JOURNAL OF CATALYSIS 5, 508–516 (1966)

# The Vanadium-Pentoxide-Catalyzed Oxidation of Pentenes

## III. The Role of the Catalyst

N. S. BUTT, A. FISH,* AND F. Z. SALEEB

*From the Department of Chemical Engineering and Chemical Technology, Imperial College, London*

Received June 16, 1965; revised October 25, 1965

Investigations of changes in the surface area and phase composition of vanadium pentoxide catalysts in contact with reacting mixtures of pent-2-ene with oxygen have been made. As a pumice-supported vanadium pentoxide catalyst is used, pentavalent vanadium is reduced gradually to tetravalent vanadium. When the latter attains a critical concentration a phase change occurs, reaction with the support giving sodium vanadyl vanadate. Simultaneously, sudden increases in the surface area and in the rate of oxidation of pentene occur but the selectivity of the oxidation falls, many new products being formed. Further use of the catalyst leads eventually to its deactivation.

Vanadium pentoxide in contact with mixtures of oxygen and unsaturated hydrocarbons contains, therefore, $V^{4+}$ ions as well as $V^{5+}$ ions. The pattern of product formation and the physicochemical properties of the catalyst support strongly the suggestion that the mechanism of oxidation involves reaction of the fuel with oxide ions, the catalyst being reduced. The function of gaseous molecular oxygen is to reoxidize the reduced catalyst and this step is rate-determining. It would appear that this mechanism is a general one for the oxidation of unsaturated hydrocarbons over vanadium pentoxide. On old catalysts containing sodium vanadyl vanadate, however, the mechanism differs considerably; free-radical chain reactions in which molecular oxygen is the active oxidant become important.

### INTRODUCTION

The pattern of formation of organic products during the oxidations over vanadium pentoxide of all five isomeric pentenes have been described in Parts I (*1*) and II (*2*) (preceding paper). The general mechanism of oxidation involves the isomerization on the catalyst surface of terminal pentenes to nonterminal pentenes followed by oxidation of the latter. On new catalysts, pentenes are converted to carbonyl and alkenic scission products together with epoxypentanes. The formation of oxygenated scission products even in the absence of gaseous oxygen suggests strongly that $O^{2-}$ is involved; an overall mechanism in which the catalyst itself is reduced by the adsorbed pentene and reoxidized by gaseous oxygen results. Use of the catalyst for about 5 hr causes, however, a marked and sudden change in the pattern of oxidation of straight-chain pentenes. The oxidation becomes more rapid but much less selective; it is likely that, under these conditions, gaseous molecular oxygen attacks the adsorbed pentene directly and that the oxidation acquires free-radical chain character.

The present paper describes attempts to correlate changes in the physicochemical properties of the catalyst as it is used with this change in the mechanism of oxidation.

### METHODS

The apparatus and procedure employed for catalytic studies and the methods of analysis of gaseous products have been described in Part I (*1*). The preparation and

---

* Present address: "Shell" Research Limited, Thornton Research Centre, P.O. Box No. 1, Chester, England.

purification of pent-2-ene has been described in Part II (*2*).

### (*1*) *Preparation of the Catalyst*

The pumice-supported vanadium pentoxide catalyst was prepared as described in Part I (*1*).

Alumina-supported catalysts were prepared by exactly similar methods, using pure $\gamma$ alumina (obtained from Peter Spence Ltd.) containing less than 1% of aluminum sulfate and only a few parts per million of other impurities.

### (*2*) *Determination of the Surface Areas of Catalysts*

The surface areas of catalyst samples were determined in a modified Brunauer-Emmett-Teller volumetric gas sorption apparatus (*3*, *4*). A sample bulb in which a known weight of catalyst was enclosed was attached to 2-mm capillary tubing leading directly to a 100-ml gas burette maintained at 25° ± 0.05°C and a wide-bore (25 mm) manometer which was used in conjunction with a cathetometer to measure equilibrium pressures lower than 80 mm Hg with an accuracy of ±0.02 mm Hg [compare ref. (*5*)]. For higher equilibrium pressures, a 10-mm bore manometer was used to measure the absolute pressure of air in a 5-liter globe which was connected to the sample bulb and gas burette through a capillary manometer which served as a null-point instrument. The dead volume of the apparatus (11.46 ml) is thus minimized but the capillary error in pressure estimation is greatly reduced.

Purified helium gas was used to determine the dead volume of the catalyst bulb at 0°C and the volumes of the other parts of the apparatus. *n*-Butane ($>99.5\%$, kindly provided by British Petroleum Ltd. and further purified by bulb-to-bulb distillation under vacuum) was used, at 0°C, as the adsorbate because of its resemblance to the hydrocarbons of interest in the catalytic oxidation studies.

Surface area determinations on new pumice-supported catalysts were carried out to determine the effects of the method of preparation of the catalyst and those of particle size and of the temperature at which the catalyst sample was degassed prior to adsorption. Suitable values for each of these parameters were then chosen and the method applied to the determination of the surface areas of used catalysts. The catalytic reactor was filled with a new activated 8–10 mesh (B.S.) pumice-supported catalyst of predetermined surface area. A mixture of pent-2-ene with oxygen and nitrogen in which the oxygen:pentene ratio was 1.25 was allowed to react at 300°C over the catalyst surface with a contact time of 33.6 sec. Samples of about 2 g of catalyst were withdrawn at intervals chosen on the basis of periodic analyses of the gaseous products of oxidation. Each sample was cooled to room temperature, weighed, and introduced into the gas-sorption apparatus. Its specific surface area was determined after degassing at 350°C and again after desorption of the butane and degassing at 500°C. This procedure was repeated for several oxidation runs under similar conditions, in each of which an identical "new" activated catalyst was employed.

The surface areas of new and used alumina-supported catalysts were determined, after degassing at 350°C, by similar methods.

### (*3*) *X-Ray Diffraction Examination of Catalysts*

Samples of pumice-supported catalyst were withdrawn from the reactor at suitable intervals during the reaction of pent-2-ene with oxygen under the conditions described in the preceding section. The vanadium pentoxide was removed from the surface of the pumice by scraping, giving a fine powder. An unused sample of pumice was also ground to a fine powder.

The X-ray diffraction pattern of each of these specimens was obtained by the Debye-Scherrer powder method, using a chromium anode X-ray tube and Philips-type camera. The pattern obtained for each sample was measured to determine the values of the spacing of the lattice planes to which each line was due. The set of values obtained for each sample was compared with sets of data obtained from known materials in order to identify the substances present.

## RESULTS

### (1) The Variation of the Course of Oxidation with Catalyst Age

The extent of consumption of fuel and of formation of major products of oxidation during the reaction of pent-2-ene with 1.25 times its own molar quantity of oxygen at a contact time of 33.6 sec and a temperature of 300°C are shown as a function of the "age" of the pumice-supported vanadium pentoxide catalyst in Fig. 1. In the first 60 min of use of a new catalyst the rate of consumption of pent-2-ene falls, then increases very slowly until about 300 min have elapsed. At this point there follows a sharp and sudden increase in the consumption of pentene, accompanied by the appearance of many new products (methanol, pentan-2-one, pentan-3-one, ethylene oxide, propylene oxide, 3-methylbutan-2-one, 2-methyl-1,2-epoxypropane, *trans*-2,3-epoxybutane, crotonaldehyde, butanone, ethanol, and butan-2-ol). (Many of these products are not shown, for reasons of clarity, in Fig. 1.) Simultaneously, ethylene and propylene disappear from the products, the amount of 2,3-epoxypentane formed is reduced and the amounts of acetaldehyde, propionaldehyde, and acetone increase slightly. Carbon dioxide is produced in much larger quantities after the change in activity.

In the life period 310–500 min, the consumption of pentene is high and substantially constant. After 500 min, however, the consumption of fuel falls quite sharply and the concentrations of all products decrease simultaneously.

### (2) The Relative Activities of Pumice-Supported and Alumina-Supported Catalysts

The relative activities in effecting the oxidation of pent-2-ene of vanadium pentoxide supported on pumice and on $\gamma$ alumina are shown in Table 1. Each of these catalysts had been used for 2 hr. Although the surface area of the alumina-supported catalyst is more than 250 times that of the pumice-supported catalyst, the activity of the former, as measured by the consumption of pent-2-ene, is only about 16% higher than that of the latter. The alumina-supported catalyst is less selective than a "new"

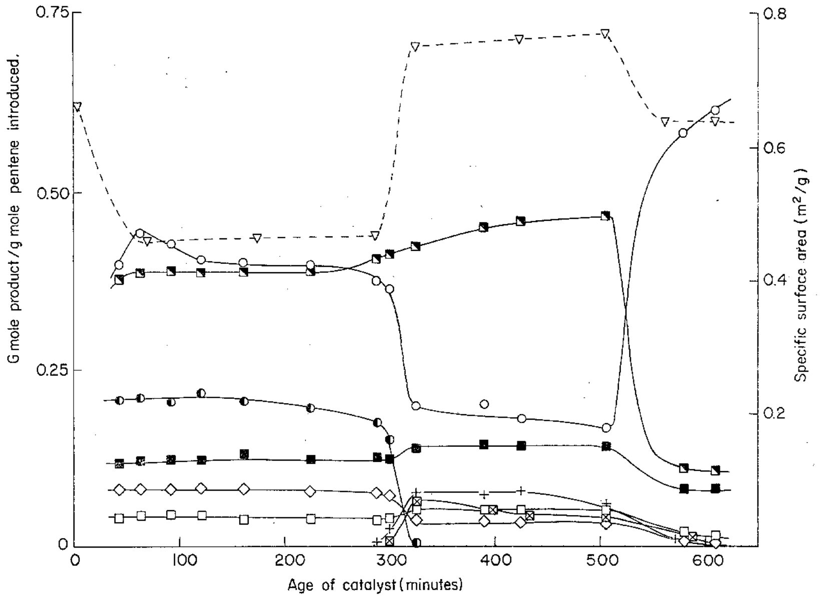

FIG. 1. The variations of product formation and of surface area with catalyst age (temperature, 300°C; pent-2-ene; oxygen: olefin = 1.25; contact time, 33.6 sec): ○, pent-2-ene; ◪ acetaldehyde; ■, propionaldehyde; □, acetone; ◇, *trans*-2,3-epoxypentane; ◐, ethylene; +, methanol; ⊠, pentanone-2 plus pentanone-3; ▽, specific surface area (after degassing at 350°C).

TABLE 1
THE OXIDATION OF PENT-2-ENE ON VANADIUM PENTOXIDE CATALYSTS SUPPORTED ON PUMICE AND ON $\gamma$ ALUMINA[a]

| | Support | |
|---|---|---|
| | 8–10 mesh pumice | 6–10 mesh alumina |
| Surface area ($m^2/g$): | 0.46 | 124.1 |
| *Products* | | |
| (g mole product/g mole pentene introduced) | | |
| Ethylene | 0.21 | 0.066 |
| Propylene | 0.03 | 0.012 |
| Pent-1-ene | 0.01 | 0.006 |
| Pent-2-ene (remaining) | 0.405 | 0.308 |
| $C_{10}$ hydrocarbons | — | 0.060 |
| Acetaldehyde | 0.39 | 0.021 |
| Propionaldehyde | 0.12 | Traces |
| Acetone | 0.04 | 0.045 |
| 2-Methyl-1,2-epoxypropane | — | Traces |
| 2,3-Epoxypentane | 0.08 | 0.003 |
| Methanol | — | 0.105 |
| Carbon dioxide | Traces | ~2.1 |

[a] Temperature, 300°C; oxygen: defin = 1.25; contact time, 33.6 sec; each catalyst had been used for 2 hr.

pumice-supported catalyst, producing large quantities of carbon dioxide but smaller quantities of individual oxygenated organic compounds. The number of products formed over the alumina-supported catalyst is smaller, however, than that over a pumice-supported catalyst more than 5 hr old, i.e., one which has suffered a decrease in selectivity.

### (*3*) *The Surface Areas of Catalysts*

#### (*a*) *The Adsorption Isotherm for n-Butane on Vanadium Pentoxide*

**(i) Supported on pumice.** The adsorption of $n$-butane on pumice-supported catalysts is reversible within the pressure range studied (0–500 mm Hg equilibrium pressure), hysteresis effects being absent. Each adsorption isotherm shows a step at a volume of adsorbed gas approximately twice the monolayer capacity, these steps being more pronounced for catalysts which have been heated to high temperatures (>400°C). No further steps were observed. Stepwise multilayer adsorption isotherms are often characteristic of adsorption on homogeneous surfaces (*6*). It is considered (*7*) that multilayer adsorption leads inevitably to stepwise isotherms and that the smoothness of the vast majority of multilayer isotherms is due to surface heterogeneity. In the present work, a change in the orientation of the adsorbed $n$-butane molecules as the adsorption progresses may also affect the shape of the isotherm but is energetically unlikely.

**(ii) Supported on $\gamma$ alumina.** The isotherm for $n$-butane on a vanadium pentoxide catalyst supported on $\gamma$ alumina, determined under experimental conditions similar to those used for the pumice-supported catalysts, shows no steps in the pressure range investigated. The amounts of $n$-butane adsorbed are far greater than those on pumice-supported catalysts, due no doubt to the porous nature of the alumina support.

#### (*b*) *The Determination of Specific Surface Area*

The adsorption of $n$-butane on pumice-supported catalysts exhibits linearity consistent with the Brunauer-Emmett-Teller multilayer adsorption isotherm (*8*) in the range of relative pressure 0.02 to 0.1 and that on alumina-supported catalysts does so in the range 0.09 to 0.36. Surface areas have been calculated, assuming that the adsorbed film of $n$-butane at 0°C is liquid-like in structure and that the molecules lie flat on the surface. The area which one molecule occupies in the completed monolayer is, therefore, 32.1 Å$^2$ (*9*). Although this value is not entirely acceptable (*10*, *11*), it suffices for the present calculations in which the aim is to determine the relative specific areas of catalysts of different histories rather than to obtain accurate absolute values.

#### (*c*) *The Effects of Degassing Temperature*

The temperature at which the catalyst was degassed prior to the adsorption of $n$-butane markedly affected the specific area. Unused samples (8–10 mesh from a given batch) each had areas of 0.66 $m^2/g$ when degassed at temperatures of 350°C or less but after degassing at temperatures of 425°C or above the same samples had areas of 0.76 m²/g. As pumice-supported vanadium pentoxide is heated to about 425°C, it would appear likely that the clearing of blocked pores and the development of crevices produces a solid of higher surface area. Also, the possibility of chemical change when the catalyst is heated cannot be neglected (see p. 514).

### *(d) The Variation in Specific Area as the Catalyst Is Used*

Systematic determinations of the variation in the specific area of a catalyst as it was used were made using a given batch of 8–10 mesh pumice-supported vanadium pentoxide. Determinations of specific area were carried out after degassing at 350°C and subsequently at 500°C, as these conditions have been shown to produce consistent results. The specific areas calculated from the linear portions of the BET isotherms obtained are given in Table 2 and shown as a function of catalyst age in Fig. 1. The specific area after degassing at 350°C falls quite sharply during the first 60 min use of the catalyst, remains constant for a further 240 min, then increases sharply to a high value exceeding the initial one. After a total of about 500 min the area falls again. The variation of specific area with catalyst age is therefore remarkably similar to the variation with age of the activity of the catalyst as measured by fuel consumption. The specific area determined after degassing at 500°C (0.76 m²/g) was independent of catalyst age; moreover, heating a catalyst of any age to 500°C causes an increase in area exactly similar to that produced by using the catalyst for the oxidation of pent-2-ene for 300–500 min.

TABLE 2
THE SURFACE AREAS AND COLORS OF VANADIUM PENTOXIDE/PUMICE CATALYSTS
THE EFFECT OF CATALYST AGE

| Catalyst age (min): | 0 | 70 | 175 | 290 | 324 | 420 | 495 | 555 | 610 |
|---|---|---|---|---|---|---|---|---|---|
| Color of catalyst[a] (at room temperature) | A | B | B | B | C | D | D | E | E |
| Specific area (m²/g) (degassed at 350°C) | 0.66 | 0.46 | 0.47 | 0.47 | 0.75 | 0.76 | 0.77 | 0.64 | 0.64 |
| Specific area (m²/g) (degassed at 500°C) | 0.76 | 0.76 | 0.76 | 0.76 | 0.75 | 0.75 | 0.77 | 0.76 | 0.77 |

[a] A, yellow-gray; B, dark brown-gray; C, dark blue-gray; D, very dark blue-gray; E, dark gray.

### *(4) The Color of the Catalysts*

All the catalysts were yellow-gray in color when new, but definite changes of color occurred during their use for the oxidation of pentenes. These changes in color correspond to changes in activity and selectivity and in surface area (Table 2). Pumice-supported catalysts which have been used for less than 300 min are dark brown-gray in color, active unselective catalysts between 300 and 500 min old are dark blue-gray and old deactivated catalysts are dark gray.

### *(5) The Diffraction of X-Rays by Pumice-Supported Catalysts*

The spacings of the lattice planes and the corresponding Miller indices, calculated from the X-ray diffraction patterns of new and used pumice-supported catalysts, are given and compared with those of known compounds in Table 3. Activated but unused catalysts and catalysts which had been used for less than 290 min gave identical line patterns which correspond with that of pure vanadium pentoxide (*12*). Catalysts which have been used for 300–500 min, i.e., those which are active but unselective, give patterns characteristic of sodium vanadyl vanadate ($Na_2O \cdot V_2O_4 \cdot 5V_2O_5$) (*13*, *14*) mixed with a small amount of vanadium pentoxide. It is evident then that the increases in activity and surface area of pumice-sup-

TABLE 3

POWDER DIFFRACTION PATTERNS OF CATALYSTS AND REFERENCE MATERIALS[a,b]

| $V_2O_5$ (Reference pattern) | | | Catalysts used for 0–280 min (Observed pattern) | | Catalysts used for 310–700 min (Observed pattern) | | $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ (Reference pattern) | | |
|---|---|---|---|---|---|---|---|---|---|
| h k l | d | $I_{rel}$ | d | $I_{rel}$ | d | $I_{rel}$ | h k l | d | $I_{rel}$ |
| | | | | | 9.52 | ms | 1 0 0 | 9.46 | s |
| | | | 8.85 | vw | 7.27 | ms | 0 0 2 | 7.28 | s |
| | | | 7.20 | vw | | | | | |
| 2 0 0 | 5.76 | m | 5.76 | ms | 5.75 | mw | | | |
| | | | | | 4.72 | mw | 2 0 0 | 4.72 | m |
| 0 0 1 | 4.38 | vs | 4.38 | vs | 4.36 | ms | | | |
| 1 0 1 | 4.09 | mw | 4.09 | mw | 4.10 | w | | | |
| | | | | | | | $\bar{1}$ 0 4 | 3.85 | mw |
| | | | | | | | 0 0 4 | 3.62 | mw |
| 2 0 1 | 3.48 | vw | | | | | | | |
| | | | | | | | 2 0 2 | 3.47 | mw |
| 1 1 0 | 3.40 | s | 3.41 | s | 3.38 | ms | | | |
| | | | | | 3.37 | s | $\bar{1}$ 1 1 | 3.37 | vs |
| | | | | | 3.19 | w | 1 1 1 | 3.20 | ms |
| | | | | | 3.06 | mw | 1 0 4 | 3.06 | s |
| | | | | | 2.91 | mw | $\bar{3}$ 0 4 | 2.92 | ms |
| 4 0 0 | 2.88 | ms | 2.88 | ms | 2.89 | mw | | | |
| 0 1 1 | 2.76 | mw | 2.76 | mw | | | | | |
| | | | | | 2.71 | mw | $\bar{2}$ 1 3<br>2 1 1 | 2.72 | ms |
| 1 1 1 | 2.69 | w | 2.68 | vw | | | | | |
| 3 1 0 | 2.61 | m | 2.61 | mw | | | | | |
| | | | | | 2.63 | w | 1 1 3 | 2.63 | w |
| 2 1 1 | 2.49 | vw | 2.49 | vw | 2.52 | w | | | |
| | | | | | | | $\bar{3}$ 1 1 | 2.445 | w |
| 4 0 1 | 2.41 | vw | | | | | 4 0 0 | 2.371 | w |
| | | | | | | | $\bar{4}$ 0 4 | 2.257 | w |
| | | | 2.24 | w | | | | | |
| 0 0 2 | 2.19 | w | 2.19 | mw | | | | | |
| | | | | | 2.17 | mw | | 2.17 | ms |
| 1 0 2 | 2.15 | w | 2.15 | vw | | | | | |
| 2 0 2 | 2.04 | vw | | | | | | | |
| 4 1 1 | 1.992 | w | 1.995 | w | | | | | |
| | | | | | 1.978 | w | | 1.97 | m |
| 6 0 0 | 1.919 | mw | 1.918 | mw | | | | | |
| 3 0 2 | 1.900 | w | 1.906 | vw | 1.908 | w | | | |
| 0 1 2 | 1.864 | w | 1.865 | vw | | | | | |
| 1 1 2 | 1.840 | vw | 1.840 | vw | | | | | |
| | | | | | 1.806 | ms | | 1.806 | ms |
| 0 2 0 | 1.778 | vw | 1.783 | mw | 1.785 | w | | | |
| 6 0 1 | 1.757 | mw | 1.761 | w | | | | | |

[a] Taken by the Debye-Scherrer method, using a chromium anode X-ray tube and Philips-type camera.

[b] Relative intensities: vs, very strong; s, strong; ms, medium to strong; m, medium; mw, medium to weak; w, weak; vw, very weak.

ported catalysts after about 300 min use are accompanied by a chemical change producing sodium vanadyl vanadate, with only a small amount of vanadium pentoxide remaining unchanged. Deactivated catalysts (more than 500 min old) again gave patterns characteristic of sodium vanadyl vanadate; no change of phase accompanies deactivation. The powdered pumice support gave a pattern consisting of two very broad bands only. It can therefore be said to be amorphous and will not have contributed to the line patterns from the catalysts.

## DISCUSSION

### (*1*) *The "Aging" of Vanadium Pentoxide Catalysts*

As vanadium pentoxide supported on pumice is used as a catalyst for the oxidation of straight-chain pentenes, changes in the activity and selectivity of the catalyst occur and are revealed both in the consumption of pentene and in the formation of gaseous products. These changes can be correlated with a series of sudden changes in the physicochemical properties (color, specific surface area, and phase composition) of the catalyst itself.

In the very early "life" of a catalyst (0–60 min), at a constant pentene input, the amount of pentene in the effluent gases gradually increases. The initially clean surface of the catalyst adsorbs pentene and increasing amounts of the fuel can be recovered as the surface approaches saturation. During this period, the surface area (after degassing at 350°C) decreases, showing that the pentene adsorbed (or some product of the surface reaction of this pentene) is not completely removed at 350°C. At temperatures above 425°C, however, adsorbed species are removed, the surface areas of new catalysts and those used for 60 min becoming identical.

During the subsequent 240 min use of the catalyst, the activity, selectivity, surface area, phase composition, and color of the catalyst all remain substantially constant.

After about 300 min use, the activity increases sharply and the selectivity falls. Simultaneously, the specific area at 350°C increases from 0.46 $m^2/g$ to 0.76 $m^2/g$ and the color changes abruptly and distinctly from brown-gray to blue-gray (the color of vanadium tetroxide). The increased activity is not due merely to the increase in surface area, however, as catalysts supported on $\gamma$ alumina, which have surface areas of about 250 times that of the selective pumice-supported catalysts, are only slightly more active than the latter and are, indeed, less active than the unselective pumice-supported catalysts. The results of X-ray diffraction studies show that the changes after about 300 min use are accompanied by a phase change producing sodium vanadyl vanadate, a compound containing vanadium in two valency states ($V^{5+}$ and $V^{4+}$). It is evident that, during the oxidation of the pentene, the vanadium pentoxide catalyst becomes partially reduced. This reduction leads eventually to a phase change which involves reaction of the vanadium oxides with the pumice support (which contains sodium) to give sodium vanadyl vanadate. As the change of activity is so sudden, it is likely that this reaction takes place when $V^{4+}$ reaches a critical concentration which may well be slightly less than one-sixth of the total vanadium, as suggested by the formula $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ and by the fact that some (but only a little) of the $V_2O_5$ remains as a separate phase. As the effects on surface area of the phase change during catalytic oxidation and of heating the unchanged catalyst to temperatures exceeding 425°C are so similar, it appears likely that sodium vanadyl vanadate is produced by the latter process also; this conclusion is supported by previous work (*14*).

Several other instances of the reduction of vanadium pentoxide to compounds containing $V^{4+}$ as well as $V^{5+}$ during its use as an oxidation catalyst have been reported. Mars and van Krevelen (*15*) have shown that vanadium pentoxide in contact with air and oxidizable substances such as anthracene will be in a partly reduced state, and Simard, Steger, Arnott, and Siegel (*16*) regard the surface of vanadium pentoxide as containing $V^{5+}$, $V^{4+}$, and $O^{2-}$ ions in continually changing structures. Changes in the physicochemical properties of catalysts attend their reduction. For example, the exposure of vanadium pentoxide to olefin-air streams lowers the electrical resistance as the oxide is reduced and re-oxidation of the catalyst will restore the resistance to its original value (*17*). When naphthalene, benzene, or *o*-xylene is oxidized on vanadium pentoxide, gradual reduction of $V^{5+}$ to $V^{4+}$ (*18*) leads eventually to the production of the phase $V_2O_{4.34}$ (*19*, *20*). These changes in catalyst composition and structure are reflected in changes in the rate of oxidation of the organic substrate; the present work shows that the mechanism of oxidation must change concurrently.

After contact for a further 200 min with a reacting pentene-oxygen-nitrogen mixture, the sodium vanadyl vanadate catalyst becomes deactivated. The consumption of fuel thereafter decreases very sharply and only small amounts of gaseous products are formed. The attendant decrease in surface area is quite small when compared with the enormous decrease in activity, and no further phase change occurs. It would appear therefore that these changes result from physical pore-blockage by reaction products with concurrent "poisoning" of the active sites. The species responsible are removed by heating the catalyst to 425°C.

### (*2*) *The Mechanism of Oxidation of Unsaturated Hydrocarbons over Vanadium Pentoxide*

The present results support strongly the suggestions that vanadium pentoxide catalysts contain $V^{4+}$ ions as well as $V^{5+}$ and $O^{2-}$ and that the mechanism of oxidation of hydrocarbons on such catalysts involves the cycle (*15*)

$$\mathrm{RH} + \text{oxidized catalyst} \rightarrow \text{products} + \text{reduced catalyst}$$

$$\mathrm{O_2} + \text{reduced catalyst} \rightarrow \text{oxidized catalyst}$$

These changes can be represented in terms of electron transfer processes, viz.,

$$m\mathrm{RH} + n\mathrm{V_2}^{5+}\mathrm{O_5}^{2-} \rightarrow \text{products} + \mathrm{V}_{2n-2m}{}^{5+}\mathrm{V}_{2m}{}^{4+}\mathrm{O}_{5n-m}{}^{2-}$$

$$\tfrac{1}{2}m\mathrm{O_2} + \mathrm{V}_{2n-2m}{}^{5+}\mathrm{V}_{2m}{}^{4+}\mathrm{O}_{5n-m}{}^{2-} \rightarrow n\mathrm{V_2}^{5+}\mathrm{O_5}^{2-}$$

During oxidation, $m$ gradually increases, the catalyst being reduced. When $m \simeq n/6$, i.e., when about one-sixth of the vanadium is tetravalent, the valency composition of the vanadium in the catalyst corresponds to that of sodium vanadyl vanadate. The mechanism is not, therefore, kinetically cyclic, indicating that re-oxidation of the catalyst is rate-determining, as has been suggested previously (*15*).

The active oxidant during catalytic oxidation over vanadium pentoxide is therefore $V^{5+}$; adsorbed alkenes are oxidized by this species to surface-bonded cations which react with $O^{2-}$ to produce carbonyl and alkenic scission products and epoxides (*1*, *2*). In contrast, the unselective oxidation of pentenes over sodium vanadyl vanadate, which produces large yields of methanol and carbon dioxide and smaller amounts of many other organic compounds (*2*), probably involves a free-radical chain reaction in which molecular oxygen is the active oxidant.

It is likely, then, that the "oxidation–reduction" mechanism postulated by Mars and van Krevelen (*15*) for the oxidation of aromatic hydrocarbons over vanadium is generally applicable to the oxidation over this catalyst of unsaturated hydrocarbons. The "hydroperoxylation" mechanism of Bretton, Wan, and Dodge (*21*) becomes important on old catalysts in which the $V^{4+}$ content is high.

## ACKNOWLEDGMENTS

The authors thank Dr. C. F. Cullis for his interest and encouragement. One of us (N.S.B.) is indebted to Pakistan Petroleum Ltd. for a scholarship. We thank Mr. R. W. Toft of Shell Research Ltd., Thornton Research Centre, P.O. Box 1, Chester for X-ray diffraction analysis of catalysts.

## REFERENCES

1. BUTT, N. S., AND FISH, A., *J. Catalysis* **5**, 205 (1966) (Part I).
2. BUTT, N. S., AND FISH, A., *J. Catalysis* **5**, 494 (1966) (Part II; preceding paper).
3. EMMETT, P. H., AND BRUNAUER, S., *J. Am. Chem. Soc.* **56**, 35 (1934).
4. EMMETT, P. H., AND BRUNAUER, S., *J. Am. Chem. Soc.* **59**, 310 (1937).
5. JURA, G., AND HARKINS, W. D., *J. Am. Chem. Soc.* **66**, 1356 (1944).
6. POLLEY, M. H., SCHAEFFER, W. D., AND SMITH, W. R., *J. Phys. Chem.* **57**, 469 (1953).
7. CHAMPION, W. M., AND HALSEY, G. D., JR., *J. Phys. Chem.* **57**, 646 (1953).
8. BRUNAUER, S., EMMETT, P. H., AND TELLER, E., *J. Am. Chem. Soc.* **60**, 309 (1938).
9. YOUNG, D. M., AND CROWELL, A. D., "Physical Adsorption of Gases," p. 226. Butterworths, London, 1962.
10. RUSSELL, A. S., AND COCHRAN, C. N., *Ind. Eng. Chem.* **42**, 1332 (1950).

*11*. Teichner, S., *J. Chim. Phys.* **47**, 118 (1950).

*12*. *Natl. Bur. Std. Circ. 539,* **8** (1958) (ASTM Powder Diffraction Index Card 9-387).

*13*. Flood, H., and Sørum, H., *Tidsskr. Kjemi Bergvesen Met.*, p. 55 (1943).

*14*. Toft, R. W., private communication.

*15*. Mars, P., and Van Krevelen, D. W., *Chem. Eng. Sci.* (*Spec. Suppl.*) **3**, 41 (1954).

*16*. Simard, G. L., Steger, J. F., Arnott, D. J., and Siegel, L. A., *Ind. Eng. Chem.* **47**, 1424 (1955).

*17*. Clark, H., and Berets, D. J., *Proc. Intern. Congr. Catalysis, 1st, Philadelphia, Penna.*, p. 204 (1956).

*18*. Weiss, J. M., Downs, C. R., and Burns, R. H., *Ind. Eng. Chem.* **15**, 965 (1923).

*19*. Korneichuk, G. P., Ushakova, V. P., and Skorbilina, T. G., *Kinetika i Kataliz* **2**, 931 (1961).

*20*. Ioffe, I. I., Ezhkova, Z. I., and Lyubarskii, H. G., *Kinetika i Kataliz* **3**, 194 (1962).

*21*. Bretton, R. H., Wan, S. W., and Dodge, B. F., *Ind. Eng. Chem.* **44**, 594 (1952).