Model vanadium-phosphorous-oxygen catalysts for the selective oxidation of C4 hydrocarbons to maleic anhydride

Thomas Patrick Moser
Iowa State University

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Moser, Thomas Patrick

MODEL VANADIUM-PHOSPHORUS-OXYGEN CATALYSTS FOR THE
SELECTIVE OXIDATION OF CARBON(4) HYDROCARBONS TO MALEIC
ANHYDRIDE

Iowa State University

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Model vanadium-phosphorus-oxygen catalysts for the selective oxidation of C₄ hydrocarbons to maleic anhydride

by

Thomas Patrick Moser

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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For the Graduate College

Iowa State University
Ames, Iowa

1986
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Summary

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GENERAL INTRODUCTION

Catalytic selective oxidation processes are some of the most important industrial routes for producing valuable chemical intermediates. To a significant extent, industrial processes for producing partially oxidized hydrocarbons by heterogeneous catalysis have relied on olefinic and aromatic hydrocarbon feedstocks. Ethylene and propylene are used in the dominant routes to ethylene oxide and acrylonitrile, respectively. Aromatics such as benzene and naphthalene can be converted to anhydrides through high-temperature selective oxidation catalysis. Methanol oxidation is also an important industrial route for producing formaldehyde, a valuable industrial chemical. A summary of some of the most significant industrial selective oxidation processes is given in Table 1 (1). In contrast, heterogeneous catalytic synthesis involving the selective oxidation of paraffins currently represents only a small portion of the total output of chemicals and intermediates in the United States; rapid growth of this processing technology has been predicted, however (2).

One significant example of paraffin conversion is the catalytic selective oxidation of n-butane to maleic anhydride. Previous routes have relied on the oxidation of benzene. The oxidation of C₄ fractions to maleic anhydride has proven to be a commercially desirable process resulting in a number of patentable catalysts. The reliance on paraffin feedstock is expected to increase significantly as benzene becomes more expensive and difficult to use, due in part to environmental restrictions.

The first production of maleic anhydride for commercial sale was in 1933, and only until very recently benzene was the preferred feedstock.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₆ + 9/2 O₂ → ( \text{C}<em>{6} \text{H}</em>{5} \text{CO}_2 \text{H} ) + 2CO₂ + 2H₂O</td>
<td>Supported V₂O₅</td>
<td>Fluidized bed</td>
</tr>
<tr>
<td>( \text{C}<em>{6} \text{H}</em>{12} ) + 3O₂ → ( \text{C}<em>{6} \text{H}</em>{6} \text{CO}_2 \text{H} ) + 3H₂O</td>
<td>Supported V₂O₅</td>
<td>Fluidized or fixed bed</td>
</tr>
<tr>
<td>C₆H₆ + 9/2 O₂ → ( \text{C}<em>{6} \text{H}</em>{5} \text{CO}_2 \text{H} ) + 2CO₂ + 2H₂O</td>
<td>Supported V₂O₅ + MoO₃</td>
<td>Fixed bed</td>
</tr>
<tr>
<td>CH₃OH + 1/2 O₂ → HCHO + H₂O</td>
<td>( \text{Fe}_2(\text{MoO}_4)_3 ) + MoO₃ or supported Ag</td>
<td>Fixed bed</td>
</tr>
<tr>
<td>H₂C=CH₂ + 1/2 O₂ + H₂C=CH₂</td>
<td>Supported Ag</td>
<td>Fixed bed</td>
</tr>
<tr>
<td>H₂C=CHCHO + 1/2 O₂ + H₂C=CH₃CO₂H</td>
<td>Mixed molybdates</td>
<td>Fixed bed</td>
</tr>
<tr>
<td>H₂C=CH₂ + 3/2 O₂ + H₂C=CH₃CO₂H</td>
<td>Mixed molybdates (two-step conversion)</td>
<td>Fixed bed</td>
</tr>
<tr>
<td>H₂C=CH₂ + NH₃ + 3/2 O₂ → H₂C=CH₃CN + 3H₂O</td>
<td>Mixed molybdates</td>
<td>Fluidized bed or fixed bed</td>
</tr>
</tbody>
</table>
In the United States, growth of maleic anhydride production has been extremely rapid. The major uses of maleic anhydride are in polyester resins, agricultural chemicals, and lubricating additives. The continually expanding role of maleic anhydride in the chemical industry has stimulated new research efforts for developing processes and catalysts that produce maleic anhydride more efficiently and economically.

Efforts to develop active, selective, and stable catalysts for n-butane oxidation have been clearly revealed in the patent literature (3). More than 70 patents that relate to the butane route were issued in the 1970s (4). The most widely claimed catalyst composition is based on vanadium, phosphorus, and oxygen; catalyst modifiers include iron, molybdenum, chromium, cobalt, nickel, zirconium, zinc, copper, and several other metals. Specific V-P-O catalyst phases have been examined because of their apparent relevance for C₄ hydrocarbon oxidation. In particular, V-P-O phases such as β-VOPO₄ (β-vanadyl phosphate) and (VO)₂P₂O₇ (vanadyl pyrophosphate) are reported to play an important role in butane and butene oxidation through a V⁵⁺/V⁴⁺ redox mechanism.

Production of Maleic Anhydride

The predominant commercial route to maleic anhydride is the vapor-phase selective oxidation of hydrocarbons over a solid catalyst. Benzene, n-butane, and butenes are used. Recovery of maleic anhydride as a by-product from phthalic anhydride manufacture provides small commercial amounts. In general, the production of maleic anhydride from hydrocarbons involves two steps. The first involves the oxidation of a relatively low concentration of hydrocarbon in air to form maleic anhydride, carbon
oxides, water, and smaller amounts of partially oxidized byproducts. Because of the large exotherm and the thermal sensitivity of the hydrocarbon oxidation, the process requires low feed concentrations, expensive heat transfer equipment, and a large gas-handling system. The exothermicity of the reaction provides an important energy source (steam). The second step involves the recovery of maleic anhydride from the dilute reactor off-gas and purification of the resultant crude product.

**Benzene route**

Historically, the catalytic selective oxidation of benzene has represented the primary route for producing maleic anhydride. A typical plant in operation today consists of a tubular reactor, a partial condenser, an absorber, a dehydration unit and a refining column. All benzene to maleic anhydride plants use multitubular, fixed-bed reactors which are cooled by molten salt. The reactors may contain as many as 15,000 tubes, each being about 25 mm in diameter and up to 4 meters long. The reactors are made of stainless steel (4).

Typically, benzene is mixed with air in concentrations from 1 to 1.4 mole percent and fed at about 200°C. The reactant mixture is rapidly preheated in the first portion of the packed tubes to a "kindling temperature" between 350 to 400°C. The reaction rate then becomes appreciable, and heat is transferred out rather than into the reactor tubes. Generally, the rate of heat transfer is insufficient to maintain isothermal conditions, and a "hot spot" develops part way down the tube. The peak temperature may be as high as 100°C above that of the coolant. As the reactant is depleted, the rate diminishes, and the gases begin to
cool. The average conversion in U.S. plants is about 94.5 percent (with an initial selectivity of over 74 percent) which decreases as the catalyst ages. Catalyst life is typically two to three years. Industrial catalysts used for benzene oxidation to maleic anhydride are reported to contain $\text{V}_2\text{O}_5$ and $\text{MoO}_3$ with additives to enhance yield being $\text{As}^+$, $\text{Co}^+$, $\text{Na}^+$, $\text{Li}^+$ or $\text{TiO}_2$, $\text{NO}_3$, and $\text{P}_2\text{O}_5$ (Table 2). Most, if not all, commercial benzene oxidation catalysts are supported. Alumina, silica, or carborundum are typical support materials (5).

**$C_4$ hydrocarbon route**

In 1981, approximately 73 percent of the U.S. maleic anhydride was produced by the oxidation of benzene, 25 percent by n-butane oxidation, and 2 percent as a byproduct of phthalic anhydride synthesis (6). By comparison, about 62 percent of the maleic anhydride produced in the Far East utilized $C_4$ feedstocks in 1980 (2). U.S. companies anticipated, however, that 85 percent of domestic maleic anhydride would be produced via the $C_4$ hydrocarbon route by 1984 (6). For economic and ecological reasons, the chemical industry has been changing to n-butane as the principal feedstock. These reasons are:

1. The cost of benzene relative to n-butane is expected to increase because of increased oil prices and the increased use of aromatics in unleaded gasolines.

2. Benzene has been labeled as a suspected carcinogen. Tight emission controls may soon be imposed by OSHA and the EPA for the use of benzene. Proposed standards would limit benzene emissions
Table 2. Benzene-maleic anhydride catalysts (5)

<table>
<thead>
<tr>
<th>Country/Company</th>
<th>Catalyst</th>
<th>Yield (mole %)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Am. Cyanamid</td>
<td>$V_2O_5MoO_3AgCe$</td>
<td>60-65</td>
<td></td>
</tr>
<tr>
<td>Allied Chem.</td>
<td>$V_2O_5MoO_3AgPO_4UO_2$</td>
<td>70-73</td>
<td>410-460°C On Alundum</td>
</tr>
<tr>
<td>Chempatents</td>
<td>$V_2O_5MoO_3Co_2O_3Li_2O CaO$</td>
<td>63-67</td>
<td>On Alundum</td>
</tr>
<tr>
<td>Hommel</td>
<td>$V_2O_5SnO_2TiO_2ZrO$</td>
<td>45-55</td>
<td>400-500°C</td>
</tr>
<tr>
<td>Monsanto</td>
<td>$V_2O_5MoO_3TiO_2$</td>
<td>55-62</td>
<td>Fixed or Fluid Bed</td>
</tr>
<tr>
<td>Pittsburgh Chem.</td>
<td>$V_2O_5MoO_3$</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>PPG</td>
<td>$V_2O_5MoO_3Co_2O_3NaCl$</td>
<td>65</td>
<td>380-420°C On Alundum</td>
</tr>
<tr>
<td>Scientific</td>
<td>$V_2O_5MoO_3NiO_2NaCl P_2O_5$</td>
<td>68-71</td>
<td>360-400°C On Alundum</td>
</tr>
<tr>
<td>Design</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>German</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Badische Anilin</td>
<td>$V_2O_5MoO_3TiO_2P_2O_5$</td>
<td>70</td>
<td>380-420°C .6-1% C_6H_6</td>
</tr>
<tr>
<td>French</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saint-Gobain</td>
<td>$V_2O_5MoO_3SnO_2TiO_2CeO_2UO_3$</td>
<td>64</td>
<td>1.3% C_6H_6</td>
</tr>
<tr>
<td>Source</td>
<td>Formula</td>
<td>Temperature</td>
<td>Notes</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------------------------</td>
<td>-------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Russian</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I. I. Jaffe et al.</td>
<td>$V_2O_5MoO_3TiO_2P_2O_5$</td>
<td>60</td>
<td>$400^\circ C$</td>
</tr>
<tr>
<td>I. A. Mozakalev</td>
<td>$V_2O_5MoO_3Co_2O_3Na_2O$</td>
<td>63-65</td>
<td>On Alundum</td>
</tr>
<tr>
<td>Indian</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. S. Trehan</td>
<td>$V_2O_5MoO_3Li^+Na^+$</td>
<td>70</td>
<td>Fluid Bed, On Quartz</td>
</tr>
<tr>
<td>S. K. Bhattacharya</td>
<td>$V_2O_5MoO_3WO_3CoO TiO_2UO_2$</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Japanese</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oriental High Pressure</td>
<td>$V_2O_5MoO_3TiO$</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Nippon Cat. Chem.</td>
<td>$V_2O_5MoO_3SnO_2$</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Takeda Chem. Ind.</td>
<td>$V_2O_5MoO_3Ag^+Na^+P_2O_5$</td>
<td>70</td>
<td>1% C$_6$H$_6$ On Alundum</td>
</tr>
</tbody>
</table>
from maleic anhydride plants to 0.3 lbs per 100 lbs of benzene fed to the process (2).

3. The development of improved butane to maleic anhydride catalysts. Butane feedstocks are currently being used by Amoco and Monsanto.

The process description and flow schemes for benzene and butane oxidation to maleic anhydride are basically the same. However, the equipment sizes and process conditions differ. n-Butane provides a higher theoretical yield of maleic anhydride than benzene; thus, 1 lb of butane can yield 1.69 lb of maleic anhydride, whereas 1 lb of benzene theoretically yields 1.26 lb of maleic anhydride. The butane process results in lower conversion and selectivity than the benzene process. Therefore, a butane plant requires larger equipment to operate at the equivalent productivity of a benzene plant. Because of the larger equipment required at equivalent capacity, the capital costs for butane-based maleic anhydride plants are greater than those for benzene. Although the butane route has a slightly higher capital cost, it is thought that the difference in feedstock prices between benzene and butane will persist. Hence, the butane process is an attractive route. The concept of the convertible plant has begun to manifest itself in practice. Argentina is currently converting its maleic anhydride plants to the dual feed construction whereby either n-butane or benzene could be used as a feedstock (5). Where n-butane is not available or where low-price benzene is available, benzene may be favored. Alternatively, if butane economics become more favorable, the plant could be converted to a C₄ feedstock.

The economic and ecological reasons for using butane as a feedstock have provided a strong impetus for research in developing C₄ processes. A
successful butane process requires (as do all partial oxidation reactions) the development of a highly selective and active catalyst. Vanadium-phosphorus-oxygen (V-P-O) catalysts alone or mixed with some activating compounds are most frequently reported in the patent literature for butane oxidation (Table 3). Catalytic operation of butane oxidation is done typically between 450 and 500°C, which is about 50 to 100 degrees higher than in the benzene process.

Selective Oxidation Reactions

The production of maleic anhydride from benzene and C_4 hydrocarbons falls under a more general class of reactions called selective oxidation reactions. A selective oxidation catalyst is designed to provide a limited amount of oxygen to a reactant, allowing formation of the desired product but restricting further oxidation that would yield CO_2 and H_2O. Reactor design is usually quite complex since the reactions are strongly exothermic and reactor temperature profiles are difficult to predict.

The mechanism for selective oxidation reactions catalyzed by metal oxides is considered to follow a two-stage redox process. This redox (reduction/oxidation) mechanism was first introduced by Mars and van Krevelen (7) in their study of naphthalene oxidation catalyzed by V_2O_5. The mechanism involves: (1) a reaction between the oxide catalyst and the hydrocarbon in which the hydrocarbon is oxidized and the catalyst is reduced, and (2) a reaction of the reduced catalyst with oxygen from the feed gas to reoxidize the catalyst. The process can be illustrated as follows:
Table 3. Patented catalysts for oxidation of n-butane to maleic anhydride (adapted from Varma and Saraf (3))

<table>
<thead>
<tr>
<th>Cat. compn.</th>
<th>Feed gas compn.</th>
<th>Temp., °C</th>
<th>Yield, %a</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_2O_5-V_2O_5$</td>
<td>1.5% butane in air</td>
<td>470</td>
<td>90(conv.)</td>
</tr>
<tr>
<td>$V_2O_5nP_2O_5$</td>
<td></td>
<td></td>
<td>90(conv.)</td>
</tr>
<tr>
<td>($n=4.1-4.5$)</td>
<td></td>
<td></td>
<td>90(sel.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>$V_2O_5-P_2O_5$</td>
<td>3 mol % butane in air</td>
<td>440</td>
<td>39</td>
</tr>
<tr>
<td>($P/V$ at 1-1.2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-P-O (contg. tetravalent V and pentavalent P)</td>
<td>butane-air</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-V-Zn</td>
<td>1 vol % butane in air</td>
<td>500</td>
<td>72(wt)</td>
</tr>
<tr>
<td>(1.15:1.0:0.19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnCl₂ as activator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-P-Zr</td>
<td>1:25 butane-air mixture</td>
<td>400</td>
<td>68</td>
</tr>
<tr>
<td>(1:1.2:0.13)</td>
<td></td>
<td></td>
<td>63.2(conv.)</td>
</tr>
<tr>
<td>V-P-Zr-O</td>
<td>butane-air</td>
<td>450</td>
<td>62.0(sel.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-P-Co</td>
<td>butane-air mixture</td>
<td>450</td>
<td>92.4(wt)</td>
</tr>
<tr>
<td>(1:1.14:0.19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCl₂ as activator</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoO₃-V₂O₅-P₂O₅</td>
<td>butane-air</td>
<td>---</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-P-Fe</td>
<td>1.59 mol % butane in air</td>
<td>495</td>
<td>25.7</td>
</tr>
<tr>
<td>(13.71:64.35:21.94)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-V-Fe-Cr-Ba</td>
<td>1.5% butane in air</td>
<td>450</td>
<td>53.0</td>
</tr>
<tr>
<td>(62.0:8.0:20.0:8.0:2.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-P-Fe-Cr</td>
<td>1.46% butane in air</td>
<td>460</td>
<td>46.5</td>
</tr>
<tr>
<td>(62.0:9.0:20.0:9.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-P-Ti</td>
<td>butane-air</td>
<td>400</td>
<td>32.5</td>
</tr>
<tr>
<td>(Ti/P=0.08:1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The yield is in mole percent based on hydrocarbon fed unless otherwise stated.
Table 3. Continued

<table>
<thead>
<tr>
<th>Cat. compn.</th>
<th>Feed gas compn.</th>
<th>Temp., °C</th>
<th>Yield, %a</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-P-Mg (1:1.1:0.05)</td>
<td>3 mol % butane in air</td>
<td>446</td>
<td>42.5</td>
</tr>
<tr>
<td>( V_{1.2}Cu_{0.026}Te_{0.026}Li_{0.039}x )</td>
<td>0.5-1.8 mol % butane in air</td>
<td>450</td>
<td>35.22</td>
</tr>
<tr>
<td>( V_{1.5}Zn_{0.19}Si_{0.167}O_x )</td>
<td>0.5-1.8 mol % butane in air</td>
<td>--</td>
<td>58.0</td>
</tr>
<tr>
<td>V-U oxide</td>
<td>1:100 butane-air mixture</td>
<td>482</td>
<td>47-50</td>
</tr>
<tr>
<td>Sb-Ni-Mo (1:0.24:0.14)</td>
<td>0.8 mol % butane in air</td>
<td>402</td>
<td>36(conv.)</td>
</tr>
</tbody>
</table>

---
1. reduction of the catalyst by the hydrocarbon molecule in feed;

\[ \text{HC}_{\text{gas}} \overset{\text{r}}{\rightarrow} \text{HC}_{\text{ads}} \]

\[ \text{HC}_{\text{ads}} + \text{CAT}_{\text{ox}} \rightarrow \text{HC-O}_{\text{ads}} + \text{CAT}_{\text{red}} \]

\[ \text{HC-O}_{\text{ads}} \rightarrow \text{HC-O}_{\text{gas}} \]

2. oxidation of the reduced catalyst by oxygen in feed;

\[ \frac{1}{2} \text{O}_2 + \text{O}_{\text{ads}} \rightarrow \frac{1}{2} \text{O}_2 \]

\[ \text{CAT}_{\text{red}} + \text{O}_{\text{ads}} \rightarrow \text{CAT}_{\text{ox}} \]

where \( \text{CAT}_{\text{red}} \) and \( \text{CAT}_{\text{ox}} \) are the reduced and oxidized forms of the catalyst, respectively, and HC is a hydrocarbon molecule.

It is generally assumed that \( \text{O}^{2-} \) from the lattice is responsible for the oxidation of the hydrocarbon. Reoxidation by gas phase oxygen is assumed to lead to formation of \( \text{O}^{2-} \) in the lattice again, but requires four electrons for every oxygen molecule, as follows from the equation

\[ \text{O}_2 + 2 \Box + 4e^- \rightarrow 2 \text{O}^{2-} \]

where \( \Box \) denotes an anion vacancy.

The mobility of oxygen both within the lattice and at the surface of an oxidation catalyst can significantly influence both selectivity and activity. Generally, highly mobile oxygen results in a very active but nonselective catalyst. On the other hand, if the oxygen is tightly bound to the catalyst, the oxide is expected to have low catalytic activity. To maximize yield, an intermediate degree of oxygen mobility is desired.
Clearly, the role of the catalyst is to promote high catalytic activity without compromising product selectivity.

Role of Selective Oxidation Catalysts

Thermodynamic considerations

Thermodynamically, the oxidation of a hydrocarbon to carbon dioxide and water is preferred over all selective oxidation reactions. To avoid numerous products with different degrees of oxidation, the use of a catalyst is obviously required. The role of the catalyst involves at least two basic functions:

1. Activation of the hydrocarbon molecule to be oxidized by chemisorption on the catalyst surface, typically in a specific orientation. Oxygen insertion may be directed to a specific site on the hydrocarbon molecule.

2. The catalyst reduces or "moderates" the activity of oxygen. The amount of energy released by the formation of C=O (86 kcal/mol) or H-O (111 kcal/mol) bonds (8) by reaction between a hydrocarbon and molecular oxygen is large enough to cause excessive fragmentation, leading to complete combustion.

For metal oxides, the degree of "moderating" is related to the free energy of transition from a higher to lower oxide (e.g. V₂O₅ → V₂O₄). A value close to zero means that the catalyst has about the same oxidation potential as molecular oxygen, while a value near 100 kcal/mol suggests negligible reactivity towards a hydrocarbon. For a selective catalyst an intermediate value is desirable. In an actual catalyst the selectivity is strongly affected by inhomogeneities in the metal oxide such as edges,
corners, defects in the lattice, and the heterogeneity of the strength of oxygen bonds at the catalyst surface.

The strength of the metal-oxygen bonds at the catalyst surface are believed to influence both catalyst activity and selectivity. The activation energy for exchange between $^{18}\text{O}_2$ in the gas phase and oxygen in the catalyst can be used as a measure of metal-oxygen bond strengths. Two types of oxygen exchange can occur (9): (1) homomolecular (involving unpairing the electrons in the oxygen-oxygen bond of the oxygen molecule); and (2) heterogeneous exchange (electrons not unpaired). Homomolecular exchange can occur by a dissociation of oxygen on the catalyst. The activity of various metal oxides towards homomolecular exchange permits one to evaluate the probability of the formation of intermediate forms of oxygen on the catalyst surface (10). Heterogeneous exchange involves both molecular oxygen and oxygen in the oxide lattice. Both homomolecular and heterogeneous exchange are believed active (10).

Haber and Grzybowska (11) have applied the principles of isotopic exchange of oxygen to correlate activity and selectivity to metal-oxygen bond strengths. Catalysts with high $^{18}\text{O}$ exchange rates led to complete combustion, whereas catalysts showing negligible exchange were most selective. This approach does have its limitation, however. In most cases the oxidation activity is considerably greater than the exchange activity. This difference exists since during oxidation catalysis the oxygen liberated from the catalyst is facilitated by the presence of a reducing agent which may form an intermediate complex (transition state) involving the active site.
Participation of lattice oxygen

The participation of lattice oxygen is generally agreed to be part of a functioning redox mechanism (12-18). Two types of experiments are commonly used to demonstrate the participation of lattice oxygen: (1) experiments in absence of gas phase oxygen, and (2) experiments conducted with labeled oxygen. The selective activity of an oxide catalyst in the absence of gas phase oxygen provides direct evidence for the participation of lattice oxygen. This type of experiment, however, does not exclude the involvement of other forms of oxygen such as adsorbed molecular or gas phase oxygen. Experiments involving labeled oxygen have utilized gas phase $^{18}$O$_2$ as an isotopic tracer (12-16), and to a lesser extent $^{18}$O labeling of the solid catalyst (12, 17, 18).

Transfer of electrons

The transfer of oxygen from the gas phase to the catalyst bulk is believed to proceed by a stepwise donation of electrons. The scheme can be represented as follows (19, 20):

$$
\begin{align*}
0_2^{\text{gas}} &\rightarrow 0_2^{\text{ads}} \quad +2e^- \\
0_2^{\text{ads}} &\rightarrow 0_2^{-}^{\text{ads}} \quad 20^{-}^{\text{ads}} \quad 20^{2-} \quad 20^{2-} \quad 20^{2-} \\
+e^- &\rightarrow 0_2^{-}^{\text{ads}} \quad +e^- \\
+2e^- &\rightarrow 20^{2-}
\end{align*}
$$

The oxidizing power of the oxygen decreases from left to right. The surface $0^{2-}$ is considered the reactive oxygen leading to selective products.
Nature of the active sites

The reaction of a hydrocarbon at the surface of a catalyst is not usually assumed to involve the presence of a particular metal ion, but instead an ensemble of metal oxygen ions that form an active site. The geometry of this site is related to the surface structure. Specific crystalline phases can be related to activity and selectivity if the bulk and surface structures are similar. In general, active sites are considered in terms of oxygen coordination, acidity (or electron affinity) and the participation of different sites in one oxidation process (bi-functional action).

Oxygen coordination  The coordination of the metal oxide is believed to play an important role in the function of an active site. Mitchell and Trifiro (21) found that a bismuth molybdate catalyst is most active if the amount of tetrahedrally coordinated molybdenum is large in comparison with octahedrally coordinated molybdenum. One problem with this interpretation is that often the coordination is changed by reduction of the catalyst or by the support interactions (22). The coordination at the catalyst surface is also very difficult to characterize.

Acid-base properties  The selective interaction of a metal oxide and a hydrocarbon molecule is a process involving electron-accepting and electron-donating, respectively. Ai et al. (23-26) described this process as being analogous to acid-base interactions. Ai (23) studied the selective oxidation of butadiene to furan using heteropoly compounds, such as 12-molybdophosphoric acid. Much like MoO$_3$-P$_2$O$_5$ and Mo$_3$-P$_2$O$_5$ catalysts, 12-molybdophosphoric acid is highly acidic with a strong affinity for basic compounds (electron donors) such as butadiene and furan, whereas it
has little affinity for acidic compounds (electron accepting) such as maleic anhydride. Consequently, the catalyst is active for butadiene and furan but inactive for maleic anhydride, preventing its further oxidation. Accordingly, the activity and selectivity would depend on the relative acidity and basicity of the active sites and the hydrocarbon to be oxidized, respectively.

**Bifunctional interactions** Catalysts are termed bifunctional if more than one active site is involved in the surface reaction. Bifunctionality in oxidation catalysis may be connected with the redox mechanism or with promoting different reaction steps. The redox mechanism is generally believed to involve at least two active sites (17, 27). The interaction of a hydrocarbon to be oxidized and the reoxidation of the reduced catalyst may occur at different functional sites. These two sites may together form one ensemble that performs the complete reaction. Likewise, the reaction mechanism may involve two sites; one for oxidative dehydrogenation and one for oxygen incorporation.

**Research Objectives**

Although vanadium–phosphorus–oxygen catalysts are extensively used industrially for $C_4$ hydrocarbon selective oxidation to maleic anhydride, a fundamental understanding of the nature of the functioning catalytic phase(s) involved is still lacking. The preparation, characterization and catalytic evaluation of two model V–P–O phases, $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$, has been previously provided (28–30). These model compounds were found to be both active and selective for n-butane conversion to maleic anhydride. The objective of this work is to obtain a more fundamental
understanding of functioning V-P-O catalysts. Particular emphasis will be given to the characterization of the functioning model compound using \textit{in situ} laser Raman spectroscopy. Complementary techniques including X-ray powder diffraction and X-ray photoelectron spectroscopy for characterization of fresh and used catalytic materials are also discussed. The \textit{in situ} Raman technique is particularly valuable since it makes possible the characterization of catalyst features during C$_4$ hydrocarbon oxidation which may otherwise be undetectable by postcatalytic characterization. The direct observations of phase stability and the participation of lattice oxygen during catalysis is also possible using the \textit{in situ} Raman technique.

Attention is also focused on the active sites responsible for selective oxidation and complete combustion using specifically labeled oxygen-18 enriched catalysts. The objective of these studies is to determine the relationship between the spectroscopic characteristics of the functioning catalyst and the catalytic behavior, i.e., the kinetics of oxygen incorporation into maleic anhydride and carbon dioxide. Experimentally this is made possible using a coupled laser Raman spectroscopy/mass spectrometry system.

The reaction network for C$_4$ hydrocarbon oxidation to maleic anhydride may involve further conversion of maleic anhydride to products such as maleic acid or combustion to CO$_2$ and water. Moser and Schrader (30) found that the further oxidation of maleic anhydride to CO$_2$ apparently was significant during n-butane oxidation. The direct conversion of maleic anhydride can be established by using maleic anhydride as the feed hydrocarbon. Evidence for the direct conversion of maleic anhydride is presented via
integral flow reactor studies utilizing a molten maleic anhydride saturator feed system. The primary objective is to determine the relationship between maleic anhydride combustion and the catalytic phase present during reaction.

Explanation of Dissertation Format

This dissertation contains three sections, each written in a form suitable for publication in a technical journal. A general introduction has been included to orient the reader to the scientific and industrial relevance of this work. The introduction is not intended to be an exhaustive literature review; such information has already been provided by this author (28, 29). A reference list is provided at the end of each section. References cited in the general introduction are given at the end of the dissertation. The research presented in each section represents original work conducted by the author.
SECTION I. MALEIC ANHYDRIDE CONVERSION BY MODEL V-P-O CATALYSTS
The vapor phase conversion of maleic anhydride was studied using two model vanadium-phosphorus-oxygen (V-P-O) catalysts, $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$. Maleic anhydride was fed directly to an integral flow reactor using a molten maleic anhydride saturator system developed for this work. Direct evidence for the combustion of maleic anhydride was established with the simultaneous production of maleic acid. The conversion of maleic anhydride increased with temperature, oxygen partial pressure, and residence time.
INTRODUCTION

The synthesis of maleic anhydride from n-butane is an important commercial example of paraffin selective oxidation. Vanadium-phosphorus-oxygen (V-P-O) catalysts with P-to-V ratios near unity have found special application for this process (1). Detailed characterization and catalytic evaluation of both model V-P-O phases (2) and high surface area industrial-type (3) catalysts have been reported. Although this process represents an important commercial advance, the mechanism of n-butane selective oxidation to maleic anhydride remains poorly understood.

The reaction pathways presented for n-butane selective oxidation to maleic anhydride are very simple. The models proposed by Wohlfahrt and Hofmann (4) and Escardino et al. (5) have implied the direct conversion of n-butane to maleic anhydride. The reaction pathway proposed by Escardino et al. (5)

\[
\text{n-butane } \xrightarrow{} \text{maleic anhydride} \tag{1}
\]

involves the formation of maleic anhydride and carbon oxides from n-butane and the combustion of maleic anhydride to CO, CO\text{, and } \text{H}_2\text{O}. Centi et al. (6) and Cavani et al. (7) have also postulated the oxidation of maleic anhydride on the basis of kinetic modeling.

This investigation provides direct evidence for the combustion of maleic anhydride by V-P-O model compounds. The effects of reaction temperature, residence time, and oxygen partial pressure on the rates of maleic anhydride disappearance and CO\text{, and } \text{H}_2\text{O} formation are presented.
EXPERIMENTAL PROCEDURE

Catalyst Preparation

Syntheses and characterization of both $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ have been described previously (2).

Maleic Anhydride Conversion Measurements

The vapor phase conversion of maleic anhydride was studied using an integral flow reactor operating at near atmospheric pressure (Figure 1). The reactor was constructed from 316 stainless-steel tubing having a 1-in. outer diameter and $\frac{5}{8}$-in. inner diameter. The overall reactor bed length was 15-in., including the $\frac{5}{8}$-in. thickness of each flange. The temperature along the reactor length and at varying radial depths was monitored by using 13 subminiature thermocouple probe assemblies (Omega Engineering). These thermocouples yielded information concerning possible axial or radial temperature gradients caused either by "hot spots" or by inadequate heating control. The entire reactor was submerged in a heated fluidized sand bath. Zoned heating of the reactor was also employed by seven independently controlled resistance elements. Typically, the temperature of the reactor bed could be maintained to within ±2°C.

Residual activity of the reactor was suppressed by preconditioning the reactor wall and the silicon carbide chips with a wash of 85 wt. % H$_3$PO$_4$ followed by calcination in oxygen at 600°C. The reactor was charged with catalyst and No. 8 mesh (2.38 mm) silicon carbide which served as a diluent. The catalyst bed consisted of a homogeneous mixture of 5.00 g of catalyst and 45 g of conditioned silicon carbide. Catalyst particles were
Figure 1. Integral flow reactor
prepared by pressing disks which were broken and sieved to between Nos. 10 and 20 mesh (1.68 to 0.84 mm).

Tylan Model FC260 mass flow controllers were used to regulate oxygen and nitrogen gas flow rates. Maleic anhydride delivery was achieved using a saturator system (Figure 2). The system consisted of a 1 liter Pyrex vessel with both inlet and outlet gas ports, a 50-ft. preheater coil made from ¼-in. copper tubing, and an air convection oven with a built-in air circulation pump. The inlet nitrogen-oxygen mixtures, delivered from the gas feed system, was preheated in the copper coil and blown just above the surface of a bath of molten maleic anhydride in the saturator vessel. The saturator temperature was regulated to within ±0.5°C by thermostat control and measured by a thermocouple probe positioned near the center of the vessel. The saturator was operated at 59°C (melting point of maleic anhydride ca. 52°C) to obtain feed concentrations of maleic anhydride of about 0.29% in air. The stability of maleic anhydride and its concentration in the feed mixture was analyzed both by gravimetric techniques and by gas chromatography. Gravimetric measurements were made by condensing the saturator effluent in a coiled Pyrex tube chilled in an ice bath.

Exit lines from the reactor were heated to 105°C to prevent maleic anhydride condensation. The composition of both the feed and product gases was analyzed by gas chromatography. The analytical system consisted of an Antex 300 gas chromatograph which was equipped with three heated sampling valves, two flame ionization detectors, and one thermoconductivity detector. The conversion of maleic anhydride was determined by analysis of the feed and product gases. The percent conversion reported in this work was defined as
Figure 2. Maleic anhydride delivery system
Rates of maleic anhydride disappearance and $\text{CO}_2$ production were normalized to a standard maleic anhydride feed of $1.575 \times 10^{-5}$ g-moles/min/g-cat.

Steady-state kinetic experiments were conducted to examine the effects of contact time (time factor), reaction temperature, and oxygen partial pressure in the feed. The time factor was defined as the ratio $W/F$, where $W$ is the weight of the catalyst (kg) and $F$ is the total molar feed rate (kmole/h at STP). The catalysts were studied as a function of the following variables: oxygen partial pressure in feed—0.05 to 0.22 atm; reaction temperature—250 to 525°C; time factor—1.55 to 9.33 kg catalyst/kmol/h.
EXPERIMENTAL RESULTS

Maleic anhydride conversion was studied under steady-state conditions using two model V-P-O catalysts; \( \beta \)-VOPO\(_4\) and \((\text{VO})_2\text{P}_2\text{O}_7\). Maleic anhydride conversion and the rate of combustion activity were measured as a function of the time factor (W/F), reaction temperature, and oxygen partial pressure in the feed gas.

Effect of Time Factor

The effect of the time factor (W/F) on maleic anhydride conversion is given in Table 1. For both \( \beta \)-VOPO\(_4\) and \((\text{VO})_2\text{P}_2\text{O}_7\), the conversion and rate of CO\(_2\) production tended to increase with increasing W/F. At high flow rates (1200 cm\(^3\)/min STP) the conversion of maleic anhydride was 24.1% for \( \beta \)-VOPO\(_4\) and 26.7% for \((\text{VO})_2\text{P}_2\text{O}_7\). The conversion was considerably greater with lower flow rates (200 cm\(^3\)/min STP): 45.3% for \( \beta \)-VOPO\(_4\) and 36.2% for \((\text{VO})_2\text{P}_2\text{O}_7\). The combustion activity was considerably higher for \( \beta \)-VOPO\(_4\) as compared to \((\text{VO})_2\text{P}_2\text{O}_7\).

Effect of Temperature

The conversion of maleic anhydride by both \( \beta \)-VOPO\(_4\) and \((\text{VO})_2\text{P}_2\text{O}_7\) increased with reaction temperature. At low temperatures, the conversion was attributed to maleic acid formation. The conversion and the rates of CO\(_2\) production and maleic anhydride disappearance are given in Table 2.

For \( \beta \)-VOPO\(_4\), maleic anhydride conversion increased from 10.4% at 250°C to 41.1% at 525°C. The corresponding combustion activity showed essentially negligible production of CO\(_2\) at 250°C but increased rapidly
Table 1. Conversion of maleic anhydride, rate of CO₂ formation and rate of maleic anhydride disappearance as a function of time factor (W/F) (T = 475°C; P₀₂ = 0.22 atm)\(^a\)

<table>
<thead>
<tr>
<th>W/F kg catalyst</th>
<th>Flow rate (sccm)</th>
<th>β-VOPO₄ conv, %</th>
<th>r₂-CO₂ (E-6)</th>
<th>-r₂-MAN (E-6)</th>
<th>(VO)₂P₂O₇ conv, %</th>
<th>r₂-CO₂ (E-6)</th>
<th>-r₂-MAN (E-6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.33</td>
<td>200</td>
<td>45.3</td>
<td>18.9 (E-6)</td>
<td>7.14 (E-6)</td>
<td>36.2</td>
<td>9.34 (E-6)</td>
<td>5.68 (E-6)</td>
</tr>
<tr>
<td>3.11</td>
<td>600</td>
<td>40.8</td>
<td>6.15 (E-6)</td>
<td>6.42 (E-6)</td>
<td>26.9</td>
<td>4.13 (E-6)</td>
<td>4.24 (E-6)</td>
</tr>
<tr>
<td>2.07</td>
<td>900</td>
<td>20.3</td>
<td>5.29 (E-6)</td>
<td>3.20 (E-6)</td>
<td>15.1</td>
<td>0.86 (E-6)</td>
<td>2.38 (E-6)</td>
</tr>
<tr>
<td>1.55</td>
<td>1200</td>
<td>24.1</td>
<td>4.59 (E-6)</td>
<td>3.79 (E-6)</td>
<td>26.7</td>
<td>2.46 (E-6)</td>
<td>4.21 (E-6)</td>
</tr>
</tbody>
</table>

\(^a\)Rates expressed as g-moles/min/g-catalyst.
Table 2. Conversion of maleic anhydride, rate of CO₂ formation and rate of maleic anhydride disappearance as a function of reaction temperature (W/F = 3.11, P₀₂ = 0.22 atm)

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>β-VOPO₄</th>
<th>(VO)₂P₂O₇</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>conv, %</td>
<td>r_CO₂</td>
</tr>
<tr>
<td>250</td>
<td>10.4</td>
<td>1.64 E-6</td>
</tr>
<tr>
<td>350</td>
<td>26.4</td>
<td>2.37 E-6</td>
</tr>
<tr>
<td>425</td>
<td>31.2</td>
<td>1.83 E-6</td>
</tr>
<tr>
<td>475</td>
<td>40.8</td>
<td>6.15 E-6</td>
</tr>
<tr>
<td>525</td>
<td>41.1</td>
<td>12.0 E-6</td>
</tr>
</tbody>
</table>

^Rates expressed as g-moles/min/g-catalyst.

^Negligible.
between 350 and 525°C. The combustion activity approximately doubled for each 50°C increase in temperature.

The conversion of maleic anhydride by \((\text{VO})_2\text{P}_2\text{O}_7\) increased from 9.0% at 250°C to 34.5% at 525°C. The combustion activity remained negligible between 250 to 350°C, but increased rapidly from 425 to 525°C. As with \(\beta\)-\text{VOPO}_4, the combustion activity approximately doubled for each 50°C increase in temperature.

Pseudo-Arrhenius plots are given in Figures 3 and 4 for maleic anhydride conversion by \(\beta\)-\text{VOPO}_4 and \((\text{VO})_2\text{P}_2\text{O}_7\), respectively. Rather low apparent activation energies for maleic anhydride conversion by \(\beta\)-\text{VOPO}_4 (4.20 kcal/mol) and \((\text{VO})_2\text{P}_2\text{O}_7\) (4.17 kcal/mol) were calculated.

**Effect of Oxygen Partial Pressure**

Maleic anhydride conversion was studied as a function of oxygen partial pressure in the feed at 475°C (Table 3).

For \(\beta\)-\text{VOPO}_4, the conversion of maleic anhydride increased slightly with increasing oxygen partial pressure. At low oxygen partial pressure (0.05 atm) the conversion was 32.1%; it increased to 40.8% at high oxygen pressures (0.22 atm). The corresponding combustion activity increased slightly with increased oxygen partial pressure.

The conversion of maleic anhydride by \((\text{VO})_2\text{P}_2\text{O}_7\) remained essentially constant (24.5 to 26.9%) with increasing oxygen partial pressure from 0.05 to 0.22 atm. The corresponding combustion activity also remained essentially constant.
Figure 3. Pseudo-Arrhenius plot of the rate of disappearance of maleic anhydride by $\beta$-VOPO$_4$. 

\[ -\frac{\ln \alpha}{T} \times 10^6 \]
Figure 4. Pseudo-Arrhenius plot of the rate of disappearance of maleic anhydride by $\text{(VO)}_{2}\text{P}_{2}\text{O}_{7}$
Table 3. Conversion of maleic anhydride, rate of $\text{CO}_2$ formation and rate of maleic anhydride disappearance as a function of oxygen partial pressure in feed ($T = 475^\circ\text{C}$; $W/F = 3.11$)$^a$

<table>
<thead>
<tr>
<th>$P_0_2$ (atm)</th>
<th>$\beta$-$\text{VOPO}_4$ conv, %</th>
<th>$r_{\text{CO}_2}$</th>
<th>$-r_{\text{MAN}}$</th>
<th>$(\text{VO})_2\text{P}_2\text{O}_7$ conv, %</th>
<th>$r_{\text{CO}_2}$</th>
<th>$-r_{\text{MAN}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>32.1</td>
<td>5.08 $E$-6</td>
<td>5.05 $E$-6</td>
<td>24.5</td>
<td>3.56 $E$-6</td>
<td>3.86 $E$-6</td>
</tr>
<tr>
<td>0.12</td>
<td>33.5</td>
<td>5.13 $E$-6</td>
<td>5.28 $E$-6</td>
<td>24.4</td>
<td>2.61 $E$-6</td>
<td>3.84 $E$-6</td>
</tr>
<tr>
<td>0.22</td>
<td>40.8</td>
<td>6.15 $E$-6</td>
<td>6.42 $E$-6</td>
<td>26.9</td>
<td>4.13 $E$-6</td>
<td>4.24 $E$-6</td>
</tr>
</tbody>
</table>

$^a$Rates expressed as g-moles/min/g-catalyst.
DISCUSSION OF RESULTS

During n-butane oxidation, Moser and Schrader (2) observed a maximum in maleic anhydride selectivity using model V-P-O catalysts. Significant combustion of n-butane and maleic anhydride was suggested for temperatures above 475°C. In this investigation, steady-state kinetic experiments were conducted to examine the conversion of maleic anhydride. Significant combustion activity was observed when maleic anhydride was fed directly to an integral flow reactor charged with model V-P-O catalysts. The complete combustion of maleic anhydride was observed for temperatures as low as 350°C for β-VOPO₄ and 425°C for (VO)₂P₂O₇. Combustion activity increased for both β-VOPO₄ and (VO)₂P₂O₇ with increasing reaction temperature. Significantly, low apparent activation energies for β-VOPO₄ (4.20 kcal/mol) and (VO)₂P₂O₇ (4.17 kcal/mol) suggests a diffusion limited reaction rate. Blank reactor runs using treated silicon carbide packing demonstrated that maleic anhydride was thermally stable at 475°C. The combustion activity observed during n-butane oxidation appears to be the result of complete combustion of maleic anhydride at the catalyst surface.

Previous (2) n-butane oxidation studies using β-VOPO₄ and (VO)₂P₂O₇ indicated that (VO)₂P₂O₇ was more selective whereas β-VOPO₄ was more active. This investigation demonstrates that the rate of maleic anhydride disappearance was larger for the oxidized (vanadium +5) β-VOPO₄ phase than for the reduced (vanadium +4) (VO)₂P₂O₇ phase. The diminished maleic anhydride combustion activity associated with (VO)₂P₂O₇ explains, at least in part, its higher selectivity during n-butane oxidation. Similar results were reported by Wenig (8) using industrial-type catalysts with
variable P-to-V ratios. The incorporation of "excess" phosphorus in the industrial catalyst formulations appeared to promote lower maleic anhydride combustion rates by stabilizing a reduced (VO)$_2$P$_2$O$_7$ phase, or by stabilizing a combination of the (VO)$_2$P$_2$O$_7$ and B-phases.

Carbon balances were calculated by comparing the flow rate of maleic anhydride which was fed to the reactor to the flow rates of unreacted maleic anhydride and carbon dioxide on a C$_4$ basis. Typically, these balances were from 80 to 95%. Analysis of the condensed solids from the reactor effluent by FT-IR spectroscopy indicated that the low material balances could be a result of maleic acid formation. Semi-quantitative FT-IR analysis indicated that 2 to 16% of the condensed solids were maleic acid.

The infrared spectrum of solid maleic anhydride, solid maleic acid, and a representative infrared spectrum of the condensed solids are given in Figure 5. The spectrum of maleic anhydride (spectrum 5a) has two intense carbonyl stretching vibrations at 1783 and 1857 cm$^{-1}$ and a =CH stretching vibration at 3131 cm$^{-1}$. Maleic acid (spectrum 5b) is characterized by a carbonyl stretching vibration at 1706 cm$^{-1}$ and a =CH stretching vibration at 3058 cm$^{-1}$. Infrared bands at 1706, 1783, 1857, 3058, and 3131 cm$^{-1}$ were observed in the condensed solids (spectrum 5c) indicating the presence of both maleic anhydride and maleic acid in the reactor effluent. The formation of maleic acid was not unexpected since maleic anhydride can be readily hydrolyzed at room temperature (9).
Figure 5. Infrared spectra of
(a) solid maleic anhydride
(b) solid maleic acid
(c) condensed solids from reactor effluent
CONCLUSIONS

The selective oxidation of n-butane by V-P-O catalysts has been established as an efficient and economical process for synthesizing maleic anhydride. Factors influencing maleic anhydride yield and selectivity are of utmost importance, particularly with regard to process development and catalyst design. Clear evidence for the complete combustion of maleic anhydride under typical industrial process conditions has been established by this investigation. Significant combustion activity was observed when maleic anhydride was fed directly to an integral flow reactor charged with model V-P-O catalysts. The conversion of maleic anhydride increased with temperature, contact time, and oxygen partial pressure. Maleic anhydride conversion was also sensitive to the catalytic phase present. Maleic anhydride combustion activity was less for (VO)$_2$$P_2$$O_7$, nominally a vanadium +4 phase. The $\beta$-VOPO$_4$ catalyst, nominally a vanadium +5 phase, resulted in increased conversions of maleic anhydride.
ACKNOWLEDGEMENT

This work was conducted through the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-ENG-82.
REFERENCES


SECTION II. STABILITY OF MODEL V-P-O CATALYSTS
FOR MALEIC ANHYDRIDE SYNTHESIS
ABSTRACT

The stability of $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ under conditions of n-butane and 1-butene oxidation was investigated using the complementary techniques of in situ laser Raman spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy (XPS). Both $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ demonstrated bulk structural integrity during n-butane oxidation. The relatively greater reducing capacity of 1-butene, however, induced a transformation of $\beta$-VOPO$_4$ to (VO)$_2$P$_2$O$_7$. The presence of V(V) and V(IV) in used $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ was detected by XPS for both hydrocarbon oxidation conditions.
INTRODUCTION

Vanadium-phosphorus oxides have a special application as catalysts for the selective oxidation of C₄ hydrocarbons to maleic anhydride. An extensive body of literature has reported the preparation, characterization, and catalytic evaluation of various V-P-O phases. Some of the crystalline phases that have been identified include α-VOPO₄ (1-3), α-II-VOPO₄ (4), β-VOPO₄ (2, 3, 5-7), (VO)₂P₂O₇ (2, 7, 8), β-(VO)₂P₂O₇ (9), VO(PO₃)₂ (2, 10), and VPO₅·2H₂O (11). Recently, Bordes and Courtine (12) discussed three additional phases: δ-VOPO₄, γ-VOPO₄, and γ-(VO)₂P₂O₇.

The structure and composition of more typical industrial catalysts revealed in the patent literature (such as the B-phase (13)) are poorly understood. It has been shown, however, that the B-phase and (VO)₂P₂O₇ have similar X-ray diffraction patterns, although the assigned structures differ.

The stability of V-P-O catalysts during C₄ hydrocarbon oxidation appears to depend strongly on the reducing environment. Investigators have principally determined phase stability by comparing X-ray diffraction patterns before and after C₄ hydrocarbon oxidation. Phases with the reduced V(IV) oxidation state such as β-(VO)₂P₂O₇ (9) and the B-phase (14), were reported to be stable under n-butane oxidation conditions. In addition, Moser and Schrader (7) provided initial findings that β-VOPO₄ (a highly oxidized V(V) phase) and (VO)₂P₂O₇ were stable during n-butane oxidation. In contrast, Bordes and Courtine (2) used X-ray diffraction before and after catalyst use to demonstrate that α-VOPO₄ and β-VOPO₄ were reduced to (VO)₂P₂O₇ under 1-butene oxidation conditions. The bulk
structural integrity of industrial B-phase (V(IV)) catalysts following 1-butene oxidation was suggested by Cavani et al. (15).

A crucial question regarding selective oxidation by V-P-O catalysts is the nature of the active phase(s) during actual reaction conditions. An initial report of the characterization of functioning β-VOPO₄ and (VO)₂P₂O₇ using in situ laser Raman spectroscopy has been provided by Moser and Schrader (7). The bulk structure of these compounds remained stable during n-butane oxidation. In this paper, further characterization of the stability of β-VOPO₄ and (VO)₂P₂O₇ for paraffin and olefin oxidation using in situ laser Raman spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy is presented. These studies have provided new insight into the nature of the active oxygen involved in C₄ hydrocarbon oxidation.
EXPERIMENTAL PROCEDURE

Catalyst Preparation

Pure β-VOPO₄ and (VO)₂P₂O₇ were synthesized by solid-state reaction techniques described previously (7).

Catalyst Activity and Selectivity

The catalytic evaluation of β-VOPO₄ and (VO)₂P₂O₇ for n-butane conversion to maleic anhydride has been previously provided (7).

In Situ Laser Raman Spectroscopy of Functioning Catalysts

In situ laser Raman spectra of the functioning catalysts were obtained using a tubular controlled atmosphere cell (Figure 1). The cell was constructed from a 8.5-cm section of 13-mm OD standard wall Pyrex tubing. An optically flat section (approximately 7 mm x 10 mm) of 1/16-in. thick borosilicate glass was fused to the center portion of the Pyrex tubing to serve as the cell window. The catalyst samples were held in an insert piece constructed from 9-mm Pyrex rod and a 9-mm OD section of standard well Pyrex tubing. Sections of the Pyrex rod and tubing were cut and fused to form a sample holding cavity (see Figure 1). Fresh powdered catalyst was packed firmly into this cavity to form a flat surface. The cell could be heated to temperatures as high as 550°C using electrical resistance heating. The temperature was determined by a subminiature thermocouple probe (Omega Engineering) placed inside the cell near the sample. A vertical mount with dual axis stages was used for alignment of the cell within the sample compartment.
Figure 1. Controlled atmosphere Raman cell
A Spex 1403 laser Raman spectrometer was used with the 514.3 nm line of a Spectra Physics Model 164 argon ion laser operated at 100 mW at the source. No thermal or photochemical decomposition of the catalyst sample occurred under these conditions. A Nicolet 1180E computer system made spectra accumulation possible. Typically ten scans were accumulated at 5 cm$^{-1}$ resolution. However, it was necessary to acquire as many as 75 to 100 scans with a typical scan speed of 3.125 cm$^{-1}$/s to obtain acceptable signal to noise ratios for experiments conducted at temperatures above 450°C.

The composition and flow rate of the gases fed to the in situ cell were controlled by Tylan mass flow controllers (Model FC260) which were calibrated for each of the specific gases. The feed gas was delivered at 50 cm$^3$/min.

Characterization Techniques for Fresh and Used Catalysts

**X-ray diffraction**

X-ray powder diffraction measurements were made with a Siemens diffractometer with a preset spinning sample mount. Cu K$_x$ radiation was used.

**X-ray photoelectron spectroscopy**

X-ray photoelectron spectra were obtained for both fresh and used catalysts using an AEI 200B spectrometer with Al K$_x$ radiation. A Nicolet 1180 computer was used for data acquisition and for signal averaging. All spectra were referenced to the carbon 1s binding energy of 285 eV.

Catalysts exposed to both n-butane and 1-butene reactive conditions were prepared for XPS analysis in reactors constructed from 6-mm OD standard
wall Pyrex tubing. Approximately one gram of loosely packed fresh catalyst was charged to each reactor and plugged on either end with quartz wool. A reactant mixture of either 1.5% n-butane or 1-butene in dry air was passed over the catalyst bed (flow rate 50 cm$^3$/min). The catalyst bed was heated to 450°C in a split tube furnace for 18 hr. Used catalysts were cooled to room temperature in the feed mixture followed by sealing under vacuum in the Pyrex reactor tube. Fresh catalyst samples were similarly sealed under vacuum. Tubes containing both the fresh and used catalysts were opened in a helium dry box (oxygen free) attached directly to the spectrometer.
EXPERIMENTAL RESULTS

In Situ Characterization of Catalysts
by Laser Raman Spectroscopy

Characterization of functioning $\beta$-VOPO$_4$

In situ Raman spectra of $\beta$-VOPO$_4$ were obtained under conditions for n-butane and 1-butene oxidation; the reducing effect of hydrogen was also examined.

Spectra for the $\beta$-VOPO$_4$ phase during exposure to 1.5% n-butane in air at temperatures from 25 to 550°C are given in Figure 2. No new bands were observed even after 12 hr of exposure. The shoulder band at 997 cm$^{-1}$ was not observable at higher temperatures because of band broadening. The band width at one-half intensity of the 987 cm$^{-1}$ peak was 11 cm$^{-1}$ at room temperature; at temperatures 250°C and above, the band width increased to 17 cm$^{-1}$. A similar effect was noticed when fresh $\beta$-VOPO$_4$ was heated in a flow of air at 450°C. At room temperature, the $\beta$-VOPO$_4$ phase had a characteristic band at 1073 cm$^{-1}$. However, after heating the sample in the n-butane-air mixture at 450 to 550°C, the position of this band shifted to 1067 cm$^{-1}$. The same effect was also observed when $\beta$-VOPO$_4$ was heated in air at 450°C. The relative intensities of the bands at 896 and 987 cm$^{-1}$ as compared to that for the 1067 cm$^{-1}$ band decreased during n-butane oxidation. All changes in the spectral features were reversible upon cooling to room temperature in the feed mixture.

Raman spectra of $\beta$-VOPO$_4$ were also accumulated using higher n-butane concentrations at 500°C. The Raman spectra remained relatively insensitive to changes in the gas feed composition.
Figure 2. *In situ* Raman spectra of $\beta$-VOPO$_4$: n-butane oxidation
Raman spectra of β-VOPO₄ during exposure to 1.5% 1-butene in air at temperatures from 25 to 550°C are given in Figure 3. The position of the β-VOPO₄ bands underwent subtle changes for temperatures from 250 to 450°C. As for the n-butane experiments and for simple heating in air, the half-width of the 987 cm⁻¹ band increased from 11 cm⁻¹ to 18 cm⁻¹, with an apparent disappearance of the shoulder band at 997 cm⁻¹. The band at 1073 cm⁻¹ also shifted to 1067 cm⁻¹ upon heating. The relative intensities of the bands at 896 and 987 cm⁻¹ as compared to that for the 1067 cm⁻¹ band decreased between 250 to 450°C.

However, there were striking changes in the spectrum at 500°C for 1-butene oxidation after 1.5 hr. The appearance of a new band at 932 cm⁻¹ was observed with a considerable decrease in the intensity of the bands at 894, 987, and 1063 cm⁻¹. This new band was characteristic of the reduced phase (VO)₂P₂O₇. After continued 1-butene oxidation for 12 hr, only a single band at 932 cm⁻¹ could be observed. This particular spectrum required 40 scans at a scan drive of 1.043 cm⁻¹/s. After 24 hr of 1-butene oxidation the sample was cooled to room temperature under a continued flow of the 1-butene-air mixture. As shown in Figure 4, bands for the original β-VOPO₄ phase were not restored.

The Raman spectrum of β-VOPO₄ was also collected during exposure to hydrogen at 450°C. Figure 5 shows the 800-1200 cm⁻¹ region of the Raman spectrum of β-VOPO₄ after 4 hr of hydrogen reduction. The same subtle changes in the Raman spectrum were observed as for the n-butane studies. After cooling to room temperature, all bands characteristic of fresh β-VOPO₄ were observable. However, the sample color changed from
Figure 3. In situ Raman spectra of β-VOPO$_4$: 1-butene oxidation
Figure 4. Raman spectrum of used β-VOPO$_4$ after 1-butene oxidation
Figure 5. **In situ** Raman spectrum of 8-VOPO$_4$ during hydrogen reduction at 450°C
yellow-green to black. A decreased signal-to-noise ratio was also observed as compared to the spectrum of a fresh $\beta$-VOPO$_4$ sample.

**Characterization of functioning (VO)$_2$P$_2$O$_7$**

*In situ* Raman spectra of (VO)$_2$P$_2$O$_7$ were accumulated during both n-butane and 1-butene oxidation; the effect of exposure to oxygen at elevated temperatures was also examined.

The spectra of the functioning (VO)$_2$P$_2$O$_7$ phase (1.5% hydrocarbon in air) during both n-butane and 1-butene oxidation are given in Figures 6 and 7, respectively. The Raman spectra were very similar for both cases. Two major bands were located at 921 and 932 cm$^{-1}$. After heating between 250 to 550°C, however, these bands evolved to a single band with a maximum at 930 cm$^{-1}$. At room temperature the band at 921 cm$^{-1}$ had a halfwidth of 11 cm$^{-1}$. The band at 930 cm$^{-1}$, for spectra accumulated between 250-550°C, had a halfwidth of 16 cm$^{-1}$. These changes were reversible upon cooling to room temperature. No significant loss in the absolute intensities (photon counts/sec) or the signal-to-noise ratio was observed during either n-butane or 1-butene oxidation. Weak bands characteristic of (VO)$_2$P$_2$O$_7$ persisted at elevated temperatures as high as 550°C.

The effect of heating (VO)$_2$P$_2$O$_7$ in a flow of oxygen was also studied; Raman spectra acquired at 450 to 550°C are given in Figure 8. Distinct changes in the spectrum were apparent, particularly with the detection of a number of new bands not characteristic of (VO)$_2$P$_2$O$_7$. After 1.5 hr of oxygen flow at 450°C, a broad feature between 250 to 550 cm$^{-1}$ was observable. The band at 930 cm$^{-1}$, characteristic of the (VO)$_2$P$_2$O$_7$ phase for elevated temperatures, remained prominent during oxygen flow at 450°C.
Figure 6. In situ Raman spectra of (VO)$_2$P$_2$O$_7$: n-butane oxidation
Figure 7. In situ Raman spectra of (VO)$_2$P$_2$O$_7$: 1-butene oxidation
Figure 8. Calcination of $(VO)\_2P\_2O\_7$ in oxygen
After 1.5 hr of oxygen flow at 500°C, however, distinct bands appeared at 320, 369, and 435 cm\(^{-1}\) (Figure 8). Other bands at 598, 651, 895, 987, and 1069 cm\(^{-1}\) also evolved with intensities comparable to the \((\text{VO})_2\text{P}_2\text{O}_7\) peak at 930 cm\(^{-1}\). These bands were characteristic of \(\beta\)-\(\text{VOPO}_4\). Upon increasing the temperature to 550°C for 12 hr these new bands became dominant, although there was clear evidence of the 930 cm\(^{-1}\) band. After cooling to room temperature, relatively larger amounts of \(\beta\)-\(\text{VOPO}_4\) were apparent.

Characterization of Used Catalysts

X-ray diffraction

The X-ray diffraction patterns of \(\beta\)-\(\text{VOPO}_4\) after n-butane and 1-butene oxidation were compared to that of fresh material. The d-spacings for fresh \(\beta\)-\(\text{VOPO}_4\) and for the catalyst after 1-butene oxidation are given in Table 1. No changes were observed after n-butane oxidation performed at 425 to 525°C. However, the X-ray data did show a phase transformation from \(\beta\)-\(\text{VOPO}_4\) to \((\text{VO})_2\text{P}_2\text{O}_7\) after 1-butene oxidation between 500 to 550°C. The primary diffraction lines of \(\beta\)-\(\text{VOPO}_4\) were not preserved (d-spacings 3.078, 3.196, and 3.416 Å); rather, the presence of the \((\text{VO})_2\text{P}_2\text{O}_7\) phase was indicated by three intense diffraction lines (among other weaker lines) at 2.989, 3.143, and 3.886 Å (2, 7). After cooling to room temperature, the diffraction pattern of used \(\beta\)-\(\text{VOPO}_4\) clearly showed a considerable amount of crystalline \((\text{VO})_2\text{P}_2\text{O}_7\).

X-ray diffraction confirmed that \((\text{VO})_2\text{P}_2\text{O}_7\) was remarkably stable during the high temperature (425 to 525°C) oxidation of both n-butane and 1-butene. A distinct phase transformation to \(\beta\)-\(\text{VOPO}_4\) was observed, however, when \((\text{VO})_2\text{P}_2\text{O}_7\) was heated in a flow of oxygen. Samples were
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<tr>
<td>1.460</td>
<td>(6.9)</td>
<td>1.840</td>
<td>(11.2)</td>
</tr>
<tr>
<td>1.475</td>
<td>(5.3)</td>
<td>1.795</td>
<td>(5.0)</td>
</tr>
<tr>
<td>1.475</td>
<td>(8.6)</td>
<td>1.750</td>
<td>(8.7)</td>
</tr>
<tr>
<td>1.475</td>
<td>(8.6)</td>
<td>1.725</td>
<td>(4.9)</td>
</tr>
<tr>
<td>1.460</td>
<td>(5.3)</td>
<td>1.702</td>
<td>(11.0)</td>
</tr>
<tr>
<td>1.475</td>
<td>(5.3)</td>
<td>1.646</td>
<td>(7.8)</td>
</tr>
<tr>
<td>1.475</td>
<td>(6.9)</td>
<td>1.606</td>
<td>(4.3)</td>
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<tr>
<td>1.475</td>
<td>(6.9)</td>
<td>1.601</td>
<td>(5.6)</td>
</tr>
<tr>
<td>1.475</td>
<td>(8.6)</td>
<td>1.576</td>
<td>(10.9)</td>
</tr>
<tr>
<td>1.475</td>
<td>(8.6)</td>
<td>1.537</td>
<td>(25.5)</td>
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<td>1.460</td>
<td>(6.9)</td>
<td>1.474</td>
<td>(6.3)</td>
</tr>
<tr>
<td>1.459</td>
<td>(9.8)</td>
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</tr>
</tbody>
</table>
obtained from the in situ Raman spectroscopy studies described previously when (VO)$_2$P$_2$O$_7$ was heated in oxygen at 500 and 550°C. The d-spacings are given in Table 1 together with relative line intensities.

**X-ray photoelectron spectroscopy**

X-ray photoelectron spectra of both fresh and used catalysts are shown in Figures 9 and 10; Table 2 provides the observed binding energies. The β-VOPO$_4$ phase was characterized by two bands at 518.2 and 525.6 eV which were assigned to the 2p$_{3/2}$ and 2p$_{1/2}$ binding energies of vanadium(V), respectively. The oxygen Is binding energy for β-VOPO$_4$ was 531.4 eV. The XPS spectra for (VO)$_2$P$_2$O$_7$ had two bands at 517.1 and 524.4 eV which were assigned to the 2p$_{3/2}$ and 2p$_{1/2}$ binding energies of vanadium(IV), respectively. An oxygen Is binding energy was observed at 531.5 eV. Similar results for these phases were reported by Shimoda et al. (16).

Following n-butane oxidation, the XPS spectra for β-VOPO$_4$ showed a -0.3 eV shift for the bands associated with the vanadium 2p$_{3/2}$ and 2p$_{1/2}$ binding energies. After 1-butene oxidation, the β-VOPO$_4$ phase spectra exhibited shifts for both vanadium 2p$_{3/2}$ (-0.8 eV) and vanadium 2p$_{1/2}$ (-0.8 eV) peaks and the oxygen Is (+0.6 eV) peak. The band halfwidths of the vanadium 2p$_{3/2}$ and oxygen Is binding energies also broadened by 0.6 eV. The XPS spectra of (VO)$_2$P$_2$O$_7$ showed small changes in peak locations following both n-butane and 1-butene oxidation. A shift occurred for the vanadium 2p$_{3/2}$ (+0.3 eV) and 2p$_{1/2}$ (+0.2 eV) peaks with a simultaneous shift for the oxygen Is (+0.4 eV) peak following n-butane oxidation. The vanadium 2p$_{3/2}$ band broadened by about 0.3 eV. The
Figure 9. X-ray photoelectron spectra of fresh and used $\beta$-VOPO$_4$

(a) fresh $\beta$-VOPO$_4$
(b) after n-butane oxidation
(c) after 1-butene oxidation
Figure 10. X-ray photoelectron spectra of fresh and used \((\text{VO})_2\text{P}_2\text{O}_7\)

(a) fresh \((\text{VO})_2\text{P}_2\text{O}_7\)
(b) after n-butane oxidation
(c) after 1-butene oxidation
<table>
<thead>
<tr>
<th>Sample</th>
<th>$W \ 2p_{3/2}$</th>
<th>$W \ 2p_{1/2}$</th>
<th>O $1s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-VO$_2$O$_4$</td>
<td>518.2 (1.6)</td>
<td>525.6 (2.1)</td>
<td>531.4 (2.0)</td>
</tr>
<tr>
<td>After n-butane oxidation</td>
<td>517.9 (1.8)</td>
<td>525.3 (2.2)</td>
<td>531.3 (2.2)</td>
</tr>
<tr>
<td>After 1-butene oxidation</td>
<td>517.4 (2.2)</td>
<td>524.8 (2.0)</td>
<td>523.0 (2.6)</td>
</tr>
<tr>
<td>($WO$)$_2$P$_2$O$_7$</td>
<td>517.1 (2.0)</td>
<td>524.4 (2.4)</td>
<td>531.5 (2.4)</td>
</tr>
<tr>
<td>After n-butane oxidation</td>
<td>517.4 (2.3)</td>
<td>524.6 (2.1)</td>
<td>531.9 (2.7)</td>
</tr>
<tr>
<td>After 1-butene oxidation</td>
<td>517.5 (2.1)</td>
<td>524.8 (2.2)</td>
<td>531.9 (2.4)</td>
</tr>
</tbody>
</table>

$^a$Binding energies referenced to Carbon $1s$ of 285 eV.

$^b$Halfwidth (eV) given in parentheses.
magnitude of the binding energy shifts were comparable following 1-butene oxidation for the vanadium $2p_{3/2}$ (+0.4 eV) and $2p_{1/2}$ (0.4 eV) peaks for the oxygen $1s$ (0.4 eV) peak.
DISCUSSION OF RESULTS

The stability of the \( \beta-\text{VOPO}_4 \) and \( (\text{VO})_2\text{P}_2\text{O}_7 \) crystalline phases under conditions associated with n-butane and 1-butene oxidation was investigated using the complementary techniques of laser Raman spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The Raman technique was particularly important because of its utility as an \textit{in situ} technique. X-ray diffraction data from post-reactor samples confirmed the Raman results with respect to bulk structural stability and transformation.

Questions regarding the catalyst oxidation states were addressed using XPS.

The \( \beta-\text{VOPO}_4 \) and \( (\text{VO})_2\text{P}_2\text{O}_7 \) bulk structures were remarkably stable during n-butane oxidation between 25 and 550°C as indicated by \textit{in situ} laser Raman spectroscopy and post-catalytic X-ray diffraction measurements. Modifications in the Raman spectra for \( \beta-\text{VOPO}_4 \) could be observed, however. The bands associated with \( \beta-\text{VOPO}_4 \) decreased in intensity by about a factor of ten over the temperature range from 25 to 550°C. This decreased signal implied that some reduction occurs, but not sufficiently throughout the entire catalyst bulk structure such that a distinct reduced V-P-O phase was formed. The decrease in the relative intensities of the bands at 896 and 987 cm\(^{-1}\) as compared by the intensity of the band at 1067 cm\(^{-1}\) implied that localized reduction occurred involving specific sites in the \( \beta-\text{VOPO}_4 \) lattice. The bands at 896 and 987 cm\(^{-1}\) have been associated by P-O stretching of the PO\(_4\) units of \( \beta-\text{VOPO}_4 \). Detailed band assignments were discussed previously by Moser and Schrader (7). The \( (\text{VO})_2\text{P}_2\text{O}_7 \) phase did not show a significant loss in Raman band intensities. Bulk reduction of \( (\text{VO})_2\text{P}_2\text{O}_7 \) reduction to a V(III) phase apparently does not occur.
X-ray photoelectron spectra of both $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ following n-butane oxidation at 450°C did show modifications in the oxidation state of the catalysts. The $\beta$-VOPO$_4$ phase was slightly reduced as indicated by a -0.3 eV shift for the binding energy of the vanadium 2p$_{3/2}$ electrons. This band shift was accompanied by a slight broadening (0.2 eV).

Conversely, (VO)$_2$P$_2$O$_7$ was slightly oxidized as indicated by a shift in the binding energy of the vanadium 2p$_{3/2}$ band from 517.1 to 517.4 eV, together with a broadening of the band (0.3 eV). These binding energy shifts likely correspond to the presence of both V(V) and V(IV). The magnitude of these shifts, however, suggest that the corresponding reduction or oxidation was rather small. Post-catalytic characterization by both Raman spectroscopy and X-ray diffraction indicated no bulk structural changes.

Transformation from $\beta$-VOPO$_4$ to (VO)$_2$P$_2$O$_7$ was clearly detected during 1-butene oxidation between 450 to 550°C as indicated by in situ laser Raman spectroscopy and post-catalytic characterization using X-ray diffraction. X-ray photoelectron spectroscopy showed further that the $\beta$-VOPO$_4$ phase was reduced during 1-butene oxidation in air at 450°C as indicated by a shift in the vanadium 2p$_{3/2}$ binding energy from 518.2 to 517.4 eV. This shift was accompanied by a rather significant broadening of both the vanadium 2p$_{3/2}$ and vanadium 2p$_{1/2}$ bands (0.6 eV), indicating that both V(V) and V(IV) were present. In comparison, (VO)$_2$P$_2$O$_7$ underwent a small, yet significant, oxidation during 1-butene oxidation. The binding energy for the vanadium 2p$_{3/2}$ electrons shifted from 517.1 to 517.5 eV.

When $\beta$-VOPO$_4$ was charged to the in situ Raman cell bands characteristic of both $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ were present during 1-butene oxidation in air. After continued 1-butene oxidation at 500°C for 12 hr, the
The \( \beta\text{-VOPO}_4 \) to \( (\text{VO})_2\text{P}_2\text{O}_7 \) transition was almost complete as indicated by a single band at 930 cm\(^{-1}\) characteristic of \( (\text{VO})_2\text{P}_2\text{O}_7 \) at elevated temperatures. In addition, the relative intensities of the P-O stretches at 896 and 987 cm\(^{-1}\) decreased as compared to the intensity of the band at 1067 cm\(^{-1}\) between 250 to 500°C. As during n-butane oxidation, it appears that oxygen vacancies were produced at P-O positions associated with the \( \text{PO}_4 \) units of \( \beta\text{-VOPO}_4 \). Because of the severity of the 1-butene reducing capacity, enough of these vacancies were created to allow the bulk restructuring to the reduced \( (\text{VO})_2\text{P}_2\text{O}_7 \) phase at 500°C. In contrast, the reduction of \( \beta\text{-VOPO}_4 \) in hydrogen at 450°C was not accompanied by a phase transformation. In situ Raman spectra collected at 450°C in hydrogen showed bands characteristic of \( \beta\text{-VOPO}_4 \). The absolute intensities of these bands, however, were rather weak as compared to similar experiments with n-butane in air. The modifications in the Raman spectrum suggests that the catalyst was reduced, possibly to an amorphous structure present together with \( \beta\text{-VOPO}_4 \). X-ray diffraction has confirmed the reduction of \( \beta\text{-VOPO}_4 \) in hydrogen can produce an amorphous material (7).

The thermal heating of either \( \beta\text{-VOPO}_4 \) or \( (\text{VO})_2\text{P}_2\text{O}_7 \) at 250°C and above caused broadening of the Raman bands with or without n-butane or 1-butene being present. In situ laser Raman spectroscopy identified this change for \( \beta\text{-VOPO}_4 \) by the merging of the P-O band at 987 cm\(^{-1}\) with the V=O band at 997 cm\(^{-1}\). The center of the composite band was located at 987 cm\(^{-1}\) (250 to 550°C). Another subtle change was associated with the P-O stretch at 1073 cm\(^{-1}\) (25°C) which shifted to 1067 cm\(^{-1}\) (250 to 550°C). This shift was likewise attributed to thermal heating effects. Finally, the \( (\text{VO})_2\text{P}_2\text{O}_7 \) phase was characterized by two intense P-O-P asymmetric stretches of the
pyrophosphate ion at 921 and 932 cm$^{-1}$. These two bands merged at elevated temperatures to become a single band at 930 cm$^{-1}$. The changes in band structure associated with thermal heating were completely reversible upon cooling the phases to room temperature.
The present investigation has examined the stability of two model V-P-O phases, β-VOPO$_4$ and (VO)$_2$P$_2$O$_7$, using in situ laser Raman spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The in situ Raman technique revealed key catalyst transformations which occurred during C$_4$ hydrocarbon oxidation which were otherwise undetectable by postcatalytic characterization. In particular, β-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ demonstrated bulk structural integrity during n-butane oxidation. Modifications in the Raman spectra of functioning β-VOPO$_4$ indicated, however, that oxygen holes were created in the lattice of β-VOPO$_4$ causing a slight reduction without bulk restructuring. Furthermore, Raman band assignments indicated these oxygen sites were associated with PO$_4$ units in the lattice of β-VOPO$_4$. The severity of the reducing environment had a marked effect on the stability of the model compounds. A 2β-VOPO$_4$ → (VO)$_2$P$_2$O$_7$ phase transformation was observed during 1-butene oxidation at 500°C. As for n-butane oxidation, oxygen vacancies were created at P-O positions in the lattice of β-VOPO$_4$; the reducing capacity of 1-butene, however, led to the specific phase transformation.
ACKNOWLEDGEMENTS

This work was conducted through the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-ENG-82. The X-ray photoelectron spectroscopy work by James W. Anderegg is gratefully acknowledged.
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SECTION III. IDENTIFICATION OF ACTIVE OXYGEN CENTERS IN A VANADIUM-PHOSPHORUS-OXYGEN CATALYST
Direct structural identification of catalytically active oxygen centers for paraffin and olefin oxidation were investigated using an $^{18}O$-enriched $\beta$-VOPO$_4$ phase catalyst synthesized by the $(VO)_2P_2O_7$ to $\beta$-VOPO$_4$ phase transformation in the presence of gaseous $^{18}O_2$. Spectroscopic characterization of the $^{18}O$-enriched $\beta$-VOPO$_4$ phase indicated the $^{18}O$ label was incorporated into discrete tetrahedral lattice positions. In situ Raman spectra of the catalyst and analysis of oxygenated products for n-butane and 1-butene oxidation were collected using a coupled laser Raman spectroscopy/mass spectrometry system. Active sites responsible for complete combustion (Site I) and selective oxidation (Site II) were identified. The function of these sites was distinctly different for paraffin and olefin oxidation. The selective route for 1-butene oxidation involved predominantly Site II centers, while Site I centers were associated with complete combustion. In contrast, n-butane oxidation required the highly active Site I centers for initial activation by oxidative dehydrogenation and for the formation of an intermediate containing two oxygen atoms. This intermediate either continued to complete combustion (Site I) or was selectively oxidized to maleic anhydride (Site II).
INTRODUCTION

Interest in vanadium-phosphorus-oxygen (V-P-O) catalysts has resulted from the high selectivity and activity these materials display in C$_4$ hydrocarbon oxidation to maleic anhydride. In the case of n-butane oxidation, V-P-O catalysts represent a significant industrial breakthrough for enabling the activation of a C-H bond at a saturated carbon center, while still providing high selectivity. Lattice oxygen appears to be extensively utilized for both n-butane (1-3) and 1-butene (3) selective oxidation, while gaseous oxygen reoxidizes the catalyst (2). Several studies have linked the catalytic activity and selectivity of V-P-O catalysts with specific catalyst phases (4-7) and with the P-to-V ratios in catalyst formulations (8-11). The active centers of V-P-O catalysts have been primarily characterized by surface acidity (12) and texture (12-14). The identification of active sites responsible for paraffin activation, oxygen incorporation, and complete combustion have yet to be addressed on the molecular scale.

The participation of lattice oxygen during the selective oxidation of hydrocarbons is a general characteristic of metal-oxide catalysts. Oxygen-18 tracer studies have proven particularly valuable in the identification of catalytically active sites for the selective oxidation of propylene to acrolein. Tracer studies utilizing both $^{18}$O$_2$ in the feed mixture (15-19) and $^{18}$O-enriched bismuth molybdate catalysts (15, 20, 21) established the extensive participation of lattice oxygen and insight into the reaction mechanism for propylene oxidation. Selective reduction of a bismuth molybdate catalyst with probe molecules such as propylene, 1-butene,
methanol, and ammonia, followed by reoxidation with oxygen-18, confirmed the existence of distinct active sites responsible for α-H abstraction and oxygen insertion (22). Laser Raman spectroscopy confirmed the bridging Bi-O-Mo oxygen centers were responsible for α-H abstraction, while oxygen incorporation into the allylic intermediate occurred at Mo-O centers. Analogous structural identification of the active sites for C₄ hydrocarbon oxidation by V-P-O catalysts is not available in the literature.

In the present study, structural identification of the catalytically active oxygens responsible for such functions as paraffin activation, oxygen incorporation, and complete combustion is obtained from the simultaneous examination of in situ Raman spectra of an ¹⁸O-enriched β-VOPO₄ catalyst and mass spectroscopic analysis of oxygenated products. The synthesis of a specifically labeled β-VOPO₄ phase provided new insight into the (VO)₂P₂O₇ to β-VOPO₄ phase transformation. Fundamental questions regarding the active sites functioning for n-butane versus 1-butene selective oxidation are discussed.
EXPERIMENTAL PROCEDURE

Synthesis of $^{18}O$-Enriched $\beta$-VOPO$_4$

Oxygen-$^{18}O$ enriched $\beta$-VOPO$_4$ was prepared by the solid state reaction of $(\text{VO})_2\text{P}_2\text{O}_7$ with gas phase $^{18}O_2$. The synthesis of $(\text{VO})_2\text{P}_2\text{O}_7$ was described previously (4). Powdered $(\text{VO})_2\text{P}_2\text{O}_7$ (0.50 g) was charged to a section of 9-mm O.D. Pyrex tubing. The tube was evacuated and backfilled with stoichiometric quantities of $^{18}O_2$ gas. The $^{18}O_2$ was obtained from Merck, Sharp, and Dohme with an atom enrichment of 97.8%. The reaction tube was heated at 550°C for 24 h followed by cooling to 200°C at a rate of 50°C per hour. The furnace power was then shut off, and the furnace and sample were allowed to cool to room temperature.

Laser Raman Spectroscopy

Laser Raman spectra were obtained using powdered samples placed in a fine capillary tube positioned in a sample holder. A Spex 1403 laser Raman spectrometer was used with the 514.3-nm line of a Spectra Physics Model 2020-05 argon ion laser operated at 100 mW at the source. A Nicolet 1180E computer system allowed for spectral accumulation. Raman spectra reported for $\beta$-VOPO$_4$ and $^{18}O$-enriched $\beta$-VOPO$_4$ represent a 40-scan accumulation at 2-cm$^{-1}$ resolution with a central slit setting of 1000 μm and a scan drive of 6.25 cm$^{-1}$/s.

Coupled Laser Raman Spectroscopy/Mass Spectrometry System

The simultaneous collection of Raman spectra of functioning $^{18}O$-enriched $\beta$-VOPO$_4$ and the analysis of oxygenated reaction products from
n-butane and 1-butene oxidation were gathered using a coupled laser Raman spectroscopy/mass spectrometry system shown in Figure 1.

**In situ** laser Raman spectra of the functioning catalyst were obtained using a tubular controlled atmosphere cell described previously (3). The cell was slightly modified to incorporate Teflon gaskets for gas-tight sealing. Fresh powdered $^{18}O$-enriched $\beta$-VOPO$_4$ (ca. 0.40 g) was packed firmly into the sample holding cavity to form a flat surface. Details concerning alignment and temperature control were described previously (3).

A Spex 1877 Tripletmate laser Raman spectrometer was used with 514.3-nm line of a Spectra Physics Model 164 argon ion laser operated at 200 mW at the source. No thermal or photochemical decomposition of the catalyst sample occurred under these conditions. An EG & G 1215 optical multi-channel analyzer and an EG & G 1420 detector made spectral accumulation possible. Typically 500 scans were accumulated in 173 seconds at 4 cm$^{-1}$ resolution. The spectrograph entrance slit was set at 50 $\mu$m using a 1200 gr/mm spectrograph grating.

The composition and flow rate of the gases fed to the **in situ** cell were controlled by Tylan mass flow controllers (Model FC260) which were calibrated for each of the specific gases. The feed gas was delivered at 50 cm$^3$/min with a composition of 2% n-butane or 1-butene (Matheson, instrument grade) in zero helium. The helium was further purified using a reduced copper catalyst bed (BASF) to remove residual oxygen. An in-line electronic manometer ensured atmospheric pressure in the Raman cell.

The incorporation of oxygen into reaction products was monitored using a UTI 100C precision quadrupole mass analyzer controlled by a PDP
Figure 1. Coupled laser Raman spectroscopy/mass spectrometry system
11/23 computer. A glass SGE single stage molecular jet separator was used for Raman cell/mass spectrometer interfacing.
EXPERIMENTAL RESULTS

Characterization of $^{18}$O-Enriched $\beta$-VOPO$_4$

The Raman spectrum of $^{18}$O-enriched $\beta$-VOPO$_4$ prepared by the solid state reaction of (VO)$_2$P$_2$O$_7$ with $^{18}$O$_2$ was compared to the Raman spectrum of similarly prepared $\beta$-VOPO$_4$ using $^{16}$O$_2$. Distinct spectral features showing the incorporation of $^{18}$O into (VO)$_2$P$_2$O$_7$ were observed following the (VO)$_2$P$_2$O$_7$ to $\beta$-VOPO$_4$ phase transformation. Raman spectra of both $^{18}$O-enriched $\beta$-VOPO$_4$ and $\beta$-VOPO$_4$ prepared in $^{16}$O$_2$ are given in Figures 2a and 2b, respectively. Raman band assignments for both $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ were discussed previously (4). Incorporated $^{18}$O was detected by an isotopically shifted P-$^{18}$O band at 886 cm$^{-1}$ being associated with the P-$^{16}$O stretch at 896 cm$^{-1}$ of equal intensity. Another isotopically shifted P-$^{18}$O band was observed at 961 cm$^{-1}$. The intensity of this band was rather weak, being about 7% of the complementary P-$^{16}$O band at 987 cm$^{-1}$. A slight broadening of the P-O band at 1072 cm$^{-1}$ was observed at the base. The magnitude of these band shifts was similar to that observed for $^{18}$O-labeled bismuth molybdates (19). The presence of unreacted (VO)$_2$P$_2$O$_7$ was detected by a very weak band at 923 cm$^{-1}$ in the $^{18}$O-enriched $\beta$-VOPO$_4$ spectrum (Figure 2a). The Raman spectrum of the control $\beta$-VOPO$_4$ prepared by the reaction of (VO)$_2$P$_2$O$_7$ with $^{16}$O$_2$ also indicated the presence of unreacted (VO)$_2$P$_2$O$_7$ (Figure 2b).

Incorporation of $^{18}$O into Reaction Products

The $^{18}$O content of maleic anhydride, carbon dioxide, and water over $^{18}$O-enriched $\beta$-VOPO$_4$ was monitored for both the selective oxidation of
Figure 2. Raman spectra of
(a) $^{18}_O$-enriched $\beta$-VOPO$_4$ prepared by reaction of (VO)$_2$P$_2$O$_7$
with $^{18}O_2$ and
(b) $\beta$-VOPO$_4$ prepared by reaction of (VO)$_2$P$_2$O$_7$ with $^{16}O_2$
n-butane and 1-butene in the absence of gas phase oxygen. The isotopic composition of oxygen in maleic anhydride was characterized by the relative abundance (specific ion current, $I_1$) of maleic anhydride molecules with mass-to-charge ratios (m/e) of 98, 100, 102, and 104, as well as by the total concentration of the label in maleic anhydride calculated by the ratio

$$\% ^{18}O_{\text{MAN}} = \frac{I_{100} + 2I_{102} + 3I_{104}}{3(I_{98} + I_{100} + I_{102} + I_{104})} \times 100$$

The concentration of label in carbon dioxide was estimated on the basis of the intensities ($I_1$) of the peaks of CO$_2$ corresponding to m/e values of 44, 46, and 48. The total concentration of label in CO$_2$ was determined by the ratio

$$\% ^{18}O_{\text{CO}_2} = \frac{I_{46} + 2I_{48}}{2(I_{44} + I_{46} + I_{48})} \times 100$$

While both CO and CO$_2$ could be observed, the CO data were significantly complicated by interferences, especially from background air (both N$_2$ and C$_{16}^1$O have m/e values of 28). The CO$_2$ data were corrected in a straightforward manner by subtracting the minor interferences at m/e 44 from n-butane or 1-butene fragmentation and background air. Finally, the $^{18}O$ content of water produced by both combustion and selective oxidation was estimated from mass spectral intensities ($I_1$) corresponding to H$_2^{16}$O (m/e 18) and H$_2^{18}$O (m/e 20). The total concentration of label in water was calculated by the ratio

$$\% ^{18}O_{\text{H}_2^0} = \frac{I_{20}}{(I_{18} + I_{20})} \times 100$$
Incorporation of $^{18}$O during n-butane oxidation

The incorporation of $^{18}$O into maleic anhydride, CO$_2$, and water was monitored under conditions of n-butane oxidation at 400 and 500°C.

The specific ion currents of maleic anhydride isotopes with m/e ratios of 98, 100, 102, and 104 are given in Figure 3 as a function of reaction time for the selective oxidation of n-butane at 400°C. The most abundant isotope produced was maleic anhydride m/e 98. Of the $^{18}$O-labeled maleic anhydride, m/e 100 was the most abundant, followed in turn by m/e 102 and 104. The $^{18}$O content of maleic anhydride, CO$_2$, and H$_2$O was very low as indicated in Figure 4. However, the tendency of $^{18}$O incorporation into maleic anhydride was approximately two to four times greater than for CO$_2$.

The isotopic composition of oxygen incorporated into n-butane oxidation products was also characterized at 500°C. Figure 5 shows the relative abundances of maleic anhydride isotopes produced. After two minutes of n-butane activity approximately equal amounts of maleic anhydride m/e 98 and 100 were produced. The production of each maleic anhydride isotope decreased steadily with time. The abundance of maleic anhydride m/e 102 was approximately 15 to 33% of the m/e 98 maleic anhydride produced. Considerably less m/e 104 maleic anhydride was detected. In addition, $^{18}$O was preferentially incorporated into maleic anhydride over CO$_2$ and H$_2$O. Figure 6 shows that the initial $^{18}$O content of maleic anhydride was 24% as compared to 4% for CO$_2$. The $^{18}$O content of water ranged from 7 to 12%.
Figure 3. Incorporation of $^{18}O$ into maleic anhydride during n-butane oxidation by $^{18}O$-enriched $\text{S}_2\text{VOP}_4$ (400°C)
Figure 4. $^{18}O$ content of maleic anhydride, CO$_2$, and H$_2$O during n-butane oxidation by $^{18}O$-enriched 8-VOPO$_4$ (400°C)
Figure 5. Incorporation of $^{18}$O into maleic anhydride during n-butane oxidation by $^{18}$O-enriched $\beta$-VOPO$_4$ (500°C)
Figure 6. $^{18}O$ content of maleic anhydride, $CO_2$, and $H_2O$ during n-butane oxidation by $^{18}O$-enriched $\beta$-VOPO$_4$ (500°C)
Incorporation of $^{18}O$ during 1-butene oxidation

The incorporation of $^{18}O$ into maleic anhydride, CO$_2$, and H$_2$O was investigated during 1-butene oxidation at 350 and 450°C.

The relative abundances of maleic anhydride produced with m/e ratios of 98, 100, 102, and 104 are given in Figure 7 for the selective oxidation of 1-butene at 350°C. The specific ion current recorded for each isotope decreased steadily between 2 to 30 minutes of reaction time. The most abundant isotope produced was m/e 104, followed by 98, 100, and 102. The corresponding $^{18}O$ content in maleic anhydride as compared to that in CO$_2$ and H$_2$O is given in Figure 8. After two minutes of reaction time, 63% of the oxygen in maleic anhydride was $^{18}O$ as compared to 24% in CO$_2$ and 4% in H$_2$O. With increased reaction time, the $^{18}O$ content of maleic anhydride decreased with a simultaneous increase in the $^{18}O$ content in both CO$_2$ and H$_2$O.

The incorporation of $^{18}O$ into maleic anhydride, CO$_2$, and H$_2$O was investigated during 1-butene oxidation at 450°C. Figure 9 shows the relative abundances of maleic anhydride isotopes produced. The most abundant isotope produced was m/e 98. Of the $^{18}O$-labeled maleic anhydride produced, m/e 104 was the most abundant, followed in turn by m/e 100 and 102. After two minutes of reaction time approximately 50% of the maleic anhydride produced was labeled with $^{18}O$ as compared to about 12% for CO$_2$ and 9% for H$_2$O (Figure 10).
Figure 7. Incorporation of $^{18}O$ into maleic anhydride during 1-butene oxidation by $^{18}O$-enriched $\beta$-VOPO$_4$ (350°C)
Figure 8. $^{18}$O content of maleic anhydride, CO$_2$, and H$_2$O during 1-butene oxidation by $^{18}$O-enriched β-VOPO$_4$ (350°C)
Figure 9. Incorporation of $^{18}\text{O}$ into maleic anhydride during 1-butene oxidation by $^{18}\text{O}$-enriched $\beta\text{-VOPO}_4$ ($450^\circ\text{C}$)
Figure 10. $^{18}$O content of maleic anhydride, CO$_2$, and H$_2$O during 1-butene oxidation by $^{18}$O-enriched β-VOPO$_4$ (450°C)
**In Situ Characterization of $^{18}$O-Enriched $\beta$-VOPO$_4$ by Laser Raman Spectroscopy**

Characterization during n-butane oxidation

**In situ** Raman spectra of $^{18}$O-enriched $\beta$-VOPO$_4$ were obtained under conditions of n-butane oxidation at 400 and 500°C.

Spectra of $^{18}$O-enriched $\beta$-VOPO$_4$ exposed to 2% n-butane in helium (400°C) are given in Figure 11. The room temperature Raman spectrum clearly showed the isotopically shifted P-$^{18}$O band at 886 cm$^{-1}$ together with the complementary P-$^{16}$O stretch at 896 cm$^{-1}$. The P-$^{18}$O shifted band at 961 cm$^{-1}$ was also observable at room temperature. No new bands were observed after 60 minutes of n-butane oxidation at 400°C. In addition, the shoulder V=O band at 997 cm$^{-1}$ was not observable at elevated temperature because of band broadening. At room temperature, the $^{18}$O-enriched $\beta$-VOPO$_4$ phase had a characteristic $\beta$-VOPO$_4$ band at 1072 cm$^{-1}$. After heating the sample in the n-butane-helium mixture at 400°C, the position of this band shifted to 1068 cm$^{-1}$. This same effect was observed when $\beta$-VOPO$_4$ was heated in air at 450°C (3). The complementary P-$^{16}$O and P-$^{18}$O bands were observed as a single band at 890 cm$^{-1}$ at elevated temperature as a result of band broadening. After two minutes of n-butane-helium exposure, the relative intensities of the composite 890 cm$^{-1}$ band decreased by 27% and the 987 cm$^{-1}$ band decreased by 44% compared to the 1068 cm$^{-1}$ band. Continued n-butane activity resulted in little change of the catalyst spectrum.

The Raman spectra of $^{18}$O-enriched $\beta$-VOPO$_4$ during exposure to 2% n-butane in helium (500°C) are given in Figure 12. As for n-butane
Figure 11. Raman spectra of $^{18}O$-enriched $\beta$-VOPO$_4$ during n-butane oxidation (400°C)
Figure 12. Raman spectra of $^{18}$O-enriched $\beta$-VOPO$_4$ during n-butane oxidation (500°C)
oxidation at 400°C, band broadening caused the apparent disappearance of the shoulder V=O band at 997 cm\(^{-1}\) and the two bands at 886 and 896 cm\(^{-1}\) appeared as a single composite band at 890 cm\(^{-1}\). The band at 1072 cm\(^{-1}\) also shifted to 1068 cm\(^{-1}\) upon heating. The relative intensity of the composite P-O band at 890 cm\(^{-1}\) (representative of both P-\(^{16}\)O and P-\(^{18}\)O stretches) and the P-O band at 987 cm\(^{-1}\) decreased as compared to the P-O band at 1068 cm\(^{-1}\). The intensity of the 987 cm\(^{-1}\) band decreased by 46, 65, and 73\% following 2, 5, and 10 minutes of reaction, respectively. In comparison, the band at 890 cm\(^{-1}\) decreased by 30, 48, and 71\% following 2, 5, and 10 minutes of reaction, respectively. After two minutes of reaction a distinct band characteristic of the reduced (VO)\(_2\)P\(_2\)O\(_7\) phase appeared at 930 cm\(^{-1}\). After continued n-butane oxidation, this band increased in intensity, with the simultaneous decrease in all bands characteristic of the \(\beta\)-VOPO\(_4\) phase. After 30 minutes of n-butane oxidation the composite band at 890 cm\(^{-1}\) was no longer observable. Weak bands at 987 and 1068 cm\(^{-1}\) persisted even after 60 minutes of reaction.

**Characterization during 1-butene oxidation**

In situ Raman spectra of \(^{18}\)O-enriched \(\beta\)-VOPO\(_4\) were obtained during 1-butene oxidation at 350 and 450°C.

Figure 13 shows the Raman spectra of \(^{18}\)O-enriched \(\beta\)-VOPO\(_4\) collected during the oxidation of 2% 1-butene in helium at 350°C. In situ Raman spectra clearly indicated the decrease of the relative intensities of the two P-O bands at 890 and 987 cm\(^{-1}\) as compared to the P-O band at 1068 cm\(^{-1}\). After two minutes of reaction, the bands at 987 and 890 cm\(^{-1}\) decreased by 69 and 67\%, respectively. In addition, the (VO)\(_2\)P\(_2\)O\(_7\) phase was detected
Figure 13. Raman spectra of $^{18}$O-enriched $\beta$-VOPO$_4$ during 1-butene oxidation (350°C).
as early as two minutes into the reaction as characterized by the strong band at 930 cm\(^{-1}\). Bands characteristic of \(\beta\)-VOPO\(_4\) remained after 60 minutes of reaction.

The increased activity associated with 1-butene oxidation at 450°C was clearly evident in the Raman spectra of functioning \(^{18}\)O-enriched \(\beta\)-VOPO\(_4\). Figure 14 shows that the \(\beta\)-VOPO\(_4\) to \((\text{VO})_2\text{P}_2\text{O}_7\) phase transformation rapidly occurred within two to five minutes of reaction. After two minutes of reaction, the band at 890 cm\(^{-1}\) was no longer present, whereas the intensities of the bands at 987 and 1068 cm\(^{-1}\) were very weak. Indeed, after five minutes of reaction the \((\text{VO})_2\text{P}_2\text{O}_7\) phase was exclusively observed as evident by the strong band at 930 cm\(^{-1}\) and two weaker bands at 1187 and 1199 cm\(^{-1}\).
Figure 14. Raman spectra of $^{18}$O-enriched $\beta$-VOPO$_4$ during 1-butene oxidation (450°C).
DISCUSSION OF RESULTS

Crystallographic Phase Transformation

In situ laser Raman spectroscopy clearly indicated the participation of lattice oxygen during the selective oxidation of n-butane and 1-butene in air (3). Modifications in the Raman spectra of \( \beta\)-VOPO\(_4\) demonstrated that oxygen vacancies were created in the lattice of \( \beta\)-VOPO\(_4\) during n-butane oxidation, causing slight reduction without bulk restructuring. Furthermore, Raman band assignments confirmed these sites were associated with PO\(_4\) units in the lattice of \( \beta\)-VOPO\(_4\). During 1-butene oxidation, sufficient oxygen vacancies were produced to allow the \( \beta\)-VOPO\(_4\) to (VO)\(_2\)P\(_2\)O\(_7\) phase transformation.

Isotopic labeling proved particularly valuable for the characterization of the (VO)\(_2\)P\(_2\)O\(_7\) to \( \beta\)-VOPO\(_4\) phase transformation. The solid state reaction of (VO)\(_2\)P\(_2\)O\(_7\) with \( ^{18}\)O\(_2\) produced an \( ^{18}\)O-enriched \( \beta\)-VOPO\(_4\) phase. From the stoichiometry of the reaction, one mole of (VO)\(_2\)P\(_2\)O\(_7\) will react with one half a mole of \( ^{18}\)O\(_2\) forming an \( ^{18}\)O-enriched \( \beta\)-VOPO\(_4\) phase:

\[
(\text{VO})_2\text{P}_2\text{O}_7 + \frac{1}{2} \text{^{18}O}_2 \rightarrow \beta\text{-VOPO}_4 + \text{(\text{\beta\text{-VOPO}_4})*}
\]

where * denotes one mole of atomic \( ^{18}\)O incorporated. The Raman spectrum of \( ^{18}\)O-enriched \( \beta\)-VOPO\(_4\) included an isotopically shifted P-\( ^{18}\)O band at 886 cm\(^{-1}\) of equal intensity to its complementary P-\( ^{16}\)O band at 896 cm\(^{-1}\). This specific incorporation of \( ^{18}\)O into the PO\(_4\) groups of the \( \beta\)-VOPO\(_4\) lattice provided strong evidence that the (VO)\(_2\)P\(_2\)O\(_7\) to \( \beta\)-VOPO\(_4\) phase transformation occurred by a distinct crystallographic rearrangement.
Conversely, it would seem plausible that the reduction of $\beta$-VOPO$_4$ to (VO)$_2$P$_2$O$_7$ by C$_4$ hydrocarbons would involve the removal of the very same oxygen from the $\beta$-VOPO$_4$ lattice. *In situ* Raman spectra gathered during C$_4$ hydrocarbon oxidation in air using $\beta$-VOPO$_4$ (3) and those reported in this present investigation for $^{18}$O-enriched $\beta$-VOPO$_4$ decidedly showed the involvement of PO$_4$ group oxygens in the $\beta$-VOPO$_4$ to (VO)$_2$P$_2$O$_7$ transformation.

The crystal structures of $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ are represented in Figure 15 and 16, respectively. The $\beta$-VOPO$_4$ structure consists of corner sharing irregular VO$_6$ octahedra which form infinite vanadate chains through V=O-V bonding (23). The structure is composed of sheets of these vanadate chains. The PO$_4$ tetrahedron shares its oxygens with four separate VO$_6$ octahedra in three separate chains. Only the equatorial oxygens in the VO$_6$ octahedron are shared between a phosphorus and a vanadium atom. Adjacent sheets are bridged through the corner sharing of two equivalent oxygens of the PO$_4$ group with VO$_6$ groups above and below (Figure 15a). The PO$_4$ group also shares corners with two octahedra in the same vanadate chain (Figure 15b). These latter two oxygens are crystallographically distinct as a result of the displacement of the V atom from the center of the octahedron.

Likewise, the crystal structure of (VO)$_2$P$_2$O$_7$ is characterized by infinite vanadate chains formed by corner sharing VO$_6$ octahedra (24). In addition, the VO$_6$ octahedra are linked in pairs through a common equatorial edge, forming double vanadate chains (Figures 16a and 16b). Each PO$_4$ tetrahedron of the pyrophosphate groups is a tridentate bridge between three different vanadate chains.
Figure 15. Idealized $\beta$-VOPO$_4$ structure

(a) overall perspective showing vanadate chains and bridging PO$_4$ groups,

(b) projection showing PO$_4$ groups sharing two oxygens with two VO$_6$ groups in the same vanadate chain
Figure 16. Idealized \((\text{VO})_2\text{P}_2\text{O}_7\) structure
(a) overall perspective showing \(\text{P}_2\text{O}_7\) groups bridging double vanadate chains
(b) projection along the (020) plane
The above structural descriptions suggest that the $\beta$-VOPO$_4$ to $(VO)_{2}\text{P}_2\text{O}_7$ transformation must involve the cooperative movement of VO$_6$ octahedra to form the double vanadate chains characteristic of $(VO)_{2}\text{P}_2\text{O}_7$. Concurrently, the phosphate tetrahedra of $\beta$-VOPO$_4$ would need to rotate to form pyrophosphate groups with neighboring phosphate groups above or below.

In the $(VO)_{2}\text{P}_2\text{O}_7$ structure no isolated PO$_4$ tetrahedron shares more than one oxygen in the same vanadate chain. In contrast, the PO$_4$ tetrahedron of $\beta$-VOPO$_4$ shares two oxygens in the same vanadate chain. It is likely that one of these corners rotates to form the pyrophosphate group of $(VO)_{2}\text{P}_2\text{O}_7$. Conversely, the $(VO)_{2}\text{P}_2\text{O}_7$ to $\beta$-VOPO$_4$ transformation should proceed by the incorporation of oxygen into the very same PO$_4$ oxygen positions of $\beta$-VOPO$_4$. The Raman spectrum of $^{18}\text{O}$-enriched $\beta$-VOPO$_4$ clearly indicated that oxygen was incorporated very specifically into the $\beta$-VOPO$_4$ structure. Furthermore, the Raman spectrum indicated that equal amounts of oxygen from the starting material ($^{16}\text{O}$) and labeled oxygen ($^{18}\text{O}$) were associated with the same lattice position, supporting the crystallographic rearrangement discussed above. During catalysis, the $\beta$-VOPO$_4$ to $(VO)_{2}\text{P}_2\text{O}_7$ phase transformation may proceed by producing vacancies at the catalyst surface which then migrate to the bulk of the material. To facilitate structural rearrangement, sufficient vacancies in the appropriate PO$_4$ oxygen positions would be required. Since both the $\beta$-VOPO$_4$ and $(VO)_{2}\text{P}_2\text{O}_7$ structures are characterized by infinite vanadate chains, it would seem reasonable that the vanadate chain is preserved during catalysis. This result is anticipated since the V=O bond is by far the strongest bond in the VO$_6$ octahedron.
Active Sites for C₄ Hydrocarbon Oxidation

The active sites responsible for complete combustion and selective oxidation for an ¹⁸O-enriched β-VOPO₄ phase catalyst were investigated using a coupled laser Raman spectroscopy/mass spectrometry system for both n-butane and 1-butene oxidation conditions. In particular, the simultaneous collection of in situ Raman spectra of the catalyst material and the gathering of kinetic data for ¹⁸O incorporation into oxygenated products allowed the identification of specific lattice oxygen centers responsible for selective oxidation and complete combustion. The mechanism and the role of active sites in paraffin versus olefin oxidation by V-P-O catalysts were addressed.

The oxidation of n-butane by ¹⁸O-enriched β-VOPO₄ resulted in the preferential incorporation of ¹⁸O into maleic anhydride over CO₂ and H₂O. For n-butane oxidation at 500°C, the initial ¹⁸O content of maleic anhydride was approximately six times greater than for CO₂. The Raman spectrum of ¹⁸O-enriched β-VOPO₄ confirmed that ¹⁸O was incorporated into a specific lattice position of the β-VOPO₄ structure. Therefore, the selective incorporation of ¹⁸O into maleic anhydride suggests that different active sites were responsible for complete combustion and selective oxidation.

From the Raman spectrum of fresh ¹⁸O-enriched β-VOPO₄, the P=¹⁸O stretch at 886 cm⁻¹ and the complementary P=¹⁶O stretch at 896 cm⁻¹ were of equal intensity, indicating 50% of the oxygens associated with this stretching vibration were labeled with ¹⁸O. A small amount of ¹⁸O "spill-over" into another lattice position of β-VOPO₄ was detected, however. The
isotopically shifted P-$^{18}O$ stretch at 961 cm$^{-1}$ was approximately 7% the intensity of the complementary P-$^{16}O$ stretch at 987 cm$^{-1}$. In situ Raman spectra of functioning $^{18}$O-enriched β-VOPO$_4$ clearly indicated the involvement of oxygen characterized by the P-O stretch at 987 cm$^{-1}$. The intensity of the 987 cm$^{-1}$ band significantly decreased with reaction time. Steady state n-butane oxidation by β-VOPO$_4$ at 500°C resulted in relatively low maleic anhydride selectivities (ca. 20%), with the greater majority of reacting n-butane undergoing complete combustion (4). Therefore, it is reasonable to hypothesize that the P-O stretch at 987 cm$^{-1}$ distinctly characterizes the active combustion site of the β-VOPO$_4$ catalyst. If the n-butane interaction was strong enough, complete combustion would result at this site with an anticipated $^{18}$O content of approximately 7% for CO$_2$. Indeed, this prediction is in good agreement with the observed $^{18}$O content of 4% for CO$_2$ and 7% for H$_2$O.

The selective route for producing maleic anhydride yielded an initial $^{18}$O content of 24% during n-butane oxidation at 500°C over $^{18}$O-enriched β-VOPO$_4$, implying the involvement of two different active sites for maleic anhydride synthesis. It is generally accepted that the first interaction of n-butane with the catalyst involves a highly active oxygen for paraffin activation via oxidative dehydrogenation (1). It is likely that this site is equivalent to the necessarily highly active combustion site described above. The $^{18}$O content of water (ca. 10%) further suggests that most oxidative dehydrogenation occurred at the combustion site. To account for the observed $^{18}$O content of maleic anhydride, CO$_2$, and H$_2$O, the selective route must first involve extensive oxidative dehydrogenation and the
incorporation of two oxygen atoms into the hydrocarbon at the combustion site (Site I). An 18O content of roughly 7% would be anticipated for this oxygenated intermediate, based on characterization of the 18O-enriched β-VOPO4 catalyst. This intermediate could undergo further oxidation to combustion products (Site I) or migrate to another active site (Site II) for perhaps final dehydrogenation and oxygen incorporation to form maleic anhydride. If Site II is characterized by the P-16O and P-18O stretches at 886 and 896 cm⁻¹, respectively, an 18O content of 21% would be predicted for maleic anhydride. This prediction is in good agreement with the observed 18O content of 24%. In addition, roughly equivalent amounts of m/e 98 and 100 maleic anhydride were produced as predicted by the active site mechanism discussed above. The involvement of Site II oxygens was further confirmed by the observed β-VOPO4 to (VO)2P2O7 transformation as characterized by in situ Raman spectroscopy.

The activity of the Site II oxygens was found to depend strongly on reaction temperature. The oxidation of n-butane at 400°C resulted in very little 18O incorporation into maleic anhydride using 18O-enriched β-VOPO4. Previous steady state experiments for n-butane oxidation by β-VOPO4 at 425°C showed very low activity and negligible selectivity to maleic anhydride (4), further confirming the inactivity of Site II centers at low temperature. Of the maleic anhydride produced only that produced at Site I was detected, with the greater majority of the reacting hydrocarbon continuing onto combustion products. The inactivity of Site II oxygens was also reflected by the Raman spectra of functioning 18O-enriched β-VOPO4. The β-VOPO4 structure remained stable during n-butane oxidation
in the absence of gas phase oxygen at 400°C. Without the involvement of Site II oxygens the \( \beta\-VOPO_4 \) to \( (VO)_2P_2O_7 \) phase transformation would not occur.

In contrast to n-butane oxidation, the activation of 1-butene is readily accomplished by dehydrogenation to an allylic surface intermediate. Therefore, the interaction with a Site I center would not be necessary for activation of the olefin as opposed to the paraffin. The present investigation indicated the selective route for producing maleic anhydride was performed with Site II type oxygens; whereas, 1-butene once absorbed at Site I positions resulted in predominantly complete combustion. The selective oxidation of 1-butene at 350 and 450°C resulted in an initial \( ^{18}O \) content for maleic anhydride of approximately 63 and 48\%, respectively. Furthermore, nearly equal amounts of m/e 98 and 104 maleic anhydride were produced, suggesting each Site II location acts as a "well" of either \( ^{16}O \) or \( ^{18}O \) atoms. The \( ^{18}O \) content of \( CO_2 \) and \( H_2O \) was considerably lower than for maleic anhydride, indicating complete combustion was associated with Site I centers of \( ^{18}O \)-enriched \( \beta\-VOPO_4 \). For 1-butene oxidation at 350°C, the \( ^{18}O \) content of \( CO_2 \) increased as a function of reaction time resulting from the production of vacancies in both Site I and Site II oxygen centers followed by reoccupation by either \( ^{18}O \) or \( ^{16}O \) from neighboring sites. The Raman spectra of functioning \( ^{18}O \)-enriched \( \beta\-VOPO_4 \) indicated the involvement of both Site I and Site II oxygens. The high reactivity of 1-butene at 450°C resulted in the rapid \( \beta\-VOPO_4 \) to \( (VO)_2P_2O_7 \) phase transformation by the creation of Site II vacancies in the
lattice of the catalyst. For 1-butene oxidation at 350°C both β-VOPO₄ and (VO)₂P₂O₇ were detected by Raman spectroscopy.
CONCLUSIONS

The synthesis of an $^{18}$O-enriched $\beta$-VOPO$_4$ catalyst provided new insight into the (VO)$_2$P$_2$O$_7$ to $\beta$-VOPO$_4$ phase transformation. In addition, the specific incorporation of $^{18}$O into the $\beta$-VOPO$_4$ structure allowed the identification of pertinent oxygen centers involved in the C$_4$ hydrocarbon combustion and selective oxidation routes. The simultaneous collection of Raman spectra of the functioning catalyst and the gathering of kinetic data for $^{18}$O incorporation into maleic anhydride, CO$_2$, and H$_2$O permitted the characterization of active sites responsible for complete combustion and paraffin activation (Site I) and selective oxidation (Site II). The function of these active sites was distinctly different for n-butane and 1-butene oxidation. In particular, the activation of the paraffin required the interaction of the hydrocarbon with a highly reactive oxygen center (Site I) for initial dehydrogenation. Limited oxygen incorporation also occurred at the Site I centers for n-butane selective oxidation, forming perhaps a highly dehydrogenated intermediate such as a cycloperoxide or a dialdehyde species. This intermediate either continued to complete combustion products or migrated to a Site II oxygen center for final oxidative dehydrogenation and oxygen insertion to form maleic anhydride. The activity of Site II centers was strongly dependent on reaction temperature for n-butane oxidation. For the model $\beta$-VOPO$_4$ catalyst the selectivity to maleic anhydride was negligible for temperatures below 425°C (4), resulting from the inactivity of Site II centers as opposed to the continued activity of Site I centers. In contrast, 1-butene adsorption at Site I oxygen centers resulted in entirely
combustion products whereas selective oxidation occurred at Site II centers. Therefore, it is possible to suggest the following active site mechanisms for the synthesis of maleic anhydride from n-butane and 1-butene:

Scheme 1. Active site mechanism for combustion and selective oxidation of n-butane

Scheme 2. Active site mechanism for combustion and selective oxidation of 1-butene

A possible representation of the active sites for C₄ hydrocarbon oxidation can be postulated by extending the bulk structure of β-VOPO₄ to a surface as in Figure 17. The surface shown is parallel to the zigzagged vanadate chain. Site I oxygen centers are shown both in the equatorial plane of the VO₆ octahedra (V-O bonds perpendicular to the surface plane)
Figure 17. Plausible surface structure of \( \beta\text{-VOPO}_4 \) showing Site I and Site II oxygen centers
and as the P-O bond (1.528 Å) extending out of the surface plane. Both of these oxygens are equivalent in the bulk structural sense. Each PO₄ group also shares two oxygen atoms with two VO₆ groups in the same vanadate chain. These two oxygens are not equivalent as a result of the displacement of the vanadium atom from the center of each octahedra, yielding two P-O bond lengths of 1.519 and 1.540 Å (23). Site II oxygen centers are likely characterized by the slightly weaker P-O bond (1.540 Å), while the remaining oxygen is unreactive.
ACKNOWLEDGEMENT

This work was conducted through the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under contract W-7405-ENG-82.
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SUMMARY AND RECOMMENDATIONS

Summary

The model vanadium-phosphorus-oxygen catalysts, $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$, provided the opportunity to investigate fundamental questions concerning catalytic phase stability, the role of the vanadium oxidation state, the participation of lattice oxygen in C$_4$ hydrocarbon oxidation, and the nature of the active sites involved in complete combustion and selective oxidation. Pure $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ were synthesized by solid-state reaction techniques which yielded highly crystalline materials. Extensive characterization of the catalysts was performed using complementary instrumentation techniques, including laser Raman spectroscopy, X-ray powder diffraction, and X-ray photoelectron spectroscopy. Since the crystal structures of the two model catalysts were discussed by previous investigators, it was possible to make detailed band assignments for the characteristic Raman spectra. Confident identification of active catalyst sites, active lattice oxygen, and phase stability was thus possible. The influence of the catalytic phase and the formal vanadium oxidation state of the catalyst was also discussed in relation to maleic anhydride stability.

The stability of V-P-O catalysts during C$_4$ hydrocarbon oxidation was strongly dependent on the reducing environment. The structural stability of $\beta$-VOPO$_4$ and (VO)$_2$P$_2$O$_7$ was investigated using in situ laser Raman spectroscopy, X-ray powder diffraction, and X-ray photoelectron spectroscopy. The in situ Raman technique revealed key catalyst transformation during C$_4$ hydrocarbon oxidation which were otherwise undetectable by
postcatalytic characterization. The bulk structural integrity of \( \beta\)-VOPO\(_4\) and \((\text{VO})\sb{2}\text{P}_2\text{O}_7\) during n-butane oxidation was clearly indicated by in situ laser Raman spectroscopy and postcatalytic X-ray powder diffraction measurements. Modifications in the Raman spectra of functioning \( \beta\)-VOPO\(_4\) indicated, however, that oxygen vacancies were created in the lattice of \( \beta\)-VOPO\(_4\) causing slight reduction without bulk restructuring. Furthermore, Raman band assignments suggest these oxygen sites were associated with \( \text{PO}_4\) units in the lattice of \( \beta\)-VOPO\(_4\). The greater reducing capacity of 1-butene, however, did result in a \( \beta\)-VOPO\(_4\) to \((\text{VO})\sb{2}\text{P}_2\text{O}_7\) phase transformation. As for n-butane oxidation, the oxygen vacancies were created at P-O positions in the lattice of \( \beta\)-VOPO\(_4\). X-ray photoelectron spectroscopy confirmed the presence of V(V) and V(IV) in used \( \beta\)-VOPO\(_4\) and \((\text{VO})\sb{2}\text{P}_2\text{O}_7\) for both hydrocarbon oxidation conditions.

Direct structural identification of catalytically active oxygen centers for paraffin and olefin oxidation was investigated using an \( ^{18}\text{O}\)-enriched \( \beta\)-VOPO\(_4\) phase catalyst synthesized by the \((\text{VO})\sb{2}\text{P}_2\text{O}_7\) to \( \beta\)-VOPO\(_4\) phase transformation in the presence of gaseous \( ^{18}\text{O}_2\). Laser Raman spectroscopy indicated the \( ^{18}\text{O}\) label was incorporated into discrete tetrahedral positions in the \( \beta\)-VOPO\(_4\) lattice. The \( ^{18}\text{O}\)-enriched \( \beta\)-VOPO\(_4\) catalyst was particularly valuable for the study of active combustion and selective oxidation sites. The relationship between the spectroscopic characteristics of the functioning catalyst and the incorporation of \( ^{18}\text{O}\) into oxygenated products such as maleic anhydride, \( \text{CO}_2\), and \( \text{H}_2\text{O}\) was investigated using a combined laser Raman spectroscopy/mass spectrometry system. Active sites responsible for complete combustion (Site I) and
selective oxidation (Site II) were identified. Both active sites were associated with PO$_4$ tetrahedral position in the $\beta$-VOPO$_4$ lattice. The function of these sites was distinctly different for paraffin and olefin oxidation. The selective route for 1-butene oxidation involved predominantly Site II centers, while Site I centers were associated with complete combustion. In contrast, n-butane oxidation required interaction with the highly active Site I centers for initial activation by oxidative dehydrogenation and for the formation of an intermediate containing two oxygen atoms. This intermediate either continued to complete combustion (Site I) or was selectively oxidized to maleic anhydride (Site II).

Direct evidence for the conversion of maleic anhydride by model V-P-O catalysts was confirmed by directly feeding maleic anhydride to an integral flow reactor. Significant combustion activity was observed with the simultaneous production of maleic acid. The reaction network for C$_4$ hydrocarbon oxidation to maleic anhydride may therefore involve the further conversion of maleic anhydride to products such as maleic acid and carbon dioxide. Maleic anhydride conversion increased with temperature, contact time, and oxygen partial pressure. The stability of maleic anhydride was particularly sensitive to the catalytic phase present. Maleic anhydride combustion activity was least for (VO)$_2$P$_2$O$_7$, nominally a vanadium +4 phase. The $\beta$-VOPO$_4$ catalyst, nominally a vanadium +5 phase, resulted in increased conversion of maleic anhydride. The greater combustion activity associated with the $\beta$-VOPO$_4$ catalyst may result from a high population of Site I oxygen centers.
Recommendations for Future Work

Interest in vanadium-phosphorus-oxygen (V-P-O) catalysts has stemmed from the high selectivity and activity these materials display in C₄ hydrocarbon oxidation to maleic anhydride. From a more fundamental viewpoint, however, the selective oxidation of n-butane by V-P-O catalysts represents a significant example of the catalytic oxidation of paraffins, which to date remains little understood or practiced industrially. The emphasis of this present work was the identification of specific catalyst features which play key roles in C₄ hydrocarbon oxidation, particularly during actual reaction conditions. In addition to contributing to the fundamental understanding of the active and selective components of V-P-O catalysts, the present investigation suggests several other ideas for future work. The following are some specific suggestions which would exploit the techniques and results presented in this current investigation, particularly with regard to catalyst synthesis, characterization, and evaluation.

1. Characterization of the solid state synthesis of β-VOPO₄ and (VO)₂P₂O₇ using in situ laser Raman spectroscopy. The controlled atmosphere Raman cell presented in this work is well suited for spectroscopic characterization during catalyst synthesis.

2. Characterization of industrial type V-P-O catalysts prepared by organic precipitation. The in situ Raman cell can be used during both the air calcination and n-butane activation steps.

3. Reactor experiments need to be performed to evaluate phosphorus loss from V-P-O catalysts with variable P-to-V ratios. Mass
spectrometry may be particularly valuable for the detection of small quantities of phosphorus compounds in the reactor effluent.

4. In general, $\beta$-VOPO$_4$ (nominally V(V)) is more active but less selective than (VO)$_2$P$_2$O$_7$ (nominally V(IV)). Flow reactor experiments need to be completed to evaluate the performance of a catalyst bed packed with $\beta$-VOPO$_4$ in the first portion of the reactor (to "activate" n-butane) and (VO)$_2$P$_2$O$_7$ in the second portion (to enhance selectivity).

5. The laser Raman spectrum of oxygen-18 enriched $\beta$-VOPO$_4$ indicated that oxygen was specifically incorporated into P-O sites associated with PO$_4$ groups. Solid state NMR studies using similarly prepared oxygen-17 enriched $\beta$-VOPO$_4$ need to be completed to determine the specific coordination of the oxygen involved during the (VO)$_2$P$_2$O$_7$-to-$\beta$-VOPO$_4$ transformation. Changes in peak position and the shape of the $^{31}P$, $^{51}V$, and $^{17}O$ NMR signals would be of particular interest.

6. The incorporation of oxygen into products of n-butane selective oxidation should be studied to determine if oxygen incorporation into maleic anhydride or CO$_2$ is via gas phase, adsorbed, or lattice oxygen. By using a micro-reactor system the catalyst should be brought to steady state with a feed consisting of n-butane, $^{16}$O$_2$, and helium. A step change to an $^{18}$O$_2$ feed would then be initiated. The incorporation of $^{18}$O$_2$ into the reaction products would be recorded by a mass spectrometer as a function of time.

7. A simple experiment can be conducted to test whether oxygen is chemisorbed on the oxide surface. The $\beta$-VOPO$_4$ phase should be
conditioned in a mixture of $^{16}\text{O}_2$ in helium. The feed oxygen supply would then be replaced by $^{18}\text{O}_2$. If oxygen is chemisorbed on the surface of the oxide, exchange products such as $^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}_2$ would be detected.

8. Pulsed reactor studies of n-butane and 1-butene oxidation both with and without $^{16}\text{O}_2$ or $^{18}\text{O}_2$ in the feed mixture should be performed. Characterization of the catalyst between pulses by laser Raman spectroscopy may provide more information regarding the catalytic components responsible for oxygen insertion into the hydrocarbon molecule.

9. Both industrial type and model V-P-0 catalysts should be evaluated for other paraffin feedstocks such as ethane, propane, and hexane.

10. The interaction of the catalyst with a support can dramatically influence its catalytic properties. A fundamental understanding of catalyst/support interactions is still lacking for V-P-0 catalysts. Specific research topics would include the preparation of V-P-0 catalysts using a series of support materials, their characterization, and catalytic evaluation.

11. Although promotional effects in industrial V-P-0 catalysts are very significant, a fundamental understanding of the nature of modified V-P-0 catalysts has yet to be developed. A comprehensive study of the synthesis, characterization, and catalytic evaluation of promoted V-P-0 is required.
ADDITIONAL LITERATURE CITED


ACKNOWLEDGEMENTS

I would like to thank Dr. Glenn L. Schrader for his guidance both in my professional development and in the completing of this research. His encouragement for my direct involvement in writing journal publications and in presenting my research at professional meetings is very much appreciated.

I would also like to thank the many friends at the First Evangelical Free Church for their prayerful support during my stay in Ames. Their encouragement and teaching helped me keep my work in perspective.

Finally, I would like to thank my wife, Janice, for her confidence in my abilities. You said I would finish this semester! I should have believed you earlier.