SOLID ELECTROLYTE POTENTIOMETRY STUDY OF BUTENE OXIDATION OVER VANADIUM PHOSPHATE CATALYSTS

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ABSTRACT
The technique of solid electrolyte potentiometry (SEP) has been used to follow the oxygen activity in vanadium phosphate (VPO) catalysts during the catalytic oxidation of butene. Reaction products and oxygen activity were monitored concurrently in an effort to correlate selectivity for partial oxidation of butene to maleic anhydride, furan and crotonaldehyde with oxygen activity in the catalyst. It was found that partial oxidation selectivity increased with decreased oxygen activity in the catalyst. Additionally, the activity for total oxidation and oxygen activity were found to be dependent on the past history of the catalyst for a catalyst with a P/V ratio of 1.07. A high temperature reduction of the catalyst was able to freeze the catalyst into a form that was selective for partial oxidation. Models to account for the rate and oxygen activity data from this study suggest that subsurface oxygen is involved in the oxidation of butene over VPO catalysts and causes the non-selective total oxidation reaction.

INTRODUCTION
Vanadium oxide catalysts are widely used to carry out partial oxidation reactions. It is commonly accepted that oxygen incorporated into the metal oxide lattice participates in the reaction [1-3]. Oxygen is exchanged between the surface and the bulk by lattice diffusion. Changes in the surface layer with gas phase composition and temperature are then mirrored in corresponding changes in the bulk of the vanadium oxide. Variations in catalyst activity and selectivity may then be expected to be correlated with the structure of the metal oxide. Several studies of vanadium phosphates (VPO) have attempted to establish correlations between activity and selectivity characteristics and various solid state properties of the catalyst, such as the crystalline phases present, the average oxidation number of the vanadium cation, and the degree of aggregation of the vanadium cations. Bordes and Courtine [4] employed a variety of techniques including X-ray and electron diffraction, infrared and uv-vis spectroscopies, and thermal gravimetric analysis to investigate a series of VPO catalysts used for butene oxidation to maleic anhydride. They found that significant selectivity for partial oxidation was observed only when VOPO₄ and (VO)₂P₂O₇ were present. Nakamura and co-workers [5] suggested that a high degree of aggregation of vanadium ions with an average oxidation number of +4 gave a high selectivity to maleic anhydride. Ai and others
have extensively studied the effect of addition of $P_2O_5$ to vanadium oxide catalysts [6,7]. They noted that acid strength and oxidation activity both decrease while selectivity to maleic anhydride increases as the phosphorus to vanadium ratio (P/V ratio) increases.

Several other studies have found a poor correlation between the bulk properties of the VPO and the catalytic performance. Buchanan et al. [8] studied the effects of pretreatments on a vanadium phosphate catalyst, and found no consistent relationship between reactivity in butane oxidation and the bulk catalyst properties. Similar results were found by Pepera et al. [9]; there was essentially no difference in the redox state of vanadium as monitored by electron spin resonance between catalysts reduced under pulses of butane and those oxidized under pulses of oxygen. Moser and Schrader found that the Raman spectrum of a $(VO)_2P_2O_7$ catalyst showed little change over a 5-8 hour activation period, even though selectivity to maleic anhydride doubled over this period [10].

Other studies have suggested that the state of an oxide catalyst, particularly the degree of reduction, is affected by the gas phase composition at the temperatures typical of reaction. Simard and co-workers [11] studied o-xylene oxidation over $V_2O_5$ in a packed bed reactor and observed that the degree of reduction of the catalyst was a function of position in the bed, and hence of the o-xylene concentration. Similarly, Wainwright and Hoffman [3] found that the activity of a reduced $V_2O_5$ catalyst could be restored by reoxidation in an oxygen atmosphere.

Trifiro and co-workers [12,13] have suggested that the gas phase composition affects the competitive adsorption of butene and butadienes on VPO catalysts which in turn influences the product selectivity. They indicated that the gas phase did not cause major changes in the makeup of the catalyst and ascribed changes in reactions to the shifts in adsorption equilibrium.

Hodnett has reviewed the parameters affecting VPO catalysts [14]. He concluded that the preparation technique, P/V ratio and activation procedure all influence the catalyst properties. Particularly noteworthy among his conclusions is that phosphorus stabilizes vanadium in a lower oxidation state, enhancing the selectivity for partial oxidation. Hodnett and Delmon [15,16] also found that phosphorus reduces oxygen mobility in VPO catalysts, suggesting that oxidation and reduction of the VPO is limited to a near surface region of the catalyst. Similar conclusions were reached by Buchanan and Sundaresan for butane oxidation over VPO catalysts [17].

It is important to understand the interactions among gas phase composition, catalyst state and activity/selectivity behavior to improve both catalyst and reactor design procedures. Given the dynamic nature of these interactions it is desirable to use an in situ probe of the catalyst so that ambiguities due to changes resulting from quenching or sample preparation may be avoided. It is also preferable to find a probe that is sensitive to changes in both the surface and bulk properties of the catalyst. To this end we have employed solid electrolyte
potentiometry (SEP) to follow the activity of oxygen in a VPO catalyst used for butene oxidation. As the bulk of the catalytic solid exchanges oxygen with the surface layer where the catalytic oxidation reactions occur, changes in the state of the surface layer resulting from changes in the gas phase composition and temperature are reflected in changes in the chemical potential in the bulk. Solid electrolyte potentiometry measures the chemical potential of oxygen in the bulk of the solid and therefore provides an in situ method of following the chemical activity of one of the reactant species in the catalyst. In this paper we describe the experimental technique of SEP applied to metal oxide catalysts. It is shown for a particular VPO catalyst with a P/V ratio of 1.2 that the oxidation activity decreases with catalyst reduction, while the selectivity for partial oxidation increases with the degree of reduction. A catalyst with a P/V ratio of 1.07 showed similar but more complex behavior. The P/V 1.07 catalyst could exist in two different forms displaying different catalytic activity and selectivity with the same reaction mixture.

SOLID ELECTROLYTE POTENTIOMETRY

The activity of oxygen at a catalyst surface can be monitored electrochemically with a solid electrolyte electrochemical cell. Zirconia, doped with 8% yttria, acts as an oxygen ion conductor at temperatures above 700 K; and below 1100 K oxygen ions are the only mobile charge carrier in the solid. A cell consisting of the solid electrolyte coated on each side with a metal electrode can be used to measure the difference in the chemical potential of oxygen on the two sides [18]. The charge transfer at the three-phase interface between the electrode, the electrolyte and the gas phase in such oxygen sensors is believed to proceed according to the reaction

$$A^0 + V_{O}^{n} + 2e^{-} \rightarrow A + O_{O}$$

(R1)

where $A$ and $A^0$ denote reduced and oxidized sites on the electrode respectively, and $O_{O}$ and $V_{O}^{n}$ are the oxygen and oxygen-ion vacancy in the electrolyte lattice respectively. It follows that the cell potential is related to the oxygen activities on the two electrodes by

$$E = \frac{RT}{2F} \log \left( \frac{a_{O}^{11}/a_{O}^{0}}{a_{O}^{1}/a_{O}^{0}} \right)$$

(1)

where $R$ is the gas constant, $T$ is the absolute temperature, $F$ is the Faraday constant and $a_{O}$ is the activity of oxygen on the electrode at the three-phase interface between the electrode, the electrolyte and the gas phase. In our measurements, side 11 refers to the reference side of the cell. If the gas phase on each side consists of oxygen and an inert gas, then the gas-solid equilibrium may be written as
2A + O₂(g) → 2AO  \hspace{1cm} (R2)

and the ratio of the oxygen activity at the two electrodes is simply given by the ratio of oxygen pressures in the gas phase to the 1/2 power, resulting in the familiar Nernst equation

\[
E = \frac{RT}{4F} \log \left( \frac{P_{O_2}^{11}}{P_{O_2}^{1}} \right)
\]

The electrochemical cells, obtained from Bendix-Autolite, were zirconia thimbles with Pt electrodes coated on the inner and outer surfaces. A gold lead wire was wrapped around the outer electrode resulting in a mechanical connection. The lead wire for the inner (reference) electrode was held in place with a cup and weight arrangement. An alumina disk was cemented to the thimble to provide a sealing surface. The seal was provided through compression of a 1.6 mm graphite gasket against the alumina disk and the flat top of the reactor. The electrochemical cell configuration is shown in Figure 1.

In order to obtain meaningful measurements of the oxygen activity it is necessary that the mobility of oxygen in the zirconia be sufficient to allow a steady state to be established in a reasonable length of time. Table 1 summarizes the response time to achieve 90% of the change in steady state voltage and the offset from the voltage predicted by the Nernst equation at a series of temperatures. These results indicate that steady state voltages are achieved in a time frame of minutes only at temperatures above 675 K. These results are consistent with previous measurements of the diffusion of oxygen in zirconia [18,19]. The results also indicate that the steady-state voltage shows an offset from the value predicted by the Nernst equation. This voltage offset appears to result from a potential difference developed between the Pt electrodes and gold lead wires used to make the external circuit connections. The magnitude of this voltage offset was an indication of how well the cell was constructed; good cells had offset voltages of 10 mV or less. The offset was found to be nearly independent of temperature when the electrodes on both sides of the cell were Pt.

A cell arrangement in which both sides of the electrolyte are coated with the same metal can be used for kinetic studies of oxidation reactions on metal catalysts when the catalyst is the same as the electrode metal. One side is left exposed to an atmosphere with a known concentration of oxygen, e.g., air, while the other side is exposed to a reactive gas mixture. Since the electrode on the reaction side serves as the catalyst for the reaction, the voltage becomes a measure of the activity of oxygen adsorbed on the catalyst surface. This technique has been used by several investigators to study a variety of oxidation reactions on Pt, Ag and Au catalysts [20-28]. The interpretation can become somewhat more complex if other species, in addition to oxygen, interact with the solid electrolyte at the three phase interface. Such a situation arises in the context of CO oxidation over platinum [24-28].
FIGURE 1 Electrochemical cell and reactor configuration.
The electrode on the reaction side may also be coated with an oxide catalyst such as VPO. The potential in the cell is then a measure of the activity of oxygen in the oxide catalyst at the interface of the electrolyte and the catalyst. This is no longer a direct measure of the oxygen activity at the catalyst surface as the oxygen must diffuse through the metal oxide to the three-phase interface between the zirconia electrolyte, Pt electrode and VPO coating. Hence, for meaningful electrochemical measurements in such cells, there is a further requirement that the temperature be high enough to assure sufficiently rapid mobility of oxygen in the metal oxide. The transient response of an electrochemical cell containing two Pt electrodes is compared to that obtained when one of the Pt electrodes was coated with the VPO catalyst in Table 1. These results indicate that a minimum temperature of 700 K is necessary to obtain reliable results. Furthermore, the results with the VPO coatings show a larger steady state offset voltage than observed with just the Pt electrodes, and this offset decreases with increasing temperature. This offset is probably related to the diffusion of oxygen through the VPO. At lower temperatures a larger electrochemical potential is required to cause diffusion of oxygen through the VPO. This complication precludes at this time making true quantitative determinations of the oxygen activity in the VPO catalyst at temperatures below 725 K. However, changes in the cell voltage will still reflect changes in the oxygen activity in the catalyst.

A problem with the study of the vanadium phosphorus oxide catalysts with SEP involved the preparation of the metal oxide coating. Several different preparation procedures were tried before a suitable method for preparing reproducible films with good adhesion characteristics was found. The catalyst preparation adopted is based on a Monsanto patent [29]. Vanadium pentoxide and phosphorous acid were combined in water with phosphoric acid added in the proper amount to give the desired P/V ratio. Boiling under reflux for 12 hours reduces the vanadium to +4

### TABLE 1

Cell voltage responses.

<table>
<thead>
<tr>
<th>Temp./K</th>
<th>t/min(^a)</th>
<th>(\Delta E_{low}) (^b)</th>
<th>(\Delta E_{high}) (^c)</th>
<th>t/min(^a)</th>
<th>(\Delta E_{low}) (^b)</th>
<th>(\Delta E_{high}) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>9.2</td>
<td>-11.0</td>
<td>-6.3</td>
<td>15.0</td>
<td>108.4</td>
<td>50.8</td>
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<tr>
<td>698</td>
<td>7.0</td>
<td>-10.0</td>
<td>-6.8</td>
<td>12.0</td>
<td>59.2</td>
<td>23.6</td>
</tr>
<tr>
<td>723</td>
<td>4.8</td>
<td>-9.7</td>
<td>-6.9</td>
<td>8.1</td>
<td>30.7</td>
<td>10.7</td>
</tr>
<tr>
<td>748</td>
<td>3.5</td>
<td>-9.9</td>
<td>-7.0</td>
<td>4.2</td>
<td>7.7</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\(^a\)Time to achieve 90% of final voltage after a change from 5% oxygen to 15% oxygen.

\(^b\)Experimental - \(E_{Nernst}\) at 5% oxygen.

\(^c\)Experimental - \(E_{Nernst}\) at 15% oxygen.
and a vanadium phosphate complex is formed. The resulting deep blue solution is boiled further until it has reached a syrupy consistency. At this time the cell with lead wire attached is dipped, resulting in a uniform coating of catalyst. The catalyst was dried in air at 390 K for 6 hours, after which the temperature was ramped at 2 K min⁻¹ to 670 K and the catalyst was calcined at 670 K for 2 hours. The VPO layer is approximately 0.1 mm thick. No exposed Pt could be detected from visual inspection with a magnifying glass. The cells were stored under nitrogen in a dessicator until used, because the catalyst irreversibly absorbs moisture from the atmosphere.

EXPERIMENTAL

The reactor was designed to minimize both homogeneous gas phase reactions and reactions catalyzed by the tubing and reactor walls. It is constructed entirely of glass and has a volume of 6 cm³ when the electrochemical cell is in place. The reactor with the electrochemical cell in place is detailed in Figure 1. It was placed in an electric furnace with temperature control to maintain a constant temperature. The feed lines to the reactor and the exhaust lines from the reactor inside the furnace were all glass, and with the reactor formed a single unit. The use of an inert material for the reactor and the heated gas flow lines, and a small reactor volume were very important to the success of these experiments. The total catalyst surface area is less than 100 cm² and homogeneous and wall-catalyzed reactions can be quite important. We found that both aluminum and stainless steel reactors were unacceptable due to large amounts of wall-catalyzed reactions.

A schematic of the flow and product analysis systems is shown in Figure 2. The experimental flow system allowed independent variation of both butene and oxygen concentrations in a helium carrier stream. The reactor effluent was analyzed using two parallel gas chromatography trains. The first separated partial oxidation products on a Porapak QS column and monitored these with a flame ionization detector. The second train consisted of an ester column which separated the hydrocarbons and CO₂, followed by a molecular sieve column which separated oxygen, nitrogen and CO. Both columns in this train employed thermal conductivity detectors.

The oxidation reaction was studied in two types of experiments. To obtain potential differences under well-defined conditions the reactor was run in a differential mode with the hydrocarbon conversion kept as low as possible, typically below 3%. The condition of near-zero conversion was accomplished by introducing the feed mixture at the maximum flow rate possible (approximately 20 cm³ s⁻¹, corresponding to a residence time of 0.3 s). Under these conditions it may be assumed that the cell voltage is a function only of the feed gas composition. In order to measure product selectivities and kinetics along different reaction pathways experiments were also done where the conversion was generally between 3 and 20% of the hydrocarbon feed. This resulted in product yields sufficient to be accurately measured with gas chromatography.
FIGURE 2 Schematic of flow and product analyses systems.
FIGURE 3 Experimental data obtained for catalyst with P/V = 1.2; T = 748 K, oxygen concentrations shown on figure. a) cell voltage (dimensionless voltage = ZFE/RT), b) rate of butene consumption, c) rate of butadiene production, d) rate of partial oxidation.
FIGURE 4 Dimensionless cell voltage as a function of oxygen partial pressure; P/V = 1.2; T = 748 K; 1.7% butene.

RESULTS

The differential reactor experiments measure an oxygen activity in the metal oxide under a gas phase with a defined composition of hydrocarbon, oxygen and helium. The oxygen activity is a steady state value, and is not an equilibrium value. More will be said about this below. Figure 3a shows the dimensionless cell voltage (defined as 2FE/RT) for a P/V = 1.2 catalyst, with reference to a Pt/air electrode, as a function of butene concentration for two different oxygen concentrations. Based on the Nernst equation, a more positive cell voltage indicates a lower oxygen activity in the catalyst. These results show that as the butene concentration is increased at a constant oxygen concentration the oxygen activity shows a rather dramatic decrease. The slope of the voltage versus hydrocarbon pressure indicates that the activity of oxygen varies as the hydrocarbon pressure to the -2.5 power. Figure 4 shows the results for varying oxygen concentration with a fixed butene concentration for the same catalyst. Here it is seen that the oxygen activity increases with oxygen concentration; the functional dependence is $a_0 \sim P_{O2}^{1/2}$.

Similar experiments were conducted with 1,3-butadiene as the hydrocarbon. These data are also presented in Figure 3a. For the same partial pressures of oxygen and hydrocarbon in the gas phase the butadiene gives almost the same voltage as butene.

The rate of butene consumption at 748 K was also measured for the P/V = 1.2 catalyst as a function of both butene and oxygen partial pressures to see if the oxygen activity could be correlated with the reaction rate. The reaction rate as a function of butene pressure at different fixed oxygen pressures is shown in Figure 3b. The butene consumption rate was first order in the hydrocarbon pressure up to a concentration of 0.6% butene, with the reaction being zero order.
at higher concentrations. This behavior is typical of that predicted from a simple redox mechanism; however the oxygen activity data are not consistent with such a simple model. The butene consumption rate as a function of oxygen pressure at various fixed hydrocarbon pressures shows a great deal of scatter, but the general trend indicates a reaction order of zero for oxygen. It was not possible to obtain reliable rate data for butene consumption at oxygen concentrations less than the stoichiometric point, as the catalyst performance and oxygen activity did not achieve steady state values except at very long times where the VPO was in a much reduced state.

The catalyst performance for partial oxidation reactions was examined by measuring the conversion of butene to partial oxidation products, which included maleic anhydride, furan and crotonaldehyde. The rates of butadiene production and partial oxidation corresponding to the results in Figure 3b are shown in Figures 3c and 3d respectively. Selectivity is defined as the butene converted to partial oxidation products divided by the butene converted to both partial oxidation products and total oxidation products (acetic acid and carbon oxides). At low butene concentrations, where the reaction was first order in butene concentration, the selectivity towards partial oxidation was low. In the concentration range where the rate of butene consumption was independent of butene concentration the selectivity was constant at a value corresponding to a selectivity of 40-50%. Over the limited range of oxygen pressures studied, no clear effect of oxygen pressure on reaction selectivity was observed.

It is well known that the P/V ratio affects the performance characteristics of the catalyst. To examine this effect a catalyst was prepared with a P/V ratio of 1.07 to compare with the P/V = 1.2 catalyst. Our initial studies with the P/V = 1.07 catalyst were perplexing; cell voltages, total reaction rate and partial oxidation selectivity were all found to show widely disparate values for the same reaction conditions. In the case of the P/V = 1.2 catalyst the catalyst history did not seem to have much effect on the experimental results. The cell voltage and catalyst activity and selectivity all lined out to constant values determined only by the feed gas composition and temperature within a couple of hours. With the P/V = 1.07 catalyst it was found that cell voltages could vary by 100 mV, and reaction rates could vary by a factor of 2 depending on the catalyst history. These findings caused us to be very systematic in examining the performance of the catalyst.

The rate of butene consumption as a function of butene concentration for a P/V = 1.07 catalyst at a fixed oxygen pressure of 15%, and a temperature of 748 K is shown in Figure 5b. The data were taken by allowing the catalyst to sit in flowing oxygen at 748 K, then incrementally increasing the butene concentration up to 2.5%. After each incremental increase in the butene concentration the system was allowed to stabilize for a period of 30 min, and then the cell voltage was recorded and the products were analyzed by gas chromatography. The procedure
FIGURE 5 Experimental data obtained for catalyst with P/V = 1.07; T = 748 K, 15.5% oxygen. Lines indicate the direction of change in the butene concentration and are not derived from the model described in the text. a) Cell voltage (dimensionless voltage = 2FE/RT), b) rate of butene consumption, c) rate of butadiene production, d) rate of partial oxidation.
FIGURE 6 Experimental data obtained for catalyst with P/V = 1.07 after three weeks of experimentation; T = 748 K, 15.5% oxygen. a) Cell voltage (dimensionless voltage =2FE/RT), b) rate of butene consumption, c) rate of butadiene production, d) rate of partial oxidation.
was then repeated, decreasing the butene concentration incrementally. The rate data shown in Figure 5b show a hysteresis in the catalytic activity with the rate of butene consumption being larger for increasing butene concentration than for decreasing butene concentration. The cell could be cycled up and down and the loop reproduced. Another interesting feature of the data is that the rate goes through a maximum as a function of the butene concentration. The rate increases to approximately the same value as observed for the P/V = 1.2 catalyst, but then at butene concentrations above 0.5% the rate drops off precipitously, in contrast to the P/V = 1.2 catalyst where it levelled off at the higher value.

The cell voltage also displayed a hysteresis between increasing and decreasing butene concentration. The cell voltage as a function of butene concentration shown in Figure 5a indicates that the oxygen activity is higher when the butene concentration is being increased. When the butene concentration is being decreased and the reaction rate is lower the cell voltage is more positive, indicating a lower oxygen activity. From a plot of cell voltage versus log(P_{butene}) during the increasing butene concentration experiments it was found that

\[ a_0 \sim P_{C_4}^{-2.5} \]

identical to the result found on the P/V = 1.2 catalyst.

Unlike the total reaction rate and the oxygen activity, the reaction rates of butadiene production (Figure 5c) and partial oxidation (Figure 5d) did not show a hysteresis. The rates of butadiene production and partial oxidation go from low values at low butene concentrations, where the rate of butene consumption is high, to nearly constant values at higher butene concentrations.

It was pointed out that the hysteresis loops in the cell voltage and catalytic activity for oxidation were reproducible. However, over longer periods of time, i.e., weeks, the behavior of the catalyst was found to change. Figures 6a and 6d show the cell voltage, rate of butene consumption, rate of butadiene production and the rate of partial oxidation as functions of increasing and decreasing butene concentration after the P/V = 1.07 catalysts has been on stream for three weeks. When compared to the same quantities for the fresh catalyst, shown in Figure 5, it is seen that activity towards butene oxidation decreased, while the partial oxidation activity increased, indicative of improved reaction selectivity. In addition, the hysteresis loop for cell voltage has also been partially closed.

The results on the P/V = 1.07 catalyst suggest that metastable phases may exist in the vanadium phosphate that display much different catalytic properties. To test this, some experiments were performed at lower temperatures where metastable phases could be stabilized for longer periods of time. From the results at 748 K it appeared that VPO catalysts treated under conditions of higher butene concentrations showed the best selectivity for partial oxidation. A P/V = 1.07 catalyst was pretreated by reacting 1.9% butene, 15% oxygen over it at 748 K. The
reactor was cooled to 673 K while maintaining the reaction gas flow. At 673 K the butene concentration was then incrementally decreased. As shown in Figure 7, the reaction selectivity started high and then decreased with decreasing butene concentration. After decreasing the butene concentration to zero the butene concentration was increased incrementally. The selectivity for partial oxidation products was observed to increase, but was distinctly lower than it had been initially. The butene was turned off and the catalyst was permitted to sit in 15% oxygen for 24 hours, and then the partial oxidation selectivity was measured again. These data, also shown in Figure 7, indicate that the catalyst characteristics were unchanged by this treatment at 673 K. This contrasts with the behavior of the catalyst at 748 K, where a similar treatment (10 hours under 16% O₂) always resulted in lower selectivity. A second pretreatment of the catalyst was to allow it to cool from 748 to 673 K in a 15% oxygen, 0.03% butene mixture. This resulted in freezing in a low selectivity state of the VPO catalyst. It was found that after this treatment the catalyst showed zero selectivity for partial oxidation, regardless of the butene concentration. The rate of butene consumption was found to be comparable for both the cases of zero selectivity and high selectivity, though generally the rate of butene consumption was greater for the catalyst with zero selectivity. Lastly the catalyst showing zero selectivity was re-exposed to 1.9% butene, 15% oxygen at 748 K for one hour and allowed to cool to 673 in this reaction mixture. This restored the catalyst to the high selectivity state, indicating these are reversible changes in the catalyst performance. It should also be noted that this quenching data for the P/V = 1.07 catalyst indicates that the hysteresis observed for reaction rate and cell voltage result from changes in the catalyst and do not arise from transport and reaction processes that are so familiar in catalytic oxidation reactions.

FIGURE 7 Selectivity of catalyst with P/V = 1.07 at 673 K following different treatments at 748 K; 15.5% oxygen.
DISCUSSION

To illustrate that the measured cell voltages are indicative of the oxygen activity in the metal oxide catalyst, the cell voltage for a Pt electrode is compared with that for a VPO covered electrode in Figure 3a. The cell voltages are substantially different both qualitatively and quantitatively. This difference assures us that the oxygen activity measurements reported in our experiments are not influenced by the Pt beneath the vanadium phosphate.

The data from the experiments reported here are more detailed than previous studies in that both reaction rates and oxygen activity of the catalyst are monitored simultaneously. These pieces of information can be used to test various models for the mechanism of butene oxidation over VPO catalysts. The most important features of the data that a viable model must reproduce are: i) the pronounced maximum in the total rate of oxidation as was observed for the P/V = 1.07 catalyst, ii) the difference in functional dependence on butene pressure of the reaction rate and oxygen activity, and iii) the greater selectivity for partial oxidation over more reduced catalysts.

The data presented here provide new information about VPO catalysts by monitoring the electrochemical potential of the VPO under reaction conditions. To show the utility of this measurement we formulate the relationship between the cell voltage and the oxygen activity in the vanadium phosphate. In the absence of any hydrocarbon in the feed gases, the dimensionless cell voltage is described by the Nernst equation

\[
\frac{2FE}{RT} \log \left\{ \frac{P_{O_2,\text{ref}}^{1/2}}{P_{O_2}^{1/2}} \right\} = \log \left\{ \frac{P_{O_2,\text{ref}}^{1/2}}{P_{O_2}^{1/2}} \right\}
\]

where \( P_{O_2,\text{ref}} \) and \( P_{O_2} \) denote the oxygen partial pressures on the reference side and the reaction side (i.e., the VPO coated electrode) respectively. Oxygen in the gas phase interacts with the surface layer of the VPO catalyst by

\[
2S + O_2(g) \xrightarrow{k_3} \frac{k_3}{k_{-3}} \rightarrow SO
\]

where \( S \) and \( SO \) denote reduced and oxidized surface sites respectively (in the spirit of the redox model). In the electrochemical cell configuration, in order that any changes in the gas phase oxygen concentration (and consequently the surface layer of the VPO) lead to changes in the cell voltage, oxygen must diffuse through the catalyst bulk. Further, an exchange of oxygen must take place between the sub-surface region (i.e., the catalyst bulk) and the surface layer exposed to the gas phase, which may be represented by the reaction,
where MO and M denote an oxygen in the catalyst (bulk) lattice and an oxygen vacancy in the catalyst bulk. The catalyst bulk exchanges oxygen with the buried platinum electrode according to the reaction

\[ \text{MO} + \text{A} \rightleftharpoons \text{A}_0 + \text{M} \quad (\text{R5}) \]

where A and A0 denote reduced and oxidized platinum sites. When the platinum on one side is covered by VPO the Nernst equation (3) obtained under non-reactive conditions is a composite outcome of reactions (R1), (R3)-(R5) at the working side and reactions (R1) and (R2) at the reference side. Assuming mass action kinetics for the above reactions, equation (3) becomes

\[ \frac{2\text{FE}}{\text{RT}} = \log \left( \frac{p_{02,\text{ref}}^{1/2} K_3^{1/2}[\text{M}]}{K_4 [\text{MO}]} \right) \]

where \( K_3 = \frac{k_3}{k_{-3}} \) and \( K_4 = \frac{k_4}{k_{-4}} \) are the equilibrium constants for the adsorption and exchange reactions. Here [M] and [MO] are the mole fractions of M and MO respectively. Equation (4) is the relationship between cell voltage and oxygen activity that should apply even under reaction conditions.

In our effort to rationalize the reaction rate, selectivity and cell voltage data, several different models for the reactions were tried, the details of which can be found elsewhere [30]. The model described below was found to be the best among those examined, the criterion for model discrimination being that the model must reproduce, at least qualitatively, the three important features of our data discussed in the beginning of this section. (See model on following page.)

Here SI and SJ denote two different adsorbed hydrocarbon intermediates. The rate of reaction 6 is dictated by the initial attack of bulk oxygen, MO, on the intermediate SI. Further reactions with surface oxygens to produce the final products are very rapid. The number of additional oxygen atoms which are required for conversion to the products is \( n_6 \). These oxygen atoms can presumably come from either the bulk or the surface. For simplicity, all are assumed to be surface oxygens. Allowing some of these to be oxygen atoms from the bulk affected only the numerical values of some of the rate constants and not the form taken by any of the quantities predicted. Similar statements can be made for reaction 8.

In reaction 9, the rate is dependent only on the concentration of SJ, and \( n_9 \) is the number of additional oxygen atoms required to produce the partial oxidation products. The loss of hydrogens from the hydrocarbon species is assumed to
MODEL

TABLE 2
Rate expressions for proposed mechanism

\[ R_3 = k_3 \text{[PO}_2\text{][S]]}^2 - k_3 \text{[SO]}^2 \]
\[ R_4 = k_4 [\text{[MO]} - k_4 \text{[SO][M]} \]
\[ R_5 = k_5 \text{[C}_4\text{H}_6\text{][SO]} \]
\[ R_6 = k_6 \text{[SI][MO]} \]
\[ R_7 = k_7 \text{[SI][SO]} \]
\[ R_8 = k_8 \text{[SJ][MO]} \]
\[ R_9 = k_9 \text{[SJ]} \]
\[ R_{10} = k_{10} \text{[SJ]} \]

Steady state balances:

\[ R_3 + R_4 - R_5 - n_6 R_6 - 1/2 R_7 - n_8 R_8 - n_9 R_9 + 1/2 R_{10} = 0 \]
\[ R_5 - R_6 - R_7 = 0 \]
\[ R_7 - R_8 - R_9 - R_{10} = 0 \]
\[ R_4 + R_6 + R_8 = 0 \]
\[ [\text{[S]} + [\text{[SO]} + [\text{[SI]} + [\text{[SJ]} = 1 \]
\[ [\text{[M]} + [\text{[MO}] = 1 \]
proceed through the formation of surface hydroxyl groups, which are in equilibrium with gas phase water vapor. The low conversions of butene result in low water concentrations so that this equilibrium lies far to the right.

The conservation equations corresponding to the above model, which must be solved to determine the rates of production of butadiene, selective oxidation products and unselective oxidation products are presented in Table 2. The cell voltage then follows from equation 4.

Several observations from our butene oxidation data were useful to note in developing the kinetic mechanism shown above. It was found that butadiene production and partial oxidation proceed by parallel reaction pathways. A plot of the rate of partial oxidation (Figure 5d) versus the rate of butadiene production (Figure 5c) for the P/V = 1.07 catalyst yields a straight line with slope 0.325. The same trend was observed for the P/V = 1.2 catalyst as well, but with a slightly different slope. It appears that the slope is dependent on catalyst age and composition. It is generally believed that there is a slow loss of phosphorus from VPO catalysts under typical reaction conditions. Thus the dependence on catalyst age is probably due to a gradual change in the P/V ratio. The fact that both butadiene production and partial oxidation show the same functional dependence on butene concentration but with different magnitudes indicates these two reactions proceed in parallel.

The products of butene oxidation were butadiene, furan, crotonaldehyde, maleic anhydride, acetic acid, carbon oxides and water vapor, while oxidation of butadiene led to the formation of furan, crotonaldehyde, maleic anhydride, carbon oxides and water vapor. The observation that acetic acid was produced only with a butene feed and not a butadiene feed suggests that there must be at least two different reaction paths through which the unselective products can be formed, with acetic acid being formed from one of these paths and carbon oxides possibly arising from both paths. Over the entire composition range of our butene oxidation experiments the gas phase concentrations of butadiene and the partial oxidation products were at least two orders of magnitude less than that of butene. Therefore, secondary reactions of butadiene and partial oxidation products have been neglected in our efforts to model the observed results, although these reactions can become significant at higher concentration levels of these species.

The maximum in the oxidation rate as a function of butene pressure for the P/V = 1.07 catalyst suggests that the rate limiting step is the reaction between adsorbed hydrocarbon intermediates and an adsorbed oxygen complex. The P/V = 1.2 catalyst differed in its behavior from the P/V = 1.07 catalyst and did not show a maximum in the butene consumption rate. It appears unlikely that a slight excess of phosphorus will change the reaction mechanism. What is more likely is that changing the P/V ratio alters the rates of the various steps involved in the mechanism to different degrees so that the rate-determining step may change with P/V ratio. Figure 3b suggests that the oxidation of butene over the P/V = 1.2 catalyst is limited by the rates of adsorption of butene and/or oxygen, and not the surface reactions.
A key feature which emerged from this study is that in order to reproduce the cell voltage data, the model must allow for a more active participation of the catalyst bulk (i.e., subsurface oxygen) in the reaction network than the simple oxygen exchange described by reaction R4. In the kinetic model the reaction of adsorbed hydrocarbon intermediates with subsurface oxygen ([MO]) as well as with surface oxygen ([SO]) was able to reproduce the high order functional dependence of oxygen activity on butene concentration. To the best of our knowledge such a participation of the subsurface oxygen in oxidation reactions over oxide catalysts has not been considered in any previous study, although it seems plausible from a mechanistic point of view.

We speculate that the interaction of adsorbed hydrocarbon intermediates with subsurface oxygen results in the scisson of C-C bonds leading to unselective oxidation products, and that the interaction of adsorbed hydrocarbons with surface oxygen results in C-H bond scission and selective oxidation products. Although these are only speculations one can cite several pieces of circumstantial evidence to support them.

(i) As the catalyst became more reduced (i.e., as [MO] decreases) we observed a shift from carbon oxides to acetic acid as the dominant total oxidation product, consistent with a decrease in C-C bond scission with reduction of the catalyst.

(ii) Although a pronounced hysteresis was observed in the cell voltage (and hence [MO]) as a function of butene concentration for the P/V = 1.07 catalyst (Figure 5a), no such hysteresis was detected in the rate of butadiene production (Figure 5c) or the rate of partial oxidation (Figure 5d), suggesting that the pathway leading to these products should not depend on [MO]. On the other hand, a pronounced hysteresis was evident in the rate of total oxidation, consistent with a decrease in the C-C bond scission with reduction of the catalyst.

(iii) Vanadium phosphate catalysts prepared in aqueous medium typically show significant increases in selectivity toward partial oxidation as the P/V ratio is increased above 1.0, for both butene oxidation [4,5] and butane oxidation [16]. Hodnett and Delmon found that catalysts prepared from an aqueous medium were quite prone to bulk oxidation and reduction [31], and that increasing the phosphorus content in the catalysts prepared from aqueous media restricted bulk oxidation and reduction [15]. They suggest that this restriction of oxygen mobility in the bulk catalyst was a means by which excess phosphorus increases selectivity [15], although the mechanism by which the oxygen mobility is related to selectivity was not discussed. We argue that the oxygen mobility in the bulk is a measure of the reactivity of bulk (subsurface) oxygen with adsorbed hydrocarbon intermediates. The excess phosphorus in catalysts prepared from aqueous media will therefore decrease the reactivity of bulk oxygen with adsorbed hydro-
carbon intermediates. Our postulate that the reaction of bulk oxygen with the adsorbed intermediates leads to unselective products then implies that the selectivity towards partial oxidation should increase with increasing phosphorus content, consistent with the experimental trends [4,5,16].

(iv) It appears from recent studies by Pepera et al. [9], Hodnett and Delmon [15] and Buchanan and Sundaresan [17] that vanadium phosphate catalysts prepared in organic media have a more limited participation of the subsurface oxygen in the reaction that those prepared in aqueous media, but have better selectivities toward partial oxidation than the latter. Our postulate that the interaction of subsurface (bulk) oxygen with adsorbed intermediates leads to unselective products is consistent with these experimental trends as well.

The results for the more reactive metastable state of the \(P/V = 1.07\) catalyst in Figures 5 a-d (i.e., the results obtained in the sequence of experiments where the butene concentration was monotonically increased) were used to estimate a set of parameter values for the model described in Table 2. The best-fit parameter values are presented in Table 3. The model predictions are compared with the experimental data in Figures 8 a-d. Considering the complexity of the reaction system, the agreement is excellent. The model does not predict the hysteresis displayed by the \(P/V = 1.07\) catalyst. This is not surprising, as the hysteresis, in our opinion, is associated with a phase transition in the vanadium phosphate catalyst and not a competition between the adsorption and reaction processes. The model does not include the possibility of such phase transitions.

**TABLE 3**

Parameter values for kinetic model.

\[
\begin{align*}
n_6 &= 10 & n_8 &= 9.5 & n_9 &= 0.8 \\
n_{3} &= 1.084 \times 10^{-2} \text{ moles min}^{-1} \text{ atm}^{-1} \\
n_{-3} &= 3.101 \times 10^{-9} \text{ moles min}^{-1} \\
n_{4} &= 6.084 \times 10^{-4} \text{ moles min}^{-1} \\
n_{-4} &= 6.084 \times 10^{-4} \text{ moles min}^{-1} \\
n_{5} &= 8.11 \times 10^{-2} \text{ moles min}^{-1} \text{ atm}^{-1} \\
n_{6} &= 6.5062 \text{ moles min}^{-1} \\
n_{7} &= 3.17335 \times 10^{-1} \text{ moles min}^{-1} \\
n_{8} &= 8.52 \times 10^{-5} \text{ moles min}^{-1} \\
n_{9} &= 9.594 \times 10^{-6} \text{ moles min}^{-1} \\
n_{10} &= 2.952 \times 10^{-5} \text{ moles min}^{-1}
\end{align*}
\]
FIGURE 8 Experimental data used to obtain parameter estimates and model predictions for \( P/V = 1.07 \) catalyst; \( T = 748 \) K, 15.5\% oxygen.
The results for the aged P/V = 1.07 catalyst are qualitatively similar to those modelled, and can be produced by the model presented with appropriate changes in the rate constants. The results for the P/V = 1.2 catalyst, while qualitatively different from those for the fresh P/V = 1.07 catalyst, can also be produced by changing the rate constants so that the adsorption step becomes rate-limiting. Therefore, by modelling the most complex of the three data sets, we have obtained a mechanism which qualitatively accounts for all three.

In addition to being sufficiently active and selective, vanadium phosphate catalysts used in industry to carry out maleic anhydride synthesis must also be robust. The role played by excess phosphorus in imparting robustness to the VPO catalysts has been considered by several investigators. For example, Nakamura and co-workers [5] and Trifiro et al. [32] have shown that when phosphorus is present at P/V ratios of one or greater the +4 oxidation state of the vanadium is stabilized. The present study demonstrates the beneficial role of excess phosphorus in a dramatic way. The P/V = 1.07 catalyst could be oxidized or reduced by a slow process, which led to slow variation in the activity and selectivity. This gave rise to the hysteresis in the catalyst behavior where the catalyst could exist in two different states with the same gas phase composition, as shown in Figures 5 and 6. Although by suitable (either oxidizing or reducing) pretreatment, the state of the catalyst could be changed reversibly, such was not possible at a lower temperature where the catalyst remained frozen into either a selective or unselective state. The P/V = 1.2 catalyst which contains more phosphorus than the P/V = 1.07 catalyst was apparently frozen into a single state and showed uniform behavior independent of its history. Industrial VPO catalysts typically contain P/V > 1.1 and generally are very robust and do not appear to undergo changes even under severe conditions [33,34]. The hysteresis characteristics of the P/V = 1.07 catalyst suggest that it may be possible to periodically treat VPO catalysts to altered feed conditions to improve overall process performance.

CONCLUSIONS

It has been shown that solid electrolyte potentiometry can be used as an in situ probe of oxygen activity in vanadium phosphate catalysts under reaction conditions. This is a very sensitive probe to the presence of hydrocarbons and shows that the adsorption of oxygen is far from equilibrium during reaction conditions. The SEP data about the oxygen activity could be coupled with reaction rate data to help elucidate the behavior of VPO catalysts. The findings of this study are:

1) The rate limiting step in the oxidation reaction over the P/V = 1.07 catalyst is the bimolecular surface reaction of adsorbed hydrocarbon intermediates with surface or subsurface oxygen. On the other hand, the oxidation of butene over the P/V = 1.2 catalyst is limited by the adsorption of butene and/or oxygen and not the surface reactions.
ii) The interaction of adsorbed hydrocarbon intermediates with subsurface oxygen results in unselective products.

iii) The selective oxidation step requires the reaction of adsorbed hydrocarbon intermediates with surface oxygen complexes exclusively.

iv) A more reduced catalyst is more selective for partial oxidation.

v) Oxidation and reduction of the bulk of VP0 catalysts is slow, and metastable states of the P/V = 1.07 catalyst could be prepared at higher temperatures and frozen into the catalyst to obtain good or bad selectivity.

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REFERENCES