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Influence of the Phosphorus/Vanadium Ratio on the Solid State Chemistry and Redox Properties of Vanadium Phosphate-Based Catalysts

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The influence of the P/V atomic ratio on the redox properties of two series of V–P–O catalysts was investigated. The catalysts were calcined at 773 or 923 K and the P/V ratio was varied in the range 0.94 to 1.07. The 4+ oxidation state of vanadium was highly stabilized during calcination at 773 K by a slight excess of phosphorus. This stabilization was less pronounced at the higher calcination temperature. The influence of the P/V ratio on the reactivity toward hydrogen of the catalysts calcined at 773 K was difficult to establish because the phase composition of these samples varied over a large range. It was established for the series calcined at 923 K that excess phosphorus, far from activating reduction of vanadium, tended to inhibit this process. Excess phosphorus also inhibited reoxidation of the bulk of these catalysts but tended to have little effect on the reoxidation of near surface layers. The catalytic activity in *n*-butane partial oxidation to maleic anhydride was compared with the redox behavior and a model for selective oxidation is presented which envisages excess phosphorus as regulating the flow of oxygen anions from the bulk to the surface. The primary interaction is postulated as being between the hydrocarbon and oxygen anions associated with a V^{5+} related phase.

INTRODUCTION

An understanding of the importance of vanadium phosphate-based catalyst for the partial oxidation of *n*-butane to maleic anhydride can be obtained from a review of the projects of major producers of this material, which indicates that they intend to change from benzene to C_4 feedstocks (*1–3*) during the 1980's. In keeping with the growing industrial importance of this system, there has been a large increase in the number of patents, especially concerning catalyst composition, awarded for this process in recent years. By contrast, the academic interest shown in this system has been very limited and certainly so by comparison with comparable catalytic C_3 partial oxidation processes (*4, 5*).

The role of phosphorus in diminishing the activity but increasing the selectivity for C_4 partial oxidation on mixed vanadium–phosphorus catalysts has been known for many years (*6*). Recent publications have emphasized the importance of the P/V atomic ratio and the calcination conditions in determining the properties of these catalysts: a high P/V ratio and reducing atmosphere favors the formation of V^{4+} (*7*). It is significant also that most patents issued for this process feature catalysts with P/V ratios much greater than 1 (*8–11*).

The role of the oxidation state of vanadium has been emphasized as an important factor in determining the selectivity of this system. A large concentration of the 4+ oxidation state favors selective oxidation whereas the 5+ state is believed to favor total oxidation processes (*12*). However, besides a recognition that phosphorus

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somehow stabilizes the 4+ oxidation state of vanadium little is known of the mechanism of this process (*6, 12*).

The concept that selective oxidation of hydrocarbons is due to their reaction with lattice oxygen has been gaining strength in recent years. This concept supports the Mars and van Krevelen (*13*) mechanism which envisages selective oxidation as involving reduction of the catalyst by the hydrocarbon with incorporation of lattice oxygen into the product, followed by reoxidation of the lattice by gas phase oxygen. The crucial role of lattice oxygen is exemplified by recent findings relating to the mobility of oxygen in bismuth molybdate C_3 oxidation catalysts which indicate that all the lattice oxygen from these catalysts, and not just surface oxygen anions, can become incorporated into the reaction products (*14*).

Further justification for the study of the solid state chemistry of this system in relation to its catalytic properties may be had from consideration of two experimental findings concerning V–P–O catalysts. The first of these is that in a recent study of the influence of P/V ratio on surface composition and selectivity, in the range where selectivity in maleic anhydride formation changed most, i.e., between P/V of 0.97 to 1.07, no change was observed in the surface P/V ratio as measured by X-ray photoelectron spectroscopy (XPS) (*15*). Second, when *n*-butane, in an oxygen-free atmosphere, was passed over some V–P–O catalysts a considerable amount of maleic anhydride was formed and continued to be formed until the catalyst had reached an average oxidation state of vanadium between 4+ and 3+, indicating that some bulk and not only surface lattice oxygen must have been incorporated into the reaction products (*16*).

This publication focuses on the behavior in reduction and oxidation of V–P–O catalysts in an attempt to clarify the role of the P/V ratio.

Toward this end two series of catalysts have been prepared in both of which the P/V ratio was varied in a small range about the value (1 : 1) for stoichiometric vanadium phosphate (*17*). By choosing to restrict the P/V ratio in this way it was hoped that each catalyst could be readily compared with the stoichiometric compound as reference. In the first of these series, calcination conditions were chosen so that the average oxidation state of vanadium and the phase composition was largely unchanged throughout the series. In the second series the P/V ratio, the phase composition, and the average oxidation state of vanadium were varied. The work reports measurements of the reduction by hydrogen and oxidation by oxygen.

EXPERIMENTAL

Catalyst Preparation and Characterization

The method of preparation of the catalysts used in this study has been fully described elsewhere (*15*). Essentially this involved reduction and dissolution of 9.1 g of V_2O_5 into 150 g of lactic acid in water by refluxing for 16 h. After a blue solution had developed, the appropriate amount of 85% *o*-H_3PO_4 in water was added and the solution refluxed for a further 4 h. Excess lactic acid and water were evaporated off and the solid precursor was calcined at 773 K for 16 h or at 923 K for 12 h. The P/V ratios of all the catalysts were in the range 0.94 to 1.07. Characterization by X-ray diffraction (XRD) and surface area measurements were by standard procedures (*15*). Average oxidation states of vanadium (*AV*) were measured by double titration with $KMnO_4$–$FeSO_4(NH_4)_2SO_4$–$(NH_4)_2S_2O_8$ (*15*). In addition the homogeneity of the P/V atomic ratio was checked by analyzing a large number of areas of each sample of diameter between 0.1 and 1 μm using electron probe microanalysis (EPMA) (*18*). It has already been established that the surface P/V ratio, as measured by XPS, essentially remained constant for bulk P/V values above 0.97 (*15*). Below this bulk composition pronounced enrichments in vanadium were observed.

In what follows a shorthand notation will be used to identify the various catalysts; thus 0.94 PV_{773} will signify that the P/V atomic ratio was 0.94 and the calcination temperature was 773 K.

Reduction and Reoxidation

The reactivities of the catalysts toward hydrogen and oxygen were measured on a McBain quartz spiral spring balance. This apparatus allowed quantitative monitoring of weight changes which occurred when vanadium phosphate catalysts were heated at various temperatures (generally between 573 and 723 K) either in an atmosphere of pure hydrogen (P_{H_2} = 760 Torr) or in pure oxygen (P_{O_2} = 150 Torr), the latter to achieve reoxidation of catalysts which had been reduced initially. In normal operation a charge of about 250 mg of catalyst was placed in the microbalance and evacuated at the temperature to which it was to be exposed to hydrogen until the weight of the catalyst had attained a constant value. Some weight losses were observed during this evacuation procedure, but it was established that this did not result from a reduction of the catalyst but rather from loss of surface water which had accumulated on these very hygroscopic catalysts during storage. After the weight had stabilized, hydrogen could be introduced into the system via a capillary leak and changes in weight during the course of the reaction were followed. The capillary leak was necessary to prevent excessive oscillation of the spiral spring due to sudden pressure changes. By virtue of this restriction it usually required 2–3 min to charge the balance with reactant gas. To ensure that the catalyst was held in a pure-hydrogen atmosphere while it was being reduced, a circulating pump was used to facilitate removal of water formed in the reduction process from the immediate vicinity of the catalyst and a liquid-nitrogen trap was incorporated into the gas circulating system to remove this water from the gas phase.

For those experiments in which the oxidizability of the catalysts was measured, the catalysts were first reduced in a hydrogen atmosphere in the manner described above. Unless otherwise stated the reductions were carried out in such a manner as to have the *AV* value of vanadium before reoxidation at 4+. The *AV* value before reduction was determined by titration, as described previously (*15*), and assuming that the vanadium was present only in its 4+ and 5+ oxidation states the weight loss necessary to transform the remaining V^{5+} to V^{4+} was calculated according to

$$2\ VOPO_4 \rightarrow (VO)_2P_2O_7 + \tfrac{1}{2}H_2O \quad (1)$$

The transformation shown in Eq. (1) corresponds to a 5% weight loss. When the desired weight loss was attained the reduction was stopped by removing the hydrogen and the system was evacuated for several hours. Then the catalyst was exposed to the desired pressure of oxygen.

RESULTS

The results of X-ray diffraction, *AV*, and surface area measurements for catalysts with P/V atomic values in the range 0.94 to 1.07 are presented in Table 1 for samples calcined at 773 K and in Table 2 for samples calcined at 923 K. For comparison the X-ray diffractogram of 1.03 PV_{773} and 1.06 PV_{923} are presented in Fig. 1. These results clearly show that whereas a slight excess of phosphorus inhibited the oxidation of vanadium and stabilized the 4+ oxidation state during calcination at 773 K the effect was less pronounced at 923 K. However, comparison of the *AV* values for 0.94–1.00 PV_{923} with that for 1.06 PV_{923} reveals that the V^{4+} oxidation state was stabilized to a remarkable extent considering the calcination temperature. In addition, the material calcined at the higher temperature was much more crystalline, as can be seen from the line widths in the diffractograms of Fig. 1, and these materials had much lower surface areas. X-Ray diffractograms of all the catalysts studied showed the presence of some β-$VOPO_4$ (*17*). How-

TABLE 1

AV^a Values, Specific Surface Areas, and Phases Present for the Series PV_{773}

P/V ratio	0.94	0.97	1.00	1.03	1.07
AV	4.97	4.92	4.86	4.39	4.04
Specific surface area (m^2g^{-1})	2.7	5.6	9.6	4.9	4.9
Phases present after calcination	β-$VOPO_4$	β-$VOPO_4$	β-$VOPO_4$ β* phase	β-$VOPO_4$ β* phase	β-$VOPO_4$ β* phase

[a] AV = average oxidation state of vanadium.

ever, the series calcined at 773 K exhibited strong peaks at d = 4.67, 4.07, 3.14, and 2.59 Å characteristic of the β* phase (*15*), whereas the series calcined at 923 K exhibited small peaks at d = 3.87, 3.14, and 2.98 Å, characteristic of the presence of a reduced phase which has been labeled in the literature as the B phase (*19, 20*), a tripolyphosphate called the β phase (*7, 21*) and $(VO)_2P_2O_7$ (*22*). The extent to which reduced phases were present in the materials after calcination increased as the P/V ratios increased, for both series of catalysts, in keeping with the lower AV values recorded.

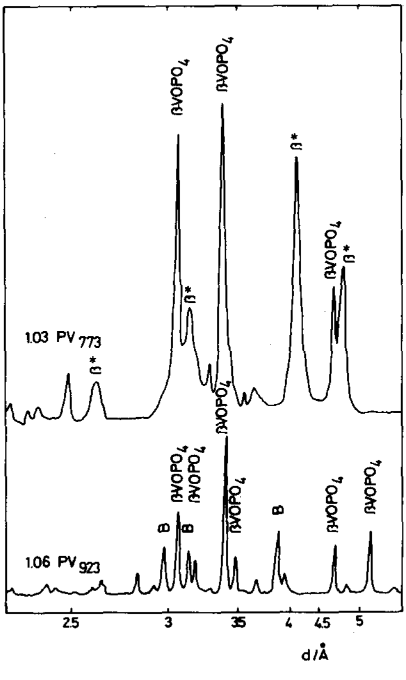

FIG. 1. X-Ray diffractograms of 1.03 PV_{773} and 1.06 $PV_{9.23}$.

Reduction of 0.94–1.07 PV_{773} at 623 K

The rates of reduction of the series 0.94–1.07 PV_{773} by hydrogen gas are presented in Fig. 2 as the percentage weight losses which occurred during the reduction process plotted as a function of time. A feature of these curves was that for the catalyst with P/V = 0.94 the initial rate of reduction was slower than the rate attained after several hours reduction. The rate of reduction of 0.94 PV_{773} was significantly higher after 10 h than at the start of the reaction.

Another significant feature of these data is that although 1.03 and 1.07 PV_{773} were characterised by AV values close to 4+ (cf. Table 1) their rates of reaction with hydrogen were still very high. To illustrate this point the data of Fig. 2 are replotted in Fig. 3 taking into account the AV values before the reduction process began and calculating

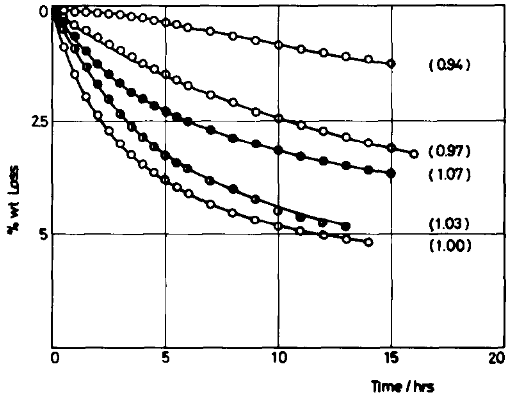

FIG. 2. Time profiles for weight losses brought about by reduction of the series PV_{773} in hydrogen at 623 K. The numbers in parentheses refer to the P/V ratios.

TABLE 2

AV Values, Specific Surface Areas, and Phases Present for the Series PV_{923}

P/V ratio	0.95	0.97	1.00	1.02	1.06
AV	4.94	4.97	4.94	4.83	4.75
Specific surface area (m^2g^{-1})	1.8	1.6	2.6	2.3	2.3
Phases present after calcination	β-$VOPO_4$	β-$VOPO_4$	β-$VOPO_4$	β-$VOPO_4$ B phase	β-$VOPO_4$ B phase

the lowering in *AV* which corresponded to the observed weight losses following Eq. (1). In this way the oxidation state of vanadium during the reduction is plotted as a function of time.

The extents to which this same series of catalysts were reduced after 0.5, 2, 4, and 14 h are presented in Fig. 4 as a function of the P/V ratio. Viewed in this way the maximum in reducibility clearly coincides with the stoichiometric P/V ratio for pure vanadium phosphate, i.e., 1, which also coincides with the maximum in surface area.

Examination of these catalysts by XRD after reduction revealed that they had become largely amorphous. However, very small peaks associated with the B phase were observed and a single small peak at *d* = 3.29 Å which could not be associated with any known phase of V–P–O catalysts (*15*).

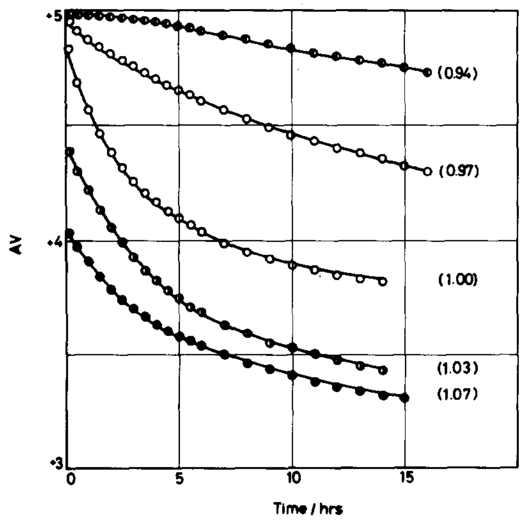

FIG. 3. Plot of average oxidation state of vanadium (*AV*) during reduction at 623 K for the series PV_{773}. The numbers in parentheses refer to the P/V ratios.

Reduction of 0.95–1.06 PV_{923} at 623 K

The rate of reduction of the series 0.95–1.06 PV_{923} by hydrogen at 623 K is presented in Fig. 5. Since the *AV* values were similar across the series of catalysts, no attempt will be made to plot this property as a function of reduction time, since this would give a curve very similar to that presented as Fig. 5. By contrast with catalysts calcined at 773 K, some irregularities were observed in initial reaction rates which were somewhat slower for all catalysts of this series by comparison with the rates which were attained after several hours reduction. As shown in Fig. 6, maxima in extents of reduction, recorded after 4, 8, and 16 h, were observed for P/V = 1. In gen-

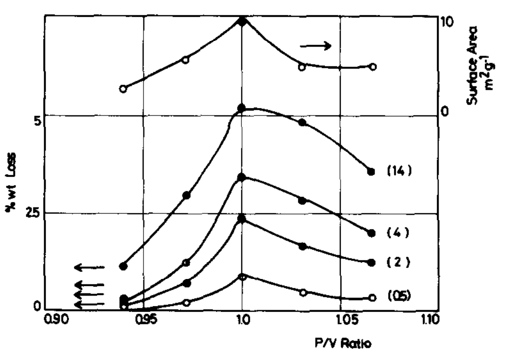

FIG. 4. Percentage weight losses at 623 K, at the times (h) indicated in parentheses, for the series PV_{773} plotted as a function of the P/V ratio. Upper trace: influence of P/V ratio on specific surface area.

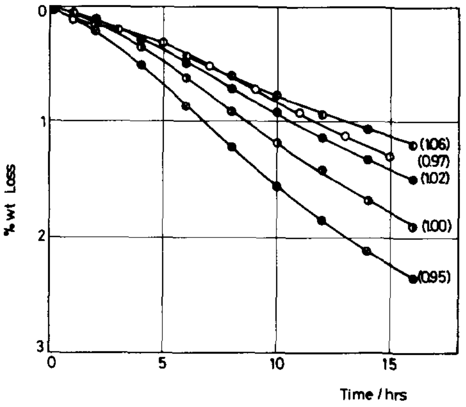

FIG. 5. Time profiles for reduction of the series PV_{923} in hydrogen at 623 K. The numbers in parentheses refer to the P/V ratios.

eral the reducibilities tended to follow the small changes observed in surface areas (Table 2) for the catalysts with P/V ratios $\geq$ 0.97. For P/V ratios less than ca. 0.97 an increase in reducibility was observed which could not be explained by an increased surface area associated with this material.

Reductions at 723 K

The rate of reduction of the series 0.94–1.07 PV_{773} with hydrogen at 723 K (Fig. 7) showed the same trends as observed at 623 K in that a maximum in initial reaction rate was observed for P/V = 1. However, it is clear from the data presented in Fig. 7 that whereas reduction of 1.07 PV_{773} stopped after it had experienced a weight loss of ca. 5%, reduction of 0.94 PV_{773} continued well beyond this point. Calculations based on the value of AV at the start of the reduction and the weight loss at the point where the reduction stopped for 1.07 PV_{773} indicates that the value of AV at the point at which the reduction stopped was close to 3+. The shape of a curve of AV as a function of reduction time would be essentially similar to those presented in Fig. 3.

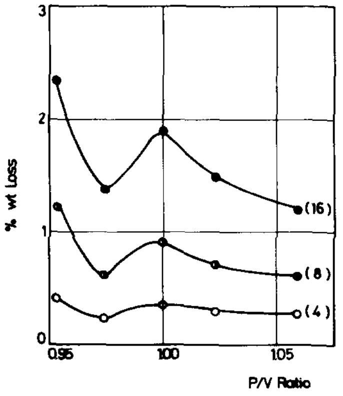

FIG. 6. Percentage weight losses at 623 K, at the times (h) indicated in parentheses, for the series PV_{923} plotted as a function of the P/V ratio.

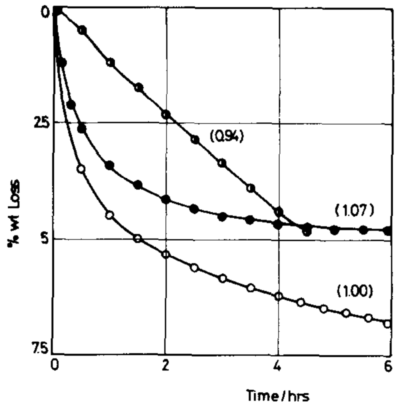

FIG. 7. Time profiles for weight losses brought about by reduction of some catalysts of the series PV_{773} at 723 K in hydrogen. The numbers in parentheses refer to the P/V ratios.

Reduction of series 0.95–1.06 PV_{923} by hydrogen at 723 K is presented in Fig. 8. The rate of reaction was much faster than at the lower temperature and lower initial reduction rates, by comparison with the rates

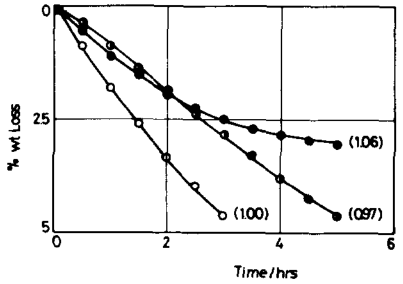

FIG. 8. Time profiles for weight losses brought about by reduction of some of the PV_{923} series at 723 K in hydrogen. The numbers in parentheses refer to the P/V ratios.

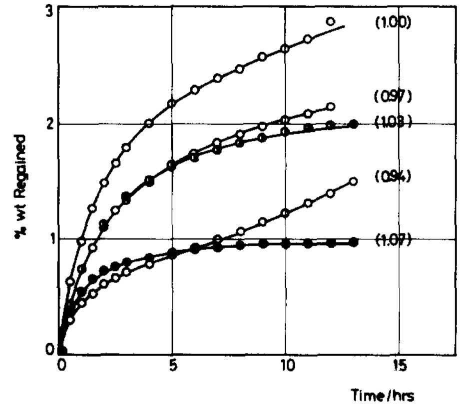

FIG. 9. Time profiles for reoxidation of catalysts of the series PV_{773} by oxygen at 723 K. The numbers in parentheses refer to the P/V ratios.

ultimately achieved, were observed only for samples with P/V ≤ 0.97. Once again it was observed that the sample with the highest P/V ratio displayed a tendency for the reduction to stop after it had reached a certain level. In this case the average oxidation state of vanadium was ca. 4.2+ at the point at which the reduction tended to stop. By contrast, considerably lower *AV* values (<4) were attained by 0.97 and 1.00 PV_{923} in spite of the fact that these catalysts were more strongly oxidized after calcination (cf. Table 2).

XRD analysis of the series PV_{773} after reduction at 723 K exhibited much the same pattern reported above for the corresponding samples analyzed after reduction at 623 K; these materials had become essentially amorphous but small peaks associated with the B phase and the β^* phase were observed as well as a single peak at $d = 3.29$ Å. Though not as pronounced, some loss of crystallinity was also observed for individual members of the series PV_{923} but the main feature in their XRD patterns was the presence of narrow lines associated with the B phase.

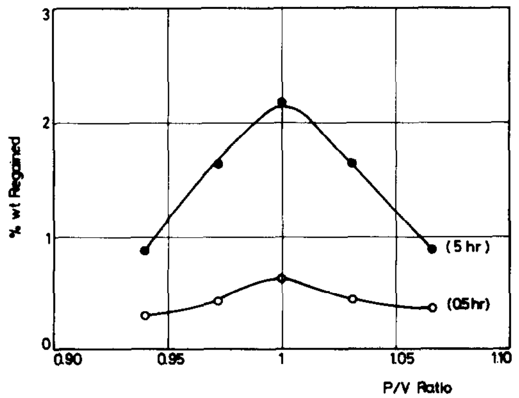

FIG. 10. Weight regained at 723 K during reoxidation of the series PV_{773} by oxygen for the times indicated in parentheses.

Reoxidation of 0.94–1.07 PV_{773}

The data presented in Fig. 9 represent the rate of reoxidation by oxygen at 723 K of vanadium phosphate catalysts which had previously been reduced by hydrogen in such a manner that their average oxidation state of vanadium was 4+. Once again a maximum in reactivity was observed for P/V = 1, as is clear from Fig. 10, which presents the extent of reoxidation after 0.5 and 5 h as a function of the P/V ratio. However, examination of Fig. 9 shows other important kinetic features. Reoxidation of 1.07 PV_{773} stopped when the sample had reached a level of reoxidation much lower than the other catalysts of the series. In addition, the initial reoxidation rate of 0.94 PV_{773} was low by comparison with 0.97 PV_{773} and tended to become slower for reaction times between 2 and 4 h. However, at the end of this time the rate of reoxidation increased again and after about 10 h its rate was the highest of the series and the extent of reoxidation increased monotonically for the duration of the experiment.

DISCUSSION

Influence of P/V Ratio on Redox Properties

It is clear from the data presented in Tables 1 and 2 that excess phosphorus stabilizes the 4+ oxidation state of vanadium during calcination at 773 K and to a lesser extent at 923 K. However, the reactivity trends of the calcined materials during reduction (Figs. 2, 4, and 5–8) indicate that catalysts with high P/V ratios do not become inherently more reactive toward hydrogen, thus indicating that the stabilization effect is not the result of the preferential formation of an inherently more stable V^{4+} containing phase when excess phosphorus is present but is the result of lower overall reactivity of V–P–O catalysts containing excess phosphorus. Indeed, the reducibility of these catalysts is not a simple problem since it may be influenced by at least two factors, namely (i) the surface areas and (ii) the *AV* values. This problem is particularly acute for the PV_{773} series since both factors vary over quite a large range. For this reason some aspects of the influence of P/V ratio on the PV_{923} series will be considered first.

An argument can be made that reactivity toward hydrogen should be normalized in terms of the fraction of V^{5+} present at the start of the reaction. Calculated in such a manner the maximum in reducibility for the PV_{923} series would not be displaced from its original value of unity. Variations in surface area of these catalysts were not large (Table 2). However, calculation of reducibility per unit surface area would displace the observed maximum toward lower P/V values. Thus for the series PV_{923} the overall reactivities toward hydrogen tend to diminish for higher P/V ratios.

A clear correlation can be seen between the specific surface areas of the PV_{773} series and their reactivities toward hydrogen in that the maxima in their plots versus P/V ratio coincided. However, this correlation cannot be regarded as rigid because the reducibility of 0.97 PV_{773} was less than that of 1.03 PV_{773} in spite of their surface areas being similar. Reducibility expressed per unit surface area would have a maximum value for P/V of 1.03. Reducibilities of the PV_{773} series at 623 K normalized in terms of the fraction V^{5+} present at the start of the reduction indicate that this value for 1.03 PV_{773} was only about 20% higher than for 1.00 PV_{773} but 1.07 PV_{773} was about 5 times more reactive. However, this value may have been artificially high since the fraction of V^{5+} present in this catalyst was very small (Table 1) (*23*).

Another factor which may be considered in this argument is that the maxima in the curves of Fig. 4 remained unaltered as a function of reduction time. It is reasonable to suggest that after calcination whatever V^{5+} was present in 1.07 PV_{773} was located near the surface. This being so, if the reducibility was strongly influenced by excess phosphorus, a maximum in the lowest curve of Fig. 4 (i.e., for reduction for short times) would be expected for the highest P/V ratio. The maximum would then be expected to move toward lower P/V ratios for extended reduction times, as the superficial V^{5+} was exhausted. Clearly this type of behavior was not observed.

In summary, the situation with regard to the PV_{773} series is rather complicated but in so far as the reactivity of the whole of the material is concerned, i.e., of V^{5+} to V^{4+} and V^{3+}, the most important factor would appear to be the dispersion. As regards the PV_{923} series, excess phosphorus did not increase but tended to diminish the reactivity toward hydrogen, even when allowance was made for the fact that some V^{4+} was already present in the freshly calcined material. It can be argued that the more reliable data come from the reducibility of the PV_{923} series, since it was there that the P/V parameter was varied while causing the minimum interruption to the *AV* and surface area parameters of the system.

The role of excess phosphorus in inhibiting the reduction process becomes manifest only after extended reaction times. Examination of the behavior of 1.07 PV_{773} (Fig. 7) and 1.06 PV_{923} (Fig. 8) in reduction at 723 K indicates that the reduction process tended to stop after relatively short reaction times, ca. 3 h. The situation with respect to 1.07 PV_{773} is again complicated because at the point where the reduction stopped its *AV* value was close to 3+, so this sample can be considered as fully reduced. However, this is not the case with 1.06 PV_{923} which contrasts strongly with 0.97 and 1.00 PV_{923} (Fig. 8) whose reduction proceeded to much greater extents without any sign of leveling off, whereas with 1.06 PV_{923} a definite plateau value was observed.

The data relating to reoxidation kinetics of these catalysts indicate that the initial rates of reoxidation correlate with the initial rates of reduction. As can be seen in Fig. 9, excess phosphorus had little effect on the initial reoxidation rates of the PV_{773} series; contrast the initial rates for 0.94 and 1.07 PV_{773}. However, at 723 K the rate of reoxidation of 1.07 PV_{773} fell to zero in a short time, thereby indicating that the excess phosphorus was inhibiting reoxidation of the bulk of this material. Finally, the relatively fast rate of reoxidation observed at extended reoxidation times for 0.94 PV_{773} is in complete contrast to the behavior observed for 1.07 PV_{773} and indicates that the phosphorus deficiency in the former was an important factor in determining the extent to which it could be successfully reoxidized.

Thus in summary it can be stated that excess phosphorus plays little role in determining the reducibility or oxidizability of the catalysts especially when initial reaction rate or reactions confined to near surface layers are considered. However, the extents to which these materials can be reduced or oxidized is very sensitive to the amount of phosphorus present. In particular excess phosphorus seems to inhibit both reduction and oxidation of the bulk of these materials.

Another aspect of the results which is particularly important for low P/V ratios is the observed lower initial reaction rates vis-à-vis rates attained after several hours for reduction and reoxidation. In general this type of behavior seemed to be associated with highly crystalline materials [hence their appearance for 0.94 PV_{773} (Figs. 2 and 9) and for most of the PV_{923} series (Fig. 5)] and could readily be interpreted in terms of a slow nucleation process for these samples (*24*). However, other factors may also have played a role. The findings of an XPS study of the PV_{773} series could also be an important factor in that lower initial reactivities could be associated with surfaces enriched in vanadium as observed for catalysts with low P/V ratios (*15*).

Relationship between Catalytic and Redox Properties

These findings must now be considered in the light of the known catalytic properties of this system. It has already been shown (*15*) that for the PV_{773} series the maximum catalytic activity was observed for intermediate P/V values but that the selectivity was highest for P/V = 1.07. These catalysts were tested in mild reaction conditions, i.e., at 673 K, such that little change occurred in their phase composition and *AV* values during testing.

The most selective catalyst, i.e., 1.07 PV_{773}, was composed mostly of the phase labeled β^* whose structure is not known, but it contains vanadium in the 4+ oxidation state, it is stabilized by excess phosphorus and slowly transforms into β-$VOPO_4$ upon heating in air at 773 K. A correlation was observed between the presence of this phase throughout the PV_{773} series and the selectivity (*15*). This phase cannot be claimed as "the active and selective phase" in butane or butene partial oxidation to maleic anhydride since other literature reports indicate that other phases such as the B phase are also active (*19, 20*). However, all these phases have in common the fact that they are composed in very large part of vanadium in the 4+ oxidation state (*7, 12, 19, 22*) and show optimum selectivities for P/V ratios between 1.05 and 1.2 (*19, 20*).

Indeed, recent work in these laboratories has shown that catalysts with quite low P/V ratios, which show zero selectivity after calcination, can be rendered partially selective by activation in reducing conditions (*16*). Catalysts treated in this way were largely amorphous, indicating that the important factor was the 4+ oxidation state of vanadium and not any one phase (*16, 25*).

There are very few reports in the literature of *n*-butane partial oxidation on this type of catalyst. Most mechanistic studies have concentrated on butene oxidation (*26–31*). These reports indicate that this is a multistep process featuring 1,3-butadiene, furan, and maleic acid as intermediates. Presumably *n*-butane partial oxidation would involve one extra dehydrogenation step. A recent report by Morselli *et al.* (*32*) suggests that catalysts with low *AV* values and high P/V ratios, i.e., 1.2–1.4, only convert butene to butadiene in the absence of gas-phase oxygen but produce furan and maleic anhydride in the presence of oxygen. Catalysts with high *AV* values produced maleic anhydride even in the absence of gas phase oxygen. These authors suggested (*32*) that the reduced phase was only capable of dehydrogenation but the V^{5+} sites were necessary for oxygen insertion.

In view of the high selectivity associated with catalysts with high V^{4+} contents, it is very tempting to suggest that it is this species which is primarily responsible by interacting directly with adsorbed hydrocarbons. However, taken together, XPS and reducibility experiments did not indicate changes in surface V^{5+}/V^{4+} ratios for the range of P/V ratios in which selectivity changed most (*15*). Taken in combination with the known catalytic activity of the PV_{773} series, this work would suggest a strong correlation between selectivity and the difficulty in reduction and particularly in reoxidation of the bulk of these catalysts. This correlation suggests that what may be of primary importance in determining selectivity is restricted availability and difficulty in recuperation of lattice oxygen. Thus catalysts with high P/V ratios would be selective not by virtue of a direct interaction between the high V^{4+} concentration and *n*-butane but by interacting specifically with the smaller amount of lattice oxygen associated with V^{5+} on the surface so as to bring about an activated intermediate. This, in turn, could further react either with more lattice oxygen or adsorbed oxygen species. This hypothesis would imply that it is only this type of lattice oxygen, i.e., associated with V^{5+}, which is sufficiently active and capable of activating the hydrocarbon by, for example, dehydrogenation. A catalyst with a low P/V ratio would be nonselective because, once activated, the complex could react nonselectively with the excess of highly active lattice oxygen. Thus within the context of a Mars and van Krevelen type mechanism (*13*), in which bulk lattice oxygen is involved in the reaction process and may become incorporated into the product, excess phosphorus can be envisaged as regulating the availability of oxygen anions.

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