In situ Vibrational Spectroscopic Investigation of C*4*
Hydrocarbon Selective Oxidation over Vanadium-phosphorus-oxide Catalysts

by

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ACKNOWLEDGEMENT
n-Butane selective oxidation over the VPO catalyst to maleic anhydride is the first and only commercialized process of light alkane selective oxidation. The mechanism of this reaction is still not well known despite over twenty years of extensive studies, which can partially be attributed to the extreme difficulties to characterize catalytic reactions real-time under typical reaction conditions. In situ spectroscopic characterization techniques such as Infrared spectroscopy and laser Raman spectroscopy were used in the current mechanistic investigations of n-butane oxidation over VPO catalysts.

To identify the reaction intermediates, oxidation of n-butane, 1,3-butadiene and related oxygenates on the VPO catalyst were monitored using FTIR spectroscopy under transient conditions. n-Butane was found to adsorb on the VPO catalyst to form olefinic species, which were further oxidized to unsaturated, noncyclic carbonyl species. The open chain dicarbonyl species then experienced cycloaddition to form maleic anhydride.

VPO catalyst phase transformations were investigated using in situ laser Raman spectroscopy. During reduction-oxidation step changes, (VO)₃P₂O₇ was readily converted to α₁⁻, δ⁻VOPO₄ and ultimately to β⁻VOPO₄ in O₂/N₂; these V⁵⁺ phases were eliminated in n-butane/N₂. A “wet” nitrogen feed (5-10% H₂O in N₂) transformed (VO)₃P₂O₇ and α₁⁻, α₃⁻, β⁻, δ⁻, γ⁻VOPO₄ to V₂O₅ at temperatures above 400°C. The presence of water vapor facilitated the loss of oxygen atoms involved in V–O–P bonding; separated vanadium oxide and phosphorus oxide species were formed. The isolated vanadium oxides than transformed to V₂O₅, and phosphorus species likely diffused from the catalyst lattice in the form of acid phosphates.
CHAPTER 1
GENERAL INTRODUCTION

Introduction

The petrochemical industry is in a transition from depending on alkenes and mono-olefins as building blocks to using alkanes as major raw materials. Alkanes are relatively inexpensive and readily available. In addition, alkane-based processes may have lower environmental impact compared with alkene-based processes. As a part of this transition, production of value-added oxygenates by single step gas phase selective oxidation of alkanes is a very active research area.

The selective oxidation of n-butane to maleic anhydride is currently the only commercialized reaction of this kind (1). Before the 1980s, vapor-phase oxidation of benzene over a vanadium-based catalyst was the dominant technique for producing maleic anhydride. The discovery of the high selectivity vanadium phosphorous oxides (VPO) has enabled the direct oxidation of n-butane to maleic anhydride to be practiced by the industry. Since the mid-1980s, all North American producers have used this n-butane oxidation process to produce maleic anhydride. Its current capacity in the U.S. is 450 million-lb.-per-year (2).

Propane ammoxidation to produce acrylonitrile is likely to be the second industrial application of alkane selective oxidation. Currently 95% of the world's output of acrylonitrile is produced by propylene ammoxidation process that was developed by Sohio in 1957 (3). Studies aimed at using propane as feedstock have been conducted for years.
Recently, BP Chemicals announced its success in ammoxidation of propane to yield acrylonitrile using a new catalyst system. According to BP, this new process can lower the production costs by 20% compared with the propylene-based approach. Production of valuable co-products (e.g. acetonitrile and hydrogen cyanide) and lower wastes (e.g. acrylic acid) are among the additional benefits (3). The selective oxidation from isobutane to methacrylic acid, ethane to acetic acid, and propane to acrylic acid are also being studied, and likely become the candidates for the next breakthrough.

In addition, processes involving the selective oxidation of diolefins have gained solid progress, particularly routes based on 1,3-butadiene. Most 1,3-butadiene is produced as a co-product from naphtha steam cracking, which is used to produce ethylene. Because of the disparity in the increments of demand for butadiene (3% per year) versus for ethylene (4.5% per year), a 2 million ton global surplus of butadiene is projected by the end of this century (4). The projected oversupply stimulates great incentive to find new applications for 1,3-butadiene. In 1996, Eastman Chemical commercialized a process for the continuous air-oxidation of butadiene to epoxybutene using a Ag-based catalyst system. Epoxybutene is a very versatile intermediate that can undergo different reactions to produce various chemical compounds to form a "chemical tree" (5). It was reported that more than 10 different chemicals would be produced from the epoxybutene in this process (6).

Catalysis obviously plays a key role in all of these new commercial developments. Understanding the mechanisms of these catalytic conversions can help to optimize the existing processes and may help in developing new catalytic reaction routes. However, the mechanistic study of heterogeneous reaction systems is a very demanding task, due to the
complexity introduced by numerous reactive species, possible changes in the catalyst during the reaction, and the complicated interaction between the reactive species and the solid catalyst.

n-Butane selective oxidation over the VPO catalyst has been studied for more than twenty years. The research in the late 70s and early 80s focused on catalyst development and reaction kinetics with the emphasis on improving the activity and selectivity of the catalyst. Since the late 80s, the focus has shifted to the investigation of the reaction mechanism using crystallographic and spectroscopic techniques in order to gain a microscopic level understanding of the reaction mechanism. The development of DuPont’s Circulating Fluidized Bed (CFB) process (7) brought new incentives to mechanistic studies. The unsteady state operation conditions adopted by DuPont’s process apparently improved the process yield for maleic anhydride. Reasons for this yield improvement, mechanistic, kinetic or else, need to be addressed. The study of reaction systems under unsteady state conditions has now become an important research topic.

Several statements about n-butane selective oxidation over the VPO catalyst can be made as the following, based on the results of numerous mechanistic studies.

- n-Butane partial oxidation on the VPO catalyst follows a redox mechanism (8).
- The reaction has multiple steps and various intermediates.
- The VPO catalyst is multifunctional and capable of alkane activation, H-abstraction, oxygen insertion, etc.
- The catalyst can exist in different phases and the reaction can induce phase transformations.
• The most active and selective phase is believed to be vanadyl pyrophosphate, (VO$_2$)P$_2$O$_7$.

There is still no definite answer to some fundamental questions: a) what is the reaction pathway; b) what is the active site responsible for each reaction step; c) how does the catalyst evolve during the reaction and how does this affect the reaction kinetics. In general, the mechanism of this reaction is not well understood.

**Research Objectives**

The primary research interest of the author is to investigate the mechanism of n-butane selective oxidation over the VPO catalyst. The research objectives are a) to identify the reaction intermediates and the reaction pathway of n-butane partial oxidation to maleic anhydride; b) to identify reaction induced phase transformations of the VPO catalyst, with emphasis on transient operation conditions.

In experimental investigations of the mechanism of a heterogeneous catalytic reaction, it would be desirable to monitor simultaneously the behavior of every species involved in the reaction system: the reactants, reaction intermediates, products, and the catalyst. Unfortunately, it is not yet practical due to instrumental and operational limitations. However a simplified approach as the following can be taken: a) investigate the nature and the dynamics of reactants, reaction intermediates, and products, b) investigate the nature of the catalyst and its dynamics in the reaction, c) investigate the reaction kinetics, d) match the data obtained in (a), (b), and (c) to form an integrated view of the reaction mechanism.

In gas-solid heterogeneous reaction systems, the reactants, products and byproducts are in the gas phase. They can be detected by analyzers such as mass spectrometry and gas
chromatography. Reaction intermediates exist only on the catalyst surface and usually have a low concentration and a short lifetime. Consequently, detection of reaction intermediates is difficult. Infrared spectroscopy is a proven to be capable of observing surface adsorbates, in situ IR is frequently used to detect reaction intermediates and monitor their evolution during the reaction. Raman spectroscopy is also a powerful characterization technique in catalysis research, particularly for metal oxide catalysts. In situ laser Raman spectroscopy is frequently used to monitor the changes that occur in the solid structure. In situ FTIR and in situ LRS combined will provide capability of studying changes in reaction intermediates and in the catalyst and they were the primary experimental techniques used in this research.

Dissertation Organization

The dissertation consists of five chapters. Chapter 1 explains the scientific and industrial relevance of studying n-butane selective oxidation over VPO catalysts and the objectives of the author's research. In Chapter 2 a literature review is given to survey the mechanistic studies in n-butane selective oxidation and to identify unsolved problems. Chapter 3 and Chapter 4 are papers written based on the author's research on reaction intermediates and on catalyst transformations in n-butane selective oxidation on VPO catalysts. The papers are in forms suitable for publication in scientific journals. Chapter 5 draws general conclusion and proposes directions for further research activities. The research presented represents original work conducted by the author.
References


4. Oil & Gas Journal, July 18, 1994, p.65


CHAPTER 2
LITERATURE REVIEW

n-Butane selective oxidation to maleic anhydride over the VPO catalyst involves abstraction of eight hydrogen atoms, insertion of three oxygen atoms, and transfer of fourteen electrons. The reaction is highly selective toward maleic anhydride at low butane conversions with carbon oxides as the only byproducts (1). The reaction is believed to follow a Mars-van Krevelen (redox) mechanism, in which the catalyst provides lattice oxygen to oxidize the adsorbed reactants and is reduced; the consumed lattice oxygen is then replenished by the surface oxygen species converted from gaseous oxygen and the catalyst is regenerated. This reaction is the focus of much research interest. The scope of previous research includes catalyst preparation, reaction pathway, reaction kinetics, catalyst structure models and the nature of active sites, etc. There are a substantial number of studies on each of these topics reported in the literature, and several reviews are available (1, 2, 3, 4, 5).

Complex Structure of (VO)$_2$P$_2$O$_7$ and VOPO$_4$ Phases

Vanadium phosphorus oxides (VPO) have many known crystalline phases, which include V$^{5+}$ compounds [e.g. $\alpha$, $\alpha_{II}$, $\beta$, $\gamma$, $\delta$-VOPO$_4$, and VOPO$_4$·2H$_2$O (dihydrate)] and V$^{4+}$ compounds [e.g. (VO)$_2$P$_2$O$_7$ and its precursor VOHPO$_4$·0.5H$_2$O (hemihydrate)] (6). Vanadyl pyrophosphate has a layered structure (Fig. 1a, b). The layers consist of pairs of edge-sharing distorted VO$_6$ octahedra equatorially linked together by corner-sharing pyrophosphate tetrahedra. The two vanadyl groups within the pair of vanadium octahedra
Fig. 1: a. Top view of (100) plane of (VO)$_2$P$_2$O$_7$ and the connection of vanadyl dimers; b. side view of the (100) plane shows the linkage between layers (Centi and Perathoner unpublished).
are trans to each other. The layers stack together through interlayer bonding formed by 
\[ V=O \cdot V=O \] chains parallel to bent pyrophosphate groups. It is further suggested that 
catalytic active \((VO)_2P_2O_7\) is characterized by a preferential exposition of the \((010)\) plane. 

SEM micrographs showed that an active VPO catalyst has stacked layer parallel to this plane 
(12). A recent XPS study suggests that the surface P/V ratio (1.098-1.136 on (010) plane) is 
much closer to bulk P/V ratio (1.00) than previously reported (1.5-2.0) (11).

These evidences allow us to view the catalyst surface by simply truncating the bulk 
structure along (010) plane: coupled vanadyl groups are isolated from each other by 
pyrophosphate groups, half of which terminate as protonated orthophosphate moieties. Half 
of the surface V atoms are coordinately unsaturated, whereas the other half terminates in 
\( V=O \) double bonds. This structure model is designated as Truncation C by Cavani and 
Trifirò (Fig. 2a) (5) and has a surface P/V ratio around unity. This proposed model allows 
the isolation of active sites: four accessible vanadium pairs surrounded by six P-OH groups 
that form a surface cavity. In Ebner and Thompson's model (7) the surface terminates with 
pendant groups of pyrophosphate (Fig. 2b). It was suggested that the adsorbed reactant 
molecules were converted to the final product in this cavity. It was also believed that active 
site isolation reduced the mobility of active surface oxygen and prevented over-oxidation of 
the products.

The structure of \( \alpha_{\Gamma}, \alpha_{\Pi}, \) and \( \beta \)-VOPO\(_4\) are also known. Different from \((VO)_2P_2O_7\), 
these phases are built form single columns of \( VO_6 \) octahedra linked together through \( PO_4 \) 
tetrahedra. For \( \alpha_{\Gamma}, \alpha_{\Pi}-VOPO_4\), every \( PO_4 \) tetrahedra shares its four oxygen atoms with four

* Also referred to as (100) plane by some authors. See pp. 263 in Reference 5 for explanation.
Fig. 2: a. Different truncations along (100) plane create surface with different P/V ratios (Reference 1.); b. Ebner and Thompson's mold (Truncation B) creates a cavity (Centi and Perathoner unpublished).
different VO₆ octahedra columns and those columns are parallel to each other. Their structures differ in the relative position of V=O as compared to the neighboring PO₄ groups: the vanadium and phosphorus atoms are on the same side of the equatorial oxygen atom plane in α₁-VOPO₄ while in α₁I-VOPO₄ they lie on the alternate sides. β-VOPO₄, on the other hand, has two of its four PO₄ oxygen atoms shared with two neighboring VO₆ octahedra in one column and other two oxygen shared with two different VO₆ columns. As a result, β-VOPO₄ does not have a layered structure.

The structural frameworks of δ- and γ-VOPO₄ have not been solved. Bordes (8) proposed that the structural building blocks of these two crystals are edge-sharing distorted VO₆ octahedra pairs and PO₄ tetrahedra based on the fact that these catalyst can be obtained by calcination of VOHPO₄*0.5H₂O in air. Ben Abdelouahab et al. (9) suggested that the structures for δ- and γ-VOPO₄ are similar to α-VOPO₄ phases with only different arrangements of the VO₆ and PO₄ units, citing the fact that all α₁-, α₁I, δ- and γ-VOPO₄ have the same hydration product: VOPO₄*2H₂O.

The Dynamics of the VPO Catalysts

The catalytic behavior of the VPO catalysts varies according to their differences in compositions (e.g. P/V ratios), precursor preparation methods (e.g. aqueous vs. organic media), activation procedures (e.g. calcination in air vs. in butane flow), and aging procedures (e.g. various times on stream) (4). Presumably the differences are due to variations in morphology and topology of the resulting catalysts. However, it is generally agreed that (VO)₂P₂O₇ is the active and selective component in converting n-butane into
maleic anhydride under steady state conditions (10). The phase transformations from \( V^{5+} \) phases and the evolution of fresh VPO catalyst into \((VO)_2P_2O_7\) has recently been confirmed by both XPS (11) and electron microscopy studies (12). The latter shows the reordering of the amorphous surface layer into layered structure of \((VO)_2P_2O_7\) as its time on stream increases, with paralleling increase in the selectivity toward maleic anhydride under steady state condition. In DuPont's Circulating Fluidized Bed (CFB) process, the catalyst is operated under unsteady state conditions. The result of XRD characterization of the catalyst after its two months' service in CFB reactor showed that \((VO)_2P_2O_7\) was the only crystalline phase in the catalyst (13). Nevertheless, phase transformations between \( V^{4+} \) and \( V^{5+} \) as well as among \( V^{5+} \) phases under various conditions have been reported. A detailed review of this topic can be found in “Introduction” of Chapter 4.

The result of studies in VPO structural alterations depicts that it is the surface layers of the catalyst which interact with n-butane and oxidize it into maleic anhydride during the reaction. The catalyst surface can undergo dynamic changes, e.g. phase transformations if the characteristic time scale of process transients is comparable to that of surface reconstruction. However, under reported transient operation conditions, e.g. up to 4 min in both reduction and reoxidation steps (14), this kind of solid state rearrangement is probably limited to the catalyst surface. Therefore, \((VO)_2P_2O_7\) appears to be an appropriate starting point to analyze the interaction between the VPO catalyst and the reactants under both steady and unsteady state operation conditions.
Reaction Mechanism

*Functionality of the Active Sites*

Reference 5 provides a comprehensive review of the proposed active sites on \((VO)\)\(_2\)\(P_2\)\(O_7\) surface and the nature of these sites published in the literature before 1994. They are summarized in Table 1(5). The current survey will focus on the information published more recently.

Table 1. Type of active sites hypothesized to be present at the surface of \((VO)\)\(_2\)\(P_2\)\(O_7\)

<table>
<thead>
<tr>
<th></th>
<th>Lewis acid sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brønsted acid sites</td>
<td>One-electron redox couple: (V^{5+}/V^{4+}), (V^{4+}/V^{3+})</td>
</tr>
<tr>
<td></td>
<td>Two-electron redox couple: (V^{5+}/V^{3+})</td>
</tr>
<tr>
<td></td>
<td>Bridge oxygen in (V-O-V) and (V-O-P) groups, or triply-bridged oxygen in (VO(P)V)</td>
</tr>
<tr>
<td></td>
<td>Terminal oxygen in ((V=O)^{3+}), ((V=O)^{2+})</td>
</tr>
<tr>
<td></td>
<td>Adsorbed molecular oxygen as (\eta^1)-peroxo and (\eta^2)-superoxo species</td>
</tr>
</tbody>
</table>

Lewis acid sites

It is believed that the unsaturated vanadium (IV) ions form Lewis acid sites on \((VO)\)\(_2\)\(P_2\)\(O_7\) (15). Lewis acid sites are thought to be responsible for the activation of C-H bond in n-butane. Busca et al. proposed that the \(\sigma\) or \(\sigma^*\) C-H orbitals interact with the d-type orbitals of a transition metal cation in which two electrons flow from the hydrocarbon to the cation, leaving a proton and a carbocation (16). It is in agreement with Centi and his coworkers' model in which Lewis sites abstract, simultaneously with an basic oxygen (triply bridged oxygen \(V-O(V^2-\)V\)), two hydrogen from two CH\(_2\) groups of n-butane via a concerted mechanism, as shown in Fig. 3 (5). The activation of C-H bonds is generally believed to be the rate-determining step in n-butane selective oxidation under steady state conditions.
Fig. 3. n-Butane activation by concerted H-abstraction on (VO)$_2$P$_2$O$_7$ and oxygen restoration (Reference 1).

Brønsted acid sites

P–OH groups are proposed to be surface Brønsted acid sites (15). As mentioned in the previous discussion (5), they may form a shallow surface cavity with the vanadium dimer pair on its bottom. P–OH groups are considered to facilitate the migration of hydrogen atoms through water elimination (7). (VO)$_2$P$_2$O$_7$ with deactivated Brønsted acid sites can not
convert butane to maleic anhydride in the presence of gaseous oxygen (17). There might be two reasons for this activity loss: a) the deactivated P–OH groups fail to provide oxygen atoms to form maleic anhydride, and b) the deactivation of P–OH groups delays the removal of hydrogen and the delay changes the relative rate of hydrogen abstraction vs. oxygen insertion.

\( \eta^1\)-peroxo and \( \eta^2\)-superoxo species

Schigtt et al. (18) suggested that oxygen molecules can adsorb on Lewis acid sites to form \( \eta^1\)-peroxo and \( \eta^2\)-superoxo species (Fig. 4). Based on extended Hückel calculation, they concluded that the energetic and geometric favorable approach is for 1,3-butadiene to interact with the terminal oxygen in V=O group in a [2+4]-like concerted mechanism to form 2,5-dihydrofuran. The generated dihydrofuran is further oxidized by adjacent \( \eta^1\)-peroxo and \( \eta^2\)-superoxo species to form lactone or maleic anhydride (19).

Agaskar et al. (20) combined Schiøtt's model with the concept of site isolation and redox cycle. They suggested that there are four types of vanadium dimer pairs with different oxidation states which involve in the catalytic redox cycle (Fig. 5). \( S_3 \) sites are similar to the \( \eta^1\)-peroxo and \( \eta^2\)-superoxo sites proposed in Schiøtt's model (18,19). The vanadium ions on these sites have a chemical valance of \( V^{5+} \). \( S_3 \) sites are responsible for converting n-butane to 1,3-butadiene through hydrogen abstractions. The resulting 1,3-butadiene further interacts with \( S_3 \) sites and is converted to maleic anhydride following the mechanism similar to that proposed by Schiøtt. After the desorption of maleic anhydride, the \( S_3 \) sites are reduced to the \( S_0 \) sites (\( V^{2+} \)). The \( S_0 \) sites can react with oxygen atoms to form \( S_1 \) (\( V^{4+} \)) or with oxygen molecules to form \( S_2 \) (\( V^{4+} \) and \( V^{5+} \)). The \( S_1 \) sites can further be converted to the \( S_3 \) sites by
Fig. 4. Proposed oxidation of adsorbed 2,5-dihydrofuran by η₁-peroxo after the formation 2,5-dihydrofuran by oxygen insertion into 1,3-butadiene (Reference 18).
Fig. 5. a. Transformation pathways linking the four distinct states of the active site and the associated substrate reactions; b. Surface dynamics of conversion of n-butane to maleic anhydride on the four-fold cluster of active sites on (VO)$_2$P$_2$O$_7$ (Reference 22).
adsorbing molecular oxygens. The $S_3$ sites can also be restored by oxygen transfer between two adjacent $S_2$ sites. In brief, $S_3$ sites are the active sites in converting n-butane to the product while other sites react with oxygen to form $S_3$ sites.

$V^{5+}$ species

It is a generally held opinion that the most selective VPO catalyst has a chemical valence of vanadium slightly over +4. This indicates that the presence of certain amount of $V^{5+}$ species is necessary for a selective catalyst. Coulston et al. (21), using in situ X-ray absorption spectroscopy, showed that maleic anhydride can only be produced when there was $V^{5+}$ species in the catalyst. In their experiment, after $V^{5+}$ signal decayed, $V^{3+}$ signal began to grow while no more maleic anhydride was produced. Although it didn't solve the problem concerning redox couples, this study monitored the dynamics of $V^{5+}$, $V^{4+}$, and $V^{3+}$ species simultaneously and directly related the states of vanadium ions to the product kinetics.

P–O–V sites

Lashier and Schrader studied the Raman spectra of $^{18}$O labeled $\beta$-VOPO$_4$ (22) and ($VO$)$_2$P$_2$O$_7$ (23) and discovered that $^{18}$O was preferentially incorporated into certain P–O–V sites. The production of n-butane oxidation over $^{18}$O labeled $\beta$-VOPO$_4$ such as maleic anhydride, carbon oxides, were analyzed using mass spectroscopy. The $^{18}$O content was significantly higher in maleic anhydride than in CO$_2$. The authors suggested that P–O–V sites were responsible for converting furan-like intermediates into maleic anhydride (Fig. 6). More recently, Numata and Ono (24) implanted $^{18}$O into $\beta$-VOPO$_4$ by reaction under a 1-butene/$^{18}$O$_2$ mixture or 1-butene – $^{18}$O$_2$ feed step change. Their analysis of obtained Raman spectra also supported that P–O–V sites are responsible for reoxidation. Using in situ
environmental high-resolution electron microscopy, Gai and Kourtakis (25, 26) observed defects nucleated at the surface of (VO₂)P₂O₇ and extended into the bulk when the catalyst was treated with either n-butane, H₂, He, N₂ or steam. The generation of these defects was attributed to oxygen vacancies due to the loss of P–O–V oxygen. Local glide shears in <201> directions were formed to reduce the misfit strain. After prolonged reaction under reducing atmosphere, an anion-deficit superstructure can be formed. In addition, the structural defect density was significantly lower in n-butane/O₂ mixture, which may suggest that gas phase oxygen replenished the P–O–V oxygen vacancies.

To summarize the current status of the research concerning the nature of active sites, the following statements can be made:

1. The adsorbed ionic oxygen species such as O₂⁻ or O⁻ have very high oxidative activity and are considered to be responsible for the total degradation of the hydrocarbon (5, 27). The suggested role and even the existence of η¹-peroxo and η²-superoxo species need further verification.

2. V⁵⁺ species might be important in catalytic conversion of n-butane to maleic anhydride. Reduction of the catalyst generates V³⁺ species. Yet it is unclear if V³⁺ species is involved in the reaction operating under near stoichiometric, steady state conditions.

3. There is no agreement on whether or not the oxygen-containing sites, e.g. P–OH, PO₄, P–O–V, V=O, V–O/V, provide lattice oxygen to the reactant. It is even more difficult to identify which one is responsible for a specific reaction step.
Fig. 6. Proposed function P-O-V oxygen in n-butane conversion to maleic anhydride (Reference 24).
Reaction Pathway

Although few chemicals other than maleic anhydride and carbon oxides have been detected under commercial reaction conditions, a complex reaction pathway from n-butane to maleic anhydride must involve many elementary steps and intermediates. The lack of the intermediate desorption is attributed to the fast reaction rates of the elementary steps following butane activation. With the support of some experimental evidences, butene, 1,3-butadiene, furan, unsaturated lactone are suggested to be intermediate products in the n-butane oxidation over VPO. The reaction pathway is described in Table 2. In order to identify the reaction pattern, studies have been conducted using suggested reaction intermediates.

Table 2. Proposed Steps in the Oxidation of n-butane to Maleic Anhydride

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane → butene</td>
<td>Oxidative dehydrogenation</td>
</tr>
<tr>
<td>butene → butadiene</td>
<td>Allylic oxidation</td>
</tr>
<tr>
<td>butadiene → 2,5-dihydrofuran</td>
<td>1,4 oxygen insertion</td>
</tr>
<tr>
<td>2,5-dihydrofuran → furan</td>
<td>Allylic oxidation</td>
</tr>
<tr>
<td>furan → lactone</td>
<td>Electrophilic oxygen insertion</td>
</tr>
<tr>
<td>lactone → maleic anhydride</td>
<td>Electrophilic oxygen insertion</td>
</tr>
</tbody>
</table>

C₄ olefins (butene and butadiene) are much more active than n-butane due to their possession of unsaturated bonds. The oxygen insertion on the adsorbed activated hydrocarbon is considered to be rate-determining in olefin oxidation (1). The kinetics of 1,3-butadiene, furan and 2,5-dihydrofuran oxidation over (VO)ₓP₂O₇ was studied by Centi and Trifirò (28). It was found that 1,3-butadiene could be converted at much lower temperatures than the temperatures at which n-butane oxidation would occur. At low temperatures
(<300°C) with low and moderate oxygen/butadiene ratios (0.7 and 3.0), furan can be the major product of butadiene oxidation. Otherwise maleic anhydride was still the predominant product. Crotonaldehyde was the by-product in this reaction. Different from butane oxidation, it was shown that higher phosphorus content in the catalyst was detrimental for the selectivity in MA and furan formation.

2,5-Dihydrofuran can react at even lower temperatures. The major products of its reaction were furan, maleic anhydride, and carbon oxides. Furan oxidation had higher selectivity to maleic anhydride than that of butadiene oxidation. Crotonaldehyde was not observed in furan oxidation.

Based on these observations, it was suggested that the electrophilic oxygen insertion on the 1,4 position of butadiene forms furan-like ring species similar to what Schiøtt et al. have suggested in their model (18). It was also reported that 1,3-butadiene causes the deactivation of the catalyst (29), presumably due to blocking of active sites by the surface carbon residue.

These differences between alkane and alkene oxidation can apparently be attributed to differences in their interactions with the VPO catalyst. 1,3-Butadiene strongly adsorbs on the catalyst surface due to the formation of π-orbitals with surface metal cations. The high surface concentration of olefinic species induces: a) the adsorption of hydrocarbon on non-active sites, b) the inhibition of oxygen chemisorption which may lead to catalyst deactivation, and c) the desorption of intermediate products (e.g. furan).
References


CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

n-Butane selective oxidation over VPO catalysts to form maleic anhydride is a complicated catalytic process. The mechanism of this reaction is still not exactly known after more than twenty years of intensive study and commercial practice. My current work using *in situ* spectroscopic characterization techniques, FTIR and laser Raman spectroscopy, made important contribution toward a deeper understanding in the reaction mechanism.

*In situ* FTIR investigation of the reaction intermediates significantly changed the view about the reaction pathway from n-butane to maleic anhydride. It revealed that open chain carbonyl species such as ketones and aldehydes are the precursors to maleic anhydride, instead of cyclic compounds furan and 2,5(6)-furanone as previously suggested. The result of this study also suggested that the strong bonding between carbonyl oxygen and the surface metal cation (C=O···M$^{n+}$) may hinder product desorption and lead to the overoxidation of the products or intermediates.

*In situ* LRS studies on the VPO catalyst transformations also made significant discoveries. It identified that in reduction-reoxidation step change reaction, α$_{II}$- and δ-VOPO$_4$ were the phases first formed in oxidation step which can be converted to β-VOPO$_4$. It also showed that these othophosphate phases can be reduced to (VO)$_2$P$_2$O$_7$ in the reduction step. All these phase transformations occurred in relatively shorts time scales (e.g. <30 min). More important is the discovery that (VO)$_2$P$_2$O$_7$ and all the othophosphate phases ($\alpha_I$- $\alpha_{II}$- $\beta$-, δ- and γ-VOPO$_4$) can be converted to V$_2$O$_5$ at around 400-600°C in presence of water vapor. This observation combined with the information available in the literature (1,
enables us to propose a three-stage solid state transformation: 1) the preferential loss of oxygen atoms in V–O–P linkage and consequently the separation of vanadium oxide and phosphorus oxide species; 2) the vanadium oxides form more close-packed structures to reduce the lattice misfit and are eventually transformed to \(\text{V}_2\text{O}_5\); and 3) the migration of phosphorus species to the surface and ultimately into the environment, possibly in the form of acid phosphates. It may further imply that the V–O–P oxygen is the most reactive lattice oxygen in VPO catalysts and may be the site responsible for the oxidation of the reactants, as has been suggested by Lashier and Schrader (3).

The information obtained in my studies is also valuable for process development and optimization. For instance, the efforts to produce furan from n-butane oxidation on VPO catalysts may not be fruitful in light of our in situ FTIR investigation which suggested that furan is not an intermediate in the main pathway. The results of our in situ LRS studies demonstrated that to obtain an optimum catalyst activity and long catalyst lifetime, it is important to maintain an optimum mixture of reducing and oxidative reactants. Excessive oxidation can cause the VPO catalyst to lose desired catalytic activity by forming orthophosphate phases (VOPO\(_4\) phases), while continuous reduction or exposure to moisture leads to depletion in active lattice oxygen and phosphorus compounds.

As the progress is being made, more questions emerge. For example, cyclic species such as furan have been detected in n-butane oxidation. Why is open chain carbonyl species oxygen-addition and cyclization a preferential path over furan oxygen-insertion to form maleic anhydride? In addition, what is the driving force for phosphorus migration to the catalyst surface? Is this related to the reported surface phosphorus enrichment? Such questions can very well be the topics for further research projects.
The current work demonstrates that \textit{in situ} characterization is extremely valuable to pinpoint the mechanism of n-butane oxidation and heterogeneous catalytic reactions in general. A catalytic reaction is often a dynamic process with changes occurring in the gas phase, gas-solid interface, and in the solid catalyst material. For instance, the VPO catalysts can be converted to V$_2$O$_5$ at high temperatures but this process can be reversed at lower temperature. Only \textit{in situ} monitoring of the reaction can catch this type of dynamics.

It is also self-evident that to obtain accurate mechanistic information, the coupling of various investigation tools is necessary. \textit{In situ} HREM provides the microscopic level identification of the change at catalyst surface while \textit{in situ} LRS pinpoints this process on a larger scale, yet FTIR can provide information complementary to what LRS observes.

As more and more being unraveled for the n-butane--VPO reaction system, alkane selective oxidation in general is becoming a mature and controllable practice, clearing the way for more efficient chemical syntheses. The state-of-the-art research techniques used in this investigation and the strategy developed in the mean time will have significant impact on future research in heterogeneous catalysis.

Reference:


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