[ \frac{\text{d}P\text{}_{\text{C}_3'}}{\text{d}t} = - k_1 P_{\text{C}_3'}^a P_{\text{O}_2}^b - k_2 P_{\text{C}_3'}^e P_{\text{O}_2}^f \]  \hspace{1cm} (IV.6)

\[ \frac{\text{d}P\text{}_{\text{O}_2}}{\text{d}t} = - k_1 P_{\text{C}_3}^a P_{\text{O}_2}^b - \frac{9}{2} k_2 P_{\text{C}_3}^e P_{\text{O}_2}^f - \frac{7}{2} k_3 P_{\text{ACR}}^c P_{\text{O}_2}^d \]  \hspace{1cm} (IV.7)

where:  \[ P_{\text{C}_3'} = \text{partial pressure of propylene} \]

\[ P_{\text{O}_2} = \text{partial pressure of oxygen} \]

\[ P_{\text{ACR}} = \text{partial pressure of acrolein} \]

\[ P_{\text{CO}_2} = \text{partial pressure of carbon dioxide} \]

\[ t = \text{reaction time} \]

\[ a,b,c,d,e,f = \text{reaction orders} \]

\[ k_1 = \text{rate constants} \]

We have not included any possible reactions to carbon monoxide as no carbon monoxide was found in the products when checked chromatographically.

In order to find the reaction orders with respect to the reactants, the initial rates of production of acrolein and CO\(_2\) were plotted on a log-log scale versus the partial pressure of one of the reactants while the other reactant partial pressure was held constant. Because there was no acrolein initially in the system, the second terms on the right
hand sides of equations IV-4 and IV-5 and the third term in equation IV.7 were zero.

The initial production rates of acrolein were almost constant over a range of oxygen partial pressures from 105 to 350 torr at 500°C when the initial partial pressure of propylene was held constant at 95 torr (Figure IV-5). This indicates that the reaction rate to acrolein was independent of the partial pressure of oxygen and is therefore zero-order in oxygen. This agrees with results of other selective oxidation catalysts, such as bismuth molybdate [12].

Figure IV-6 shows a similar plot of initial rate to acrolein at 500°C over a range of propylene partial pressures from 28 to 132 torr while the oxygen partial pressure varied over the range 97 to 350 torr. However, since the reaction is zero order in oxygen over this range of oxygen partial pressures, the rate dependence is due solely to the changing propylene partial pressure. The log-log plot of the initial rate of acrolein formation versus the initial partial pressure of propylene shows a straight line and a least-squares linear regression gives the slope as 0.96. Thus, the reaction is essentially first-order in propylene which agrees with other investigators on different catalysts [12].

The reaction order to carbon dioxide with respect to the partial pressure of propylene was studied over a range of 40 to 132 torr partial pressure of propylene at 500°C while the partial pressure of oxygen was kept nearly constant (97 to 114 torr). These data are plotted on log-log scale and a least-squares linear-regression gives a slope of 1.0 (Figure IV-7). Some of the scatter depicted in Figure IV-7 is due to slight differences in the initial oxygen partial pressure. But it is
Figure IV-5  Initial acrolein production rate for various oxygen pressures. Propylene pressure constant at 95 torr.
Figure IV-6  Initial acrolein production rate for various propylene pressures. Oxygen pressure 97 to 114 torr.
Figure IV-7  Initial carbon dioxide production rate for various propylene pressures. Oxygen pressure 97 to 114 torr.
still apparent that the reaction rate of propylene oxidation to carbon
dioxide is first-order with respect to the partial pressure of
propylene.

Similar experiments also show a first-order dependence on oxygen
partial pressure for the formation of CO₂ from propylene at 500°C over a
range of 105 to 257 torr of oxygen partial pressure. The partial
pressure of propylene was held constant at 95 torr for this experiment.
Figure IV-8 depicts the data and a calculated slope of 0.97 is obtained.

Efforts have been made to determine the kinetics of the oxidation
of acrolein. Because high concentrations of acrolein in the reactor
system tend to polymerize, it was impossible to make direct observations
on the acrolein plus oxygen system. But using a Runge-Kutta method to
solve equations IV.4 through IV.7 simultaneously and minimizing the
squares of the errors between the predicted and experimental values, we
were able to model the experimental data reasonably well.

In the simulation model, all the known reaction orders for the
oxidation of propylene to acrolein and carbon dioxide were fixed at
their experimental values. Corrections for losses due to sampling,
which amounted to about one percent of the material per sample, were
made in a material balance. Then, a least square multi-dimensional
search together with a Runge-Kutta method to solve differential
equations were performed to find the optimal values of the reaction
orders with respect to oxygen and acrolein for acrolein oxidation and
all the rate constants over five sets of data. The result suggested
that the oxidation of acrolein was 0.44 and 0.60 order with respect to
the partial pressure of acrolein and oxygen, respectively. The rate
constants k₁, k₂ and k₃ (expressed in units of torr and minutes) were
Figure IV-8  Initial carbon dioxide production rate for various oxygen pressures. Propylene pressure constant at 95 torr.
1.26 \times 10^{-1}, 6.64 \times 10^{-4} and 1.28 \times 10^{-5}, respectively. Figure IV-9 shows a full set of predicted curves and experimental data points of each component for a typical run with the optimal rate constants and reaction orders for acrolein oxidation. The highest absolute error was less than 1\%. Ten sets of data had been used to examine the model with the searched optimal values of rate constants and reaction orders of acrolein oxidation. The highest absolute error between predicted and experimental values of all components was 2.42\%. Figure IV-10 presents the predicted curves and experimental points of seven sets of data points of propylene among these ten sets of data with these optimal values. In the same figure, three sets of corresponding data for acrolein are shown. All others have the same behavior. The model gave reasonable results, but we cannot base any firm conclusions on these results since there were so many adjustable parameters in the model.

The temperature dependence of equation IV.4 may be written by the Arrhenius equation

$$\frac{dP_{ACR}}{dt}\bigg|_{t=0} = A \exp \left[-\frac{E}{RT}\right] P_{C_3}$$

(IV.8)

Here, we have utilized previous results which indicated zero-order in oxygen and first-order in propylene.

If the partial pressures of the reactants are held constant, the activation energy can be found by taking the ratio of reaction rates at different temperatures:

$$\frac{\left[\frac{dP_{ACR}}{dt}\right]_{T_1}}{\left[\frac{dP_{ACR}}{dt}\right]_{T_0}}\bigg|_{t=0} = \frac{A \exp \left[-\frac{E}{RT_1}\right] P_{C_3}}{A \exp \left[-\frac{E}{RT_0}\right] P_{C_3}}$$

(IV.9)
Figure IV-9  Comparison of the predicted values and experimental data for a typical propylene oxidation reaction.
Figure IV-10  Comparison of the predicted values and experimental data for the propylene oxidation reaction for several different initial compositions.
Taking the log of both sides

\[
\left. \ln \left[ \frac{dP_{ACR}}{dt} \right] \right|_{T_1}^{t=0} = - \frac{E}{R} \left[ \frac{1}{T_1} - \frac{1}{T_0} \right]
\]

(Figure IV.10)

Five runs with nearly identical initial partial pressures of propylene and oxygen were carried out in a temperature range of 447°C to 500°C. Because of the same initial conditions, the effect of acrolein partial pressure in equation IV.4 could be removed by using the initial rates. Then, \( \ln \left[ \left( \frac{dP_{ACR}}{dt} \right)_{T_1} / \left( \frac{dP_{ACR}}{dt} \right)_{T_0} \right] \) of acrolein versus \( 1/T \) was plotted according to equation IV.10 (Figure IV-11). All the points fell in a straight line and linear regression gave the activation energy of oxidation of propylene to acrolein as 35 kcal/mole (correlation coefficient, \( R = -0.9979 \)). This agrees with literature values on other catalysts near 35 kcal/mole [9,20,21].

The same method and data were used to find the activation energy for the oxidation of propylene to carbon dioxide. These are shown in Figure IV-12. Linear regression gave the activation energy as 41 kcal/mole (\( R = -0.9957 \)).

The selectivities to acrolein, defined as \( \frac{P_{ACR}}{P_{ACR} + \frac{1}{3} P_{CO_2}} \) decreased as the reaction temperature increased. The values varied from 0.901 - 0.762 at 450°C to 0.900 - 0.721 at 470°C and 0.763 - 0.667 at 500°C, depending upon the conversion.

b. Oxidation of 1-Butene

The reaction network for 1-butene oxidation (Figure IV-13) is somewhat more complicated than that for propylene oxidation. As in the
Figure IV-11 Arrhenius plot for acrolein production. Rates relative to the rate at 500°C.
Figure IV-12 Arrhenius plot for carbon dioxide production. Rates relative to the rate at 500°C.
acrolein reaction, no carbon monoxide was observed as a reaction product.

\[
\begin{align*}
\text{1-butene} + \text{O}_2 & \rightarrow \text{1,3-butadiene} + \text{water} \\
\text{2-butenes} + \text{O}_2 & \rightarrow \text{carbon dioxide and water}
\end{align*}
\]

Figure IV-13 Reaction network of 1-butene oxidation

The production of 2-butenes depends on the partial pressure of 1-butene as well as the density of Brönsted acid sites on the catalyst as we will discuss later. Because of the small amounts of 2-butenes produced, the fact that the rate of double bond isomerization is smaller than the rate of oxidation [22], and since we use the initial reaction rate for kinetic studies, the following treatment will not include the effects of 2-butenes.

Based on a model of irreversible power law kinetics, the production rate of 1,3-butadiene and carbon dioxide can be written as:

\[
\begin{align*}
\frac{dP_{\text{BTD}}}{dt} &= k_4 P_{C_4}^h P_{\text{O}_2}^i - k_6 P_{\text{BTD}}^i P_{\text{O}_2}^j \\
\frac{dP_{\text{CO}_2}}{dt} &= 4k_5 P_{\text{C}_4}^k P_{\text{O}_2}^1 + 4k_6 P_{\text{BTD}}^i P_{\text{O}_2}^j
\end{align*}
\] (IV.11) (IV.12)

where:

\[
\begin{align*}
P_{\text{BTD}} &= \text{partial pressure of butadiene,} \\
P_{C_4} &= \text{partial pressure of 1-butene,} \\
P_{\text{CO}_2} &= \text{partial pressure of carbon dioxide,} \\
P_{\text{O}_2} &= \text{partial pressure of oxygen,}
\end{align*}
\]

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\[ t = \text{reaction time}, \]
\[ g, h, i, j, k, l = \text{reaction orders}, \]
\[ k_i = \text{rate constants}. \]

The reaction order for the oxidation of 1-butene to 1,3-butadiene with respect to the partial pressure of oxygen under constant partial pressure of 1-butene at 107 torr was studied over a range of 120 to 294 torr partial pressure of oxygen with a reaction temperature of 340°C. The rate was found to be independent of the partial pressure of oxygen over this range (Figure IV-14). The reaction order for the oxidation of 1-butene to carbon dioxide with respect to the partial pressure of oxygen was found to be 0.49 (Figure IV-15). A slight difference in initial 1-butene partial pressures, 108.8 and 105.4 torr caused some of the scatter in the data for oxygen partial pressures of 235.3 and 294.5 torr.

The reaction order for the oxidation of 1-butene to 1,3-butadiene with respect to the partial pressure of 1-butene was studied over a range of 28 to 400 torr partial pressure of 1-butene at 340°C under constant partial pressure of oxygen at 225 torr. The data points were plotted on log-log scale in Figure IV-16 and the linear regression gave a slope of 0.85. This result was similar to the literature value of first-order for 1-butene oxidation to 1,3-butadiene over bismuth molybdates [12]. The data for the initial rate of the oxidation of 1-butene to carbon dioxide with respect to the partial pressure of oxygen are also shown in Figure IV-17. The reaction order for this pathway was 0.54 from linear regression. No attempt has been made to simulate the entire system as with the propylene reaction.
Figure IV-14  Initial butadiene production rate for various oxygen pressures. 1-Butene pressure constant at 107 torr.
Figure IV-15  Initial carbon dioxide production rate for various oxygen pressures. 1-Butene pressure constant at 107 torr.
Figure IV-16  Initial butadiene production rate for various 1-butene pressures. Oxygen pressure constant at 225 torr.
Figure IV-17 Initial carbon dioxide production rate for various 1-butene pressures. Oxygen pressure constant at 225 torr.
The temperature dependence of 1-butene oxidation was studied by taking the ratio of initial rates at different temperatures versus the reciprocal of the temperatures from 320°C to 350°C and keeping all the initial partial pressures of the reactants constant. Figures IV-18 and IV-19 are the Arrhenius plots of the initial rates of oxidation of 1-butene to 1,3-butadiene and carbon dioxide, respectively, versus the reciprocal of temperature. The activation energy for the oxidation of 1-butene to 1,3-butadiene was found to be 33 kcal/mole \((R = -0.9749)\), which is close to the literature value of 36 kcal/mole for the non-inhibited reaction over bismuth molybdates [15,16]. On the other hand, the activation energy for the oxidation of 1-butene to carbon dioxide was found to be 29 kcal/mole \((R = -0.8922)\) over this temperature range by linear regression.

The selectivities to 1,3-butadiene increased as the reaction temperature increased. The selectivities to 1,3-butadiene (defined as \(\frac{P_{\text{BTD}}}{P_{\text{BTD}} + \frac{1}{4} P_{\text{CO}_2}}\)) changed from 0.266 - 0.20 at 320°C, to 0.308 - 0.219 at 340°C and 0.33 - 0.24 at 350°C.

B. Pulse Experiments

A series of 25 pulse reactions was executed by passing pulses of 7.31x10^{-5} moles 1-butene through a 1 g catalyst bed at 340°C with 8.7 ml/min helium carrier gas. The pulse size was 600 torr 1-butene in a 2.28 ml chamber. The interval between each pulse was about 45 minutes except as noted in Figure IV-20. There were 5 treatments in this process:

1) activation of the catalyst at 350°C for 20 hours before the first pulse,
Figure IV-18 Arrhenius plot for butadiene production. Rates relative to the rate at 350°C.
Figure IV-19  Arrhenius plot for carbon dioxide production. Rates relative to the rate at 350°C.
2) re-oxidation of the catalyst at 350°C for 20 hours after the 5th pulse,
3) allowing the catalyst to remain idle at 340°C for 20 hours after the 10th pulse,
4) same as 3) after the 15th pulse,
5) same as 2) after the 20th pulse.

Figure IV-20 shows the fractional conversion, which was calculated as $1 - \frac{P_{C_4}}{(P_{C_4} + \frac{1}{4} P_{O_2} + P_{BD})}$, versus the number of pulses. Generally, the fractional conversion decreased as the catalyst was reduced, but then increased almost to the same conversion as before when the catalyst was reoxidized. The fractional conversion remained essentially constant during two pulse regions; the eighth through the thirteenth pulses had converted about 9% of the 1-butene while the fourteenth through the twentieth pulses reached about 7% conversion of the 1-butene. There was an increment starting at the eleventh pulse, which deviated from this constant conversion. However, the probable cause is the migration of lattice oxygen from deeper layers to the surface.

These two constant conversion levels between the eighth to thirteenth pulses and fourteenth to twentieth pulses were analyzed to ultimately determine the number of oxide layers removed. This was calculated from the volume and conversion of 1-butene associated with a pulse and the average number of oxygen atoms per unit surface area which is taken to be $1 \times 10^{19}$ atoms/m². The calculated number of oxide layers removed corresponded to roughly one layer of lattice oxide at pulse 10 and a total of 1.7 layers of lattice oxide at pulse 20.
Figure IV-20 Conversion of 1-butene for pulse experiments at 340°C. 
See text for explanation of events.
Figure IV-21 shows the simultaneous selectivities during the pulse reaction to 1,3-butadiene and carbon dioxide. The selectivity, as before, is defined as \( \frac{P_{\text{BTD}}}{P_{\text{BTD}} + \frac{1}{4} P_{\text{CO}_2}} \) and \( \frac{P_{\text{CO}_2}}{P_{\text{BTD}} + \frac{1}{4} P_{\text{CO}_2}} \) for butadiene and carbon dioxide, respectively. These selectivities remained essentially constant over the entire pulse procedure in spite of the relationship between conversion and the degree of catalyst reduction presented in Figure IV-20. This implies that the relative ratio of the selective oxidation sites and combustion sites is independent of degree of reduction.

Figure IV-22 shows the ratio of cis- and trans-2-butene isomers to 1,3-butadiene versus the number of pulses during the same reaction depicted in Figure IV-19. In these pulse reactions, the amount of cis-2-butene was always about 1.5 times the amount of trans-2-butene. The ratio of 2-butenes to 1,3-butadiene increased as the catalyst was reduced and decreased when the catalyst was reoxidized; this trend was the opposite of that for 1-butene conversion as a function of catalyst treatment. However, the total amount of 2-butenes produced also increased when the catalyst was reoxidized (Figure IV-23). So, reoxidation of the catalyst increased the activities of the isomerization and the oxidative products to different degrees.

It is worth noting that when pulse sizes were decreased during the pulse reactions, selectivities of 96% to 1,3-butadiene with 1-butene conversions of 92% have been observed. This was the highest yield obtained with these catalysts.
Figure IV-21 Selectivities for the 1-butene pulse experiments. See text for explanation of events.

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Figure IV-22 Ratio of 2-butene isomers to butadiene for the 1-butene pulse experiments at 340 °C. See text for explanation of events.
Figure IV-23. Production of 2-Butene Isomers for the 1-Butene Pulse Experiments at 340°C. See Text for Explanation of Events.
C. Isotopic Tracer Experiments

1. Exchange of Lattice Oxide and Gaseous Oxygen

A mixture of about 50/50 oxygen-16 and oxygen-18 was used in a recirculation reaction to test the effect of the exchange of lattice oxide and gaseous oxygen over catalyst α.

The reaction was run at 500°C, the same as for the regular catalytic reaction, except the samples for GC/MS were taken by expanding the gas-phase mixture into a pre-evacuated sample bottle and then analyzing by GC/MS. Thus, a significant amount of reaction mixture was taken away as each GC/MS sample was drawn. The partial pressure of oxygen (without isotopic discrimination) was obtained with the usual gas chromatograph. The fractions of oxygen isotopes were the normalized values of the MS intensities of their parent mass/charge (m/e) peaks. The corresponding partial pressures of oxygen isotopes were simply the product of the partial pressures of total oxygen and the corresponding fraction. The results are presented in Table IV-1.

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>pressure (torr)</th>
<th>fraction (I_x/I_total)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total</td>
<td>160_2</td>
</tr>
<tr>
<td>0</td>
<td>104.3</td>
<td>45.7</td>
</tr>
<tr>
<td>11</td>
<td>93.4</td>
<td>43.2</td>
</tr>
<tr>
<td>47</td>
<td>79.8</td>
<td>37.5</td>
</tr>
</tbody>
</table>

If there is no exchange between the lattice oxide and the gas phase oxygen, all of the oxygen isotopes, m/e = 32, 34 or 36, should remain at
their normal isotope ratio. However, the fraction of $^{16}_2$O in the gas phase increased at the beginning of the reaction and then reached a constant level (Figure IV-24), while the fractions of $^{16}_0$-180 and 1802 in the gas phase decreased corresponding to the increase of 1602 and then approached a steady level. The increase of 1602 in the first eleven minutes corresponded to a 2.3 torr (5.19x10^19 molecules of oxygen, about 5 layers of lattice oxides) change between 1602 and 1802.

From this data it is apparent that an exchange between the lattice oxygen-16 and the gas phase 1802 atoms took place. This is also proven by the increase of 1602 in the gas phase when the reduced catalyst was reoxidized by pure oxygen-18.

2. Oxidation of Propylene by Oxygen-18

In order to understand how lattice oxides are involved in the oxidation of propylene, we substituted part of the lattice oxides with labelled oxygen-18 during the reduction-reoxidation cycle and examined the distribution of oxygen-18 in the reaction products. Basically the chance for an oxidation reaction to incorporate the oxygen-16 or -18 of a catalyst is determined by the available quantities of both species in the catalyst assuming there is no kinetic isotope effect which is taken to be small for the two oxygen isotopes. There are three possible types of carbon dioxide, $^{16}_2$O, $^{16}_0$180 and $^{18}_2$O, involved. A binomial distribution of the three types of carbon dioxide will be observed if either oxygen atom is added consecutively and randomly in a stepwise manner or if the oxygen isotopes are scrambled prior to addition to carbon.
Figure IV-24 Isotopic distribution in gaseous oxygen of propylene oxidation.
The distribution data of these three different carbon dioxides were obtained from the GC/MS analysis of the products from the propylene oxidation over the oxygen-18 reoxidized catalyst at 500°C. The catalyst was reduced with propylene and then reoxidized with oxygen-18 alternately. The amount of reactants and the reaction time of each step are presented in Table IV-2. After each reduction step, the reaction mixture was trapped with liquid nitrogen, evacuated (to remove most of the helium) and then transferred to a pre-evacuated vial, and taken to the GC/MS for analysis. Note that the last sample, a fresh catalyst with an oxygen-18/propylene mixture was used in a usual catalytic reaction. The isotopic distribution of oxygen in the carbon dioxide, along with the fraction of oxygen-18 in the acrolein is listed in Table IV-2.

The average number of oxygen-18 atoms per molecule of carbon dioxide, \( \Phi_{CO_2} \), can be calculated as follows:

\[
\Phi_{CO_2} = \frac{\sum X_i N_i}{\sum X_i}
\]

where \( X_i \) = the fraction of carbon dioxide which contained \( i \) oxygen-18 atoms

\( N_i \) = the number of oxygen-18 atoms per carbon dioxide molecule.

The average number of oxygen-18 atoms per molecule of carbon dioxide are tabulated in Table IV-2.

Half of the average number of oxygen-18 atoms per molecule of carbon dioxide is the probability of picking up a single oxygen-18 atom as we have two consecutive drawings of oxygen from the catalyst. Thus, we have the possibility of obtaining none, one or two oxygen-18 atoms per carbon dioxide molecule. In order to compare the experimental
Table IV-2 Isotopic distribution of oxygen in carbon dioxides

<table>
<thead>
<tr>
<th>Condition</th>
<th>Sample</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
<th>Fresh Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene (torr)</td>
<td></td>
<td>30.0</td>
<td>29.7</td>
<td>29.8</td>
<td>30.1</td>
<td>98.†</td>
</tr>
<tr>
<td>Time (min)</td>
<td></td>
<td>48</td>
<td>65</td>
<td>57</td>
<td>66</td>
<td>88</td>
</tr>
<tr>
<td>$\phi_{CO_2}$</td>
<td></td>
<td>*</td>
<td>.955</td>
<td>.943</td>
<td>.907</td>
<td>.268</td>
</tr>
<tr>
<td>$\phi_{ACR}$</td>
<td></td>
<td>*</td>
<td>.044</td>
<td>.058</td>
<td>.093</td>
<td>.460</td>
</tr>
<tr>
<td>Reoxidation</td>
<td></td>
<td>*</td>
<td>.002</td>
<td>.002</td>
<td>.273</td>
<td></td>
</tr>
<tr>
<td>Oxygen-18 (torr)</td>
<td></td>
<td>9.5</td>
<td>9.9</td>
<td>9.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (hr)</td>
<td></td>
<td>9.5</td>
<td>8</td>
<td>8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Distribution not obtained - no oxygen-18 present

† 116 torr of oxygen-18 included in the reaction mixture
isotopic distribution with a theoretic, probability based distribution, binomial distributions calculated for equivalent levels of exchange in carbon dioxide were obtained, and are presented in Table IV-3.

Table IV-3 Calculated binomial distribution for oxygen-18 in CO₂

<table>
<thead>
<tr>
<th>Probability</th>
<th>0.022</th>
<th>0.031</th>
<th>0.048</th>
<th>0.500</th>
</tr>
</thead>
<tbody>
<tr>
<td>C¹⁶O₂</td>
<td>0.957</td>
<td>0.939</td>
<td>0.906</td>
<td>0.250</td>
</tr>
<tr>
<td>C¹⁶O¹⁸O</td>
<td>0.043</td>
<td>0.060</td>
<td>0.091</td>
<td>0.500</td>
</tr>
<tr>
<td>C¹⁸O₂</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
<td>0.002</td>
</tr>
</tbody>
</table>

From Tables IV-2 and IV-3, we see that the oxygen-18 distributions followed the binomial distribution very well. This result may indicate that the incorporation of oxygen with hydrocarbons to form carbon dioxide is by two independent steps.

3. Isotope Effect with Deuterated Propylene

Perdeuterated propylene was used to test for an isotope effect in the oxidation reaction of propylene. Figure IV-25 shows the partial pressures of acrolein and carbon dioxide versus time for the perdeuterated and non-deuterated propylene reactions. Both of the reaction rates to acrolein and carbon dioxide of perdeuterated propylene oxidation are lower than that of non-deuterated propylene by a factor of about 0.5. This is a typical isotope effect on the reaction rate of deuterated hydrocarbon compared to the non-deuterated hydrocarbon due to the difference of the dissociation energies of C-H and C-D bonds. Thus, the rate-determining step of propylene oxidation could be the abstraction of a hydrogen from propylene. The results also indicate that the rate limiting step for selective oxidation is the same.
Figure IV-25 Isotopic effect of perdeuterated propylene oxidation.
as for deep oxidation since both carbon dioxide and acrolein production are equally effected.

D. Physical Measurements

1. X-Ray Powder Diffraction

Figure IV-26 and Table IV-4 show the X-ray powder diffraction pattern for catalyst β. The two strong signals at \( D = 3.40 \) and 2.98 are the characteristic peaks of paratellurite \((\text{TeO}_2)\) [69] and the signals at \( D = 3.26, 2.53 \) and 1.70 indicate the presence of iron (III) tellurate (VI), \( \text{Fe}_2\text{TeO}_6 \), in this catalyst [70]. The diffraction pattern for catalyst \( \alpha \) (Figure IV-27 and Table IV-5) shows qualitatively the same spectrum except it had more crystalline structure; i.e., the total amount of crystalline material is greater, as evidenced by the higher intensities and narrower peak widths of the characteristic peaks of \( \text{Fe}_2\text{TeO}_6 \). These observations are consistant with the higher calcination temperatures and lower surface area catalyst \( \alpha \).

From Bayer's paper [70], \( \text{Fe}_2\text{TeO}_6 \) was thought to be trirutile structure. It's unit cell has \( a_0 = 4.59 \pm 0.01 \) Å and \( c_0 = 9.125 \pm 0.01 \) Å.

2. Mössbauer Spectroscopy

The room temperature iron Mössbauer spectrum of catalyst \( \alpha \) (Figure IV-28) shows a doublet adsorption at a Doppler velocity of 0.380 and -0.134 mm/sec. The isomer shift at approximately 0.123 mm/sec gives strong evidence of ferric \((\text{Fe}^{3+})\) ions in the catalyst [71] though the non-symmetrical nature may be due to two types of \( \text{Fe}^{3+} \) locations. But, there is no evidence of the hyperfine splitting characteristics of an
Table IV-4  X-ray powder diffraction pattern of catalyst β

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>θ</th>
<th>D</th>
<th>I</th>
</tr>
</thead>
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<td>1</td>
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<td>3</td>
<td>27.410</td>
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<td>2.9834</td>
<td>95</td>
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<td>5</td>
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<td>2.7056</td>
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<td>6</td>
<td>35.240</td>
<td>2.5446</td>
<td>14</td>
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<tr>
<td>10</td>
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<td>53.690</td>
<td>1.7057</td>
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<tr>
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<td>14</td>
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<tr>
<td>15</td>
<td>68.000</td>
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<td>16</td>
<td>77.630</td>
<td>1.2289</td>
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<tr>
<td>17</td>
<td>88.430</td>
<td>1.1045</td>
<td>17</td>
</tr>
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</table>

* wavelength = CuKα
Table IV-5 X-ray powder diffraction pattern for catalyst α

<table>
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<th>Peak Number</th>
<th>2θ</th>
<th>D</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.330</td>
<td>5.1126</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>26.150</td>
<td>3.4048</td>
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</tr>
<tr>
<td>3</td>
<td>26.420</td>
<td>3.3706</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>27.110</td>
<td>3.2864</td>
<td>14</td>
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<tr>
<td>5</td>
<td>27.322</td>
<td>3.2613</td>
<td>26</td>
</tr>
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<td>29.895</td>
<td>2.9863</td>
<td>90</td>
</tr>
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<td>7</td>
<td>30.200</td>
<td>2.9568</td>
<td>13</td>
</tr>
<tr>
<td>8</td>
<td>33.230</td>
<td>2.6938</td>
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</tr>
<tr>
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<td>2.5348</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>35.570</td>
<td>2.5217</td>
<td>13</td>
</tr>
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<td>11</td>
<td>37.261</td>
<td>2.4111</td>
<td>16</td>
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<td>42.260</td>
<td>2.1367</td>
<td>13</td>
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<td>13</td>
<td>47.720</td>
<td>1.9042</td>
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</tr>
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<td>1.8646</td>
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<td>53.780</td>
<td>1.7031</td>
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<td>20</td>
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<td>1.4903</td>
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<td>21</td>
<td>76.760</td>
<td>1.2406</td>
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<tr>
<td>22</td>
<td>80.750</td>
<td>1.1891</td>
<td>12</td>
</tr>
</tbody>
</table>

* wavelength = CuKₐ
α-Fe$_2$O$_3$ phase. This is consistent with the X-ray diffraction data which also showed no α-Fe$_2$O$_3$.

The Mössbauer spectrum (Figure IV-29) of the reduced catalyst α (described in IV.C.6.b.) had seven peaks with Doppler velocity at 8.351, 5.026, 1.748, 0.345, -0.584, -4.192 and -7.638 mm/sec. These seven peaks can be separated into two groups, a set of six peaks and a center singlet, corresponding, respectively, to α-Fe$_2$O$_3$ and Fe$^0$ in the form of very small particles.

The same reduced sample was allowed to sit idle for several days and the spectrum was taken over again. This spectrum (Figure IV-30) remained basically the same information with the set of six peaks unchanged but with a set of doublet signals at 0.616 and 0.075 mm/sec instead of the singlet. It may be explained by atmospheric reoxidation of Fe$^0$ to Fe$^{+3}$ but not to α-Fe$_2$O$_3$.

Catalyst β showed two sets of doublets merged into a triplet (Figure IV-31) indicative of the same Fe$^{+3}$ compound as in catalyst α.

3. Infra-red Spectroscopy

Figure IV-32 shows the IR spectra in the range 300 to 1400 cm$^{-1}$ of unactivated and activated catalysts α. Because of low transparency, nothing is noticeable in the field higher than 1400 cm$^{-1}$. The absorption peaks of Fe$_2$TeO$_6$ as reported by Von G. Bayer [70] at 690 (strong), 639 (medium, shoulder), 571 (medium) and 506 (strong) cm$^{-1}$, were evident in our spectrum. TeO$_2$ has IR absorption bands at 760-770 (medium) and 520-660 (strong, broad) [72]. In the IR spectrum (Figure IV-32, spectrum i) of low temperature calcined catalyst α, bands at 770 and 671 cm$^{-1}$ were the result of a mixture of TeO$_2$ and Fe$_2$TeO$_6$. There
Figure IV-29 Mössbauer spectrum for reduced catalyst α.
Figure IV-31 Mössbauer spectrum for catalyst β.
i unactivated catalyst α
ii 500 torr oxygen, 650-675 °F, 10 hours
iii 500 torr oxygen, 925-975 °F, 10 hours

Figure IV-32 IR spectra for unactivated and activated catalyst α.
was another absorption peak at 1110 cm$^{-1}$ (weak, broad) which fell in the range of bridged O-O stretching, 1075 to 1195 cm$^{-1}$ [73], indicative of the superoxide $O_2^-$ ion, M-O-O-M.

As the catalyst was calcined at higher temperature by 500 torr oxygen for 10 hours at 650 to 675°F (Figure IV-32, spectrum ii) and 925 to 950°F (Figure IV-32, spectrum iii), the absorption peaks at 650 and 500 cm$^{-1}$ increased and a shoulder appeared at 575 cm$^{-1}$, while the relative intensity of absorption at 760 to 770 cm$^{-1}$ was reduced. This observation can be correlated by the increasing crystalline structure of Fe$_2$TeO$_6$. The absorption at 1110 cm$^{-1}$ remained unchanged.

An experiment designed to provide information on the state of the catalyst during reaction was performed. A standard recirculation experiment with catalyst $\alpha$ was stopped after 80 minutes of reaction and the catalyst removed from the reactor in the glove box. A portion of the catalyst was mixed with KBr and a pellet for IR study was produced (Figure IV-33, spectrum vi). Basically, this spectrum remained unchanged from that of the activated catalyst (Figure IV-33), but showed some water production. Thus, the catalyst is in a highly oxidized state under normal catalytic reaction conditions.

Catalysts which were more highly reduced with an excess of propylene were examined by IR in a similar way. The IR spectrum (Figure IV-33, spectrum iv) indicated the presence of $\alpha$-Fe$_2$O$_3$ at 552, 470, 375 and 357 to 340 cm$^{-1}$. The spectrum also showed absorption at 1383 and 1260 cm$^{-1}$ probably due to symmetric $\text{C}^\equiv\text{H}$ deformation [74]. The absorption peak at 800 cm$^{-1}$ might be attributed to the presence of an intermediate species of catalyst. The reduced catalyst was reoxidized by oxygen at 950°F for 16 hours which restored its original bands as shown in Figure IV-33 (Figure IV-33, spectrum v).
iv 265 torr propylene, 500 °C, 2.5 hours
v reduced and reoxidized catalyst α
vi under catalytic reaction

Figure IV-33 IR spectra for unactivated and activated catalyst α.
The IR spectra for different degrees of reduction of the activated acrolein catalyst were also studied. Five 5 mg portions of activated catalyst α were mixed with propylene at pressures of 0, 25, 50, 75 and 472 torr and were sealed in 6 mm ID x 13 cm glass vial. These vials were then heated at 950°F in a muffle furnace for 12 hours. The catalysts were removed and pelletized with KBr under an argon atmosphere and the IR spectra determined (Figure IV-34). These wafers of catalyst were shown to be stable in the atmosphere over a several hour period by taking several spectra and comparing them. The characteristic absorption bands of Fe₂TeO₆ present in these catalyst decreased corresponding to an increase in the degree of reduction of the catalyst. Meanwhile, the absorption bands of α-Fe₂O₃ increased as the degrees of reduction of the catalysts increased. A band at 800 cm⁻¹ was detected during the reducing process, but disappeared as the catalyst was totally reduced. Most important of all was the absorption at 835 cm⁻¹ of the activated catalyst, (which had been heated to 950°F under vacuum), which shifted to 800 cm⁻¹ in the reduced catalyst. This absorption decreased with increasing degree of reduction and eventually disappeared as the catalyst was reduced totally. It is understood that the peroxide ion (O₂⁻) has bridging O-O stretching between 790-930 cm⁻¹ and triangular O-O stretching at about 850 cm⁻¹ [74].

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vii 25 torr propylene, 925-975 °F
viii 50 torr propylene, 925-975 °F
ix 75 torr propylene, 925-975 °F
x 472 torr propylene, 925-975 °F

Figure IV-34 IR spectra for catalyst α with different degrees of reduction.

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V. DISCUSSION

A. Kinetics

Both the selective oxidation reactions of propylene and 1-butene were found to be zero-order with respect to the partial pressure of oxygen. Selective oxidations of 1-butene and propylene over several other mixed oxide catalysts were reported to be independent of the partial pressure of oxygen [12,15,16]. This zero-order kinetics in oxygen partial pressure implies that the reaction takes place between hydrocarbon and lattice oxide, not gaseous oxygen. However, the extensive oxidation reactions of propylene and 1-butene were dependent on the partial pressure of oxygen to the first and half-order, respectively. The higher oxygen order for the extensive oxidation of propylene indicates a lower selectivity for the propylene reaction compared to the 1-butene reaction as observed.

The reaction orders for the selective oxidation of propylene and 1-butene with respect to propylene and 1-butene were found to be 1 and 0.85, respectively. The reaction order with respect to 1-butene indicates that reaction is probably inhibited by 1,3-butadiene. Schuit et al. [15,16] showed that the dependence of the oxidation reaction on 1-butene was first-order over bismuth molybdate catalysts without product inhibition. Even with product inhibition in the 1-butene case, both cases still satisfied the first-order, single site adsorption rate equation proposed by Schuit et al. [16].

Also for the case of the extensive oxidation of 1-butene, product inhibition is the probable cause for the reduced order with respect to
the 1-butene partial pressure of 1/2. In the case of the extensive oxidation of propylene, there was a first-order dependence on the partial pressure of propylene.

The activation energies of the selective oxidation of 1-butene and propylene were found as 33 and 35 kcal/mole, respectively. Meanwhile, the activation energies of extensive oxidation of 1-butene and propylene were found as 29 and 41 kcal/mole, respectively. These values are rather typical of selective oxidation reactions [15,19,20]. The magnitude of the activation energy and linearity of the activation energy plots also indicate an absence of diffusional limitations.

The change of selectivities to 1,3-butadiene and acrolein with different reaction temperatures, stated in the previous chapter, correlate well with that expected from the activation energy effects. Based on the activation energies, the selective oxidation of 1-butene would be preferred at higher temperature while the propylene oxidation should be run at a lower temperature in order to obtain higher selectivities. However, the stability of catalyst $\beta$ prevented running the selective oxidation of 1-butene higher than 350°C. The low activity caused by low surface area of catalyst $\alpha$ required higher temperatures to obtain reliable data; products from lower temperature reactions were too small to measure accurately.

In general, the selectivity to the selective products will increase as the ratio of hydrocarbon to oxygen in the initial reactants increase; i.e., the reducing environment favors the selective products. However, there is an upper limit on the hydrocarbon/oxygen ratio since the catalyst can be irreversibly affected by over reduction.
B. Pulse Experiments

The results of pulse experiments imply that selective oxidation sites are the same sites as those for deep oxidation, since the ratio of selective oxidation to deep oxidation remained constant in the pulse experiments even as the catalyst was cycled and the conversion changed. This conclusion seems inconsistent in light of different reaction orders for deep versus selective oxidation. However, the same active sites do not imply similar mechanisms for deep and selective oxidation. The number of active sites may change, but the relative rates do not change. Furthermore, the kinetic experiments were performed with gas phase oxygen and therefore, adsorbed oxygen may play an important role. The role of adsorbed oxygen is not addressed with the pulse reactions. Clearly, isomerization sites are distinct from the selective oxidation and deep oxidation sites as shown in the pulse experiments.

Pulse experiments also indicate the mobility of lattice oxygen atoms. When the catalyst is allowed to remain idle after being reduced, some activity is restored. This is probably due to migration of lattice oxygen to the surface layers. Obviously, the process slows after part of the first layer has been replenished by oxygen migration during the first idle period as evidenced by the lack of an increase in activity after a second idle period.

C. Oxygen-18 Tracer Experiments

The results of oxygen-18 tracer experiments show that the distribution of oxygen-18 in carbon dioxide follows a binomial distribution. The average number of oxygen-18 atoms in the catalyst increased as the catalyst was reoxidized by gaseous oxygen-18, according
to the average number of oxygen-18 atoms in the carbon dioxide produced. Roughly, the oxygen contained in the catalyst was about twice as much as the gaseous oxygen-18 used for oxidation during this experiment. However, the average number of oxygen-18 atoms in acrolein remained at a lower level than that of carbon dioxide. The result appears different from that of pulse experiment, which suggests that the selective and deep oxidation sites are the same. However, as mentioned in the previous section, the same sites do not imply similar mechanisms for deep and selective oxidation. In the perdeuterated propylene oxidation experiment, both selective and deep oxidation show isotope effects compared to the non-deuterated propylene oxidation, which implies that they have the same initial and rate-determining step. Most likely, abstraction of the first hydrogen forming the allylic ion corresponds to this step and is common to both CO$_2$ and acrolein production. However, deep oxidation must take place on different sites than selective oxidation after this step in order for CO$_2$ to show different oxygen-18 levels than acrolein.

In the experiment of catalytic reaction of propylene and pure oxygen-18, the average number of oxygen-18 atoms in carbon dioxide, 1.005, is much higher than that of acrolein, 0.005. Note that the catalyst had not been previously exposed to oxygen-18 and all oxygen in the catalyst should be oxygen-16 except the amount of natural abundance of oxygen-18 during the initial stages of the reaction. The very low value for the average number of oxygen-18 atoms in acrolein implies that all the oxygen in acrolein came from lattice oxides and the high value of oxygen-18 in carbon dioxide gives a strong evidence that adsorbed oxygen plays an important role in the deep oxidation process.
D. Isotope Effect with Perdeuterated Propylene Oxidation

From the results of the oxidation of perdeuterated propylene, both rates to CO\(_2\) and acrolein are about half of those from non-deuterated propylene oxidation. This is the typical isotope effect due to the different dissociation energies of C-H and C-D bonds. It indicates that the abstraction of hydrogen is the first and rate-determining step for both CO\(_2\) and acrolein production [12,15,16]. The results also indicate that both selective and deep oxidations share the same initial step, though the reaction mechanism is clearly different from that point.

E. Spectroscopic Analyses

1. X-Ray Powder Diffraction

X-ray data have been particularly useful in several aspects concerning the nature of this catalytic system. First of all, the X-ray diffraction patterns showed that the catalyst consisted of iron(III) tellurate, which is a trirutile structure (Figure V-1). The data have indicated that there is little chemical difference between catalyst \(\alpha\) and \(\beta\). The high annealing temperature and low surface area of catalyst \(\alpha\) are consistent with the X-ray observation of bigger Fe\(_2\)TeO\(_6\) crystals. Studies on the activity of catalyst \(\alpha\) for 1-butene oxidation have shown that the catalyst is selective but only very weakly active. Propylene oxidation on catalyst \(\beta\) shows a high activity but little selectivity. Apparently, the relatively high surface area of catalyst \(\beta\) causes such a high activity for propylene oxidation that essentially all of the propylene is converted completely to CO\(_2\). Catalyst \(\alpha\), on the other hand, simply does not have enough surface area to efficiently convert 1-butene. It appears that there is no significant difference between
Figure V-1  Trirutile structure of $\text{Fe}_2\text{TeO}_6$ [70]

- ○: oxygen
- ●: iron
- ◦: tellurium

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catalyst \( \alpha \) and \( \beta \) other than the surface area and that the Fe\(_2\)TeO\(_6\) phase is the active species.

The Fe\(_2\)TeO\(_6\) phase contains tellurium in the +6 oxidation state. Many other investigators have also concluded that Te\(^{6+}\) is the active species in tellurium containing catalysts [56, 63, 64, 65]. For instance, Forzatti et al. [56] have studied the effects of addition of varying amounts of tellurium to mixed molybdates such as CaMoO\(_4\), CoMoO\(_4\), Fe\(_2\)(MoO\(_4\))\(_3\) and MnMoO\(_4\). They speculated that the active site is a Te\(^{6+}\) site which is stabilized above 300°C. However, the fact remains that the catalysts studied by Forzatti et al. [56] contain oxidation and isomerization sites which are interconvertible. Our results indicate that two types of sites are prevalent on Fe\(_2\)TeO\(_6\). The first type of site is responsible for initiation of both deep and selective oxidation and is probably a Te\(^{6+}\) site and the second type of site is responsible for isomerization activity. There is no evidence which indicates the isomerization sites can be converted to oxidation sites.

2. Mössbauer Spectroscopy

The iron Mössbauer spectrum of virgin catalyst \( \alpha \) shows Fe\(^{3+}\) but no \( \alpha\)-Fe\(_2\)O\(_3\). The Fe\(^{3+}\) species is most likely due to the Fe\(_2\)TeO\(_6\) phase which was detected via X-ray diffraction. The non-symmetrical nature of the Fe\(^{3+}\) resonance is probably due to the two different Fe\(^{3+}\) lattice locations in Fe\(_2\)TeO\(_6\). When the catalyst was extensively reduced, \( \alpha\)-Fe\(_2\)O\(_3\) and elemental iron were detected via Mössbauer. This implies that, under extensive reduction, Fe\(_2\)TeO\(_6\) is converted to \( \alpha\)-Fe\(_2\)O\(_3\) and even to Fe\(^0\) if the degree of reduction is great enough. However, no Fe\(^{2+}\) was detected under any condition indicating that there is no
The formation of metallic iron parallels the formation of Te$^0$ which is lost from the catalyst upon extensive oxidation. Forzatti et al. [66] reported that tellurium doped catalyst will lose tellurium at high reaction temperatures. The formation of Fe$^0$ and Te$^0$ have not been thoroughly studied since under normal selective oxidation conditions, the elements remain in their oxidized states.

3. IR Spectroscopy

The absorption patterns of TeO$_2$ and Fe$_2$TeO$_6$ were evident in the IR experiments agreeing with the X-ray powder diffraction patterns. The increase of the Fe$_2$TeO$_6$ absorption bands with high temperature annealing was also apparent with IR.

The IR spectrum of the reduced catalyst also showed absorption bands at 1383 and 1260 cm$^{-1}$. The absorption at 1383 cm$^{-1}$ may be assigned to the symmetrical C-H deformation of $\equiv$CH$_2$ group [74] and is therefore due to adsorbed hydrocarbon.

The IR absorption at 1110 cm$^{-1}$ appears under all of the catalyst conditions except for that of totally reduced catalyst and is in the range of 0-0 stretching of superoxide ion, $O_2^-$ [73]. It may be rationalized as the effect of two adjacent oxygen atoms in the catalyst.

The IR absorption at 800 cm$^{-1}$ appears only in the reduced catalyst and falls in the range of the peroxide ion, $O_2^{2-}$ [73]. This band is very likely due to oxygen anions near anion vacancies which must appear as the catalyst is reduced. Further reduction of the catalyst shows bands which can be assigned to $\alpha$-Fe$_2$O$_3$. This result is consistent with Mössbauer observations.
F. The Nature of Catalytic Activity

From the above discussion, the nature of catalytic activity may be summarized as followed:

1) The active phase of catalyst is Fe$_2$TeO$_6$.
2) Te$^{6+}$ is the exclusive active site for selective oxidation processes; iron is not involved in the redox cycle.
3) The abstraction of the first hydrogen from the hydrocarbon is the first and rate-determining step for both CO$_2$ and acrolein production.
4) α-Fe$_2$O$_3$, elemental iron, and tellurium may be produced under extensively reduced conditions.
5) The lattice oxides in deep layers possess the mobility to diffuse to the surface layers.
6) Lattice oxides are responsible for selective oxidation while both lattice oxygen and adsorbed oxygen are responsible for deep oxidation.
7) The reduced catalyst may be reoxidized by gaseous oxygen to its original state.
8) Catalyst α and β are not appreciably different.

From this information, we are able to derive more detailed information about the mechanism of the reaction. Information pertaining to catalyst α may be applied to catalyst β and vice versa.

G. Reaction Mechanism

According to the trirutile structure of Fe$_2$TeO$_6$, the catalyst could be represented by the intersections of four- and eight-member rings

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(Figure V-2). Te$^{6+}$ is octahedrally surrounded with six oxygen anions in this compound.

The first step of the selective oxidation of olefins over mixed oxide catalysts is widely accepted as the abstraction of the allylic hydrogen to form an adsorbed, resonant stabilized species and an OH group. This step is also generally accepted to be the rate-determining step of the process.

The isotope effect with perdeuterated propylene provides evidence that the oxidation of propylene over catalyst $\alpha$ also follows this first step.

Due to the resonant structure of the allyl formed by the first step, both carbons at the ends of the hydrocarbon chain are identical and have equal chance to execute further reactions.

The second step proposed is the incorporation of oxygen onto the allyl group by attaching itself to a nearby oxygen anion. Then, Te$^{6+}$ is reduced to Te$^{4+}$ by abstraction of a second proton to form a second hydroxyl group and dissociation of the tellurium-carbon bond through electron rearrangement. The two hydroxyl groups then form a water molecule leaving an anion vacancy. Meanwhile, acrolein is dissociated from the tellurium ion and forms an anionic surface species. Migration of this species to other sites probably results in CO$_2$ formation while the selective process continues near the tellurium site. These two free electrons may be absorbed by the reduction of tellurium (VI) to tellurium (IV). The tellurium (IV) may be restored to tellurium (VI) via oxidation with gas phase oxygen.

If no gas phase oxygen is present, the reaction may proceed by further reduction of Te$^{4+}$ following the same mechanism.
Figure V-2  Ring Structure of Fe$_2$TeO$_6$
The proposed reaction mechanism is sketched in Figure V-3. It is also formulated in Figure V-4.

In summary, tellurium has been reported as a good doping element for selective oxidation catalysts but is not stable [66]. In the mechanism proposed here, it is suggested that Te\(^{6+}\) has the capability to conduct selective oxidation of propylene by itself provided that there is an environment to stabilized Te\(^{6+}\). In Fe\(_2\)TeO\(_6\), iron does not participate in the catalytic reaction but provides the environment for stable Te\(^{6+}\).
Figure V-3 Proposed mechanism of propylene oxidation over catalyst $\alpha$. Structural representation.
Figure V-4 Proposed mechanism of propylene oxidation over catalyst α. Stoichiometric representation.
VI. SUMMARY

Tellurium has been used as a doping agent for the mixed oxide catalysts for selective oxidation of propylene and 1-butene. It has been rationalized that tellurium may either act as an active site in the form of Te$_{6+}$ or a modifier of metal oxygen double bonds. Fe$_2$O$_3$ is the most active catalyst for selective oxidation among those pure oxides of the first row transition metals. Thus, a mixed iron tellurium oxide is expected to be a good selective oxidation catalyst.

A recirculation reactor system was built to conduct this research work. The catalysts have been made by the solid state reaction of iron hydroxide and tellurium oxide. Isotopic tracers and spectroscopic analyses were used to study the catalyst.

The kinetic study was based on a power law model and the data were taken from the initial reaction rates. The results can be expressed as follows:

For propylene oxidation:
\[
\frac{dP_{ACR}}{dt} = k_1 P_{C_3}^3 \quad \text{with activation energy 35 kcal/mole}
\]
\[
\frac{dP_{CO_2}}{dt} = k_2 P_{C_3} P_{O_2} \quad \text{with activation energy 41 kcal/mole}
\]

For 1-butene oxidation:
\[
\frac{dP_{BTD}}{dt} = k_4 P_{C_4}^{0.85} \quad \text{with activation energy 33 kcal/mole}
\]
\[
\frac{dP_{CO_2}}{dt} = k_5 P_{C_3}^{0.5} P_{O_2}^{0.5} \quad \text{with activation energy 29 kcal/mole}
\]

The catalyst consists of different active sites for isomerization and oxidation reactions. However, the active sites for selective and
extensive oxidation appear to be identical, at least during the initial and rate-determining step.

The catalyst is identified as trirutile Fe$_2$TeO$_6$ by X-ray powder diffraction pattern. The oxidation reaction is supposed to take place only at surface layers and the oxides in these surface layers will either be substituted by gaseous oxygen or deep layer oxides.

A mechanism which suggested that Te$^{6+}$ is the active site is proposed. Iron does not participate in the catalytic reaction unless the catalyst is destroyed and iron oxide is formed. Obviously, an environment which can stabilize Te$^{6+}$ is essential, and iron appears to provide the environment.

The results from this novel catalyst, which contains tellurium in a binary mixed oxide, may provide a basic explanation for the role of tellurium as a good doping agent. The philosophy of selecting this catalyst may also provide an alternative theoretical background for selecting catalysts.
VII. REFERENCES


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VITA

Yan-Nian Shyr was born in Hsin-chu, Taiwan, Republic of China on October 5, 1949. He graduated from Hsin-chu High School in 1967.

He started his undergraduate work in Chemical Engineering at Chung Chen Institute of Technology, Taiwan, R.O.C., and received a B.S. degree in June, 1971. He enrolled in the Department of Applied Chemistry, College of Chinese Culture in September, 1974 and obtained his M.S. degree in May, 1976. In June, 1980, he began his graduate career in the Department of Chemical Engineering, LSU. In May, 1982, he received his M.S. degree in Chemical Engineering at LSU.

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EXAMINATION AND THESIS REPORT

Candidate: Yan-Nian Shyr

Major Field: Chemical Engineering

Title of Thesis: Studies on the Selective Oxidation Activity of Fe-Te-O Catalysts

Approved:

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Major Professor and Chairman

Dean of the Graduate School

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Date of Examination: November 23, 1983