AlPO$_4$ as a Support Material for VPO Catalysts

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AlPO$_4$ has been demonstrated to be a good support material for vanadium–phosphorus oxide (VPO) catalysts in selective oxidation of 1-butene to maleic anhydride. The advantages of using AlPO$_4$ as the support include (i) strong thermal stability suitable for the highly exothermic reaction, (ii) large pore diameter to minimize pore diffusion resistance, and (iii) the positive support–catalyst interaction to make the supported VPO more selective to maleic anhydride production. When compared to VP$_{1.6}$O$_x$/SiO$_2$, VP$_{1.6}$O$_x$/AlPO$_4$ showed a lower activity in overoxidation. Increasing the reaction temperature from 400 to 500°C caused little selectivity loss on VP$_{1.6}$O$_x$/AlPO$_4$. While on VP$_{1.6}$O$_x$/SiO$_2$, a temperature increase over 450°C resulted in significant overoxidation and the loss of maleic anhydride selectivity. © 1989 Academic Press, Inc.

INTRODUCTION

Vanadium–phosphorus oxide (VPO) catalyst is catalytically active in making maleic anhydride from C$_4$ hydrocarbons via selective oxidation (*1, 2*). Its industrial importance resulted in intensive studies in recent years, mainly concentrated on catalyst preparation (*3–5*) and activation (*4–6*), the effect of P/V ratio (*7–9*), the search for active phases (*10–12*), and the reaction mechanism (*13–16*). Most studies were made on unsupported VPO catalysts.

The reaction, however, is strongly exothermic. The theoretical heat of reaction is −1315 kJ/mole based on the reaction

$$C_4H_8 + 3O_2 \rightarrow C_4H_2O_3 + 3H_2O$$
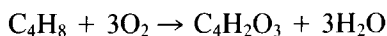
The practical heat release is even higher due to a significant extent of overoxidation to carbon oxides. For this highly exothermic reaction, a fluidized reactor is particularly advantageous for its good heat transfer characteristics. Problems like hot spot and run-away that occur in a fixed-bed reactor can be avoided. For fluidized operation, however, a supported catalyst is usually needed. Supported VPO catalysts have been studied and reported in the literature.

Silica has been used as the support material in most studies (*17–22*), and only a very limited number of studies used other supports like alumina (*3, 23*), titania (*24, 25*), and zeolites (*26*). Silica, due to its weak thermal stablity, is not practically a good support material for VPO catalysts, which may suffer from a serious local heating within the catalyst particles. Also, with a system of easy overreaction, pore diffusion resistance should be minimized to reduce the degree of overreaction. An ideal support should therefore have high thermal stability and large pores. With this in mind, our attention was drawn to aluminum phosphate (AlPO$_4$), a material with good thermal stability and large pores.

Aluminum phosphate belongs to a family of recently developed high-surface-area support material, aluminophosphate. This group of materials received an intensive study in recent years as potential supports for polymerization catalysts (*27, 28*) and hydrogenation catalysts (*29*). The material is usually made by coprecipitation of Al^{3+} and PO$_4^{3-}$ from an aqueous solution by controlling the pH value of the solution and followed by high-temperature calcination of the precipitate. When excess Al^{3+} is present in the solution, the precipitation usually results in the formation of alu-

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minophosphate with a P/Al ratio lower than 1.0. When PO_4^{3-} is in sufficient excess, however, $AlPO_4$ with P/Al ratio equal to unity is always obtained (30). Aluminophosphates thus prepared are amorphous in general, although a certain degree of crystallinity can be developed after high-temperature calcination (31). The specific surface area and average pore diameter of this material can be well controlled by varying the P/Al ratio of the precipitate. As reported by Cheung et al. (30), samples with specific surface area from 100 to 450 m^2/g and average pore diameter from 0.01 to 0.1 μm can be made. The largest pore diameter is achieved when the P/Al ratio reaches unity. Another characteristic property of this material is its good thermal stability. Take $AlPO_4$ as an example: calcination from 200 to 800°C resulted in a loss of surface area in less than 10% (30).

Another possible advantage of using $AlPO_4$ as the support for VPO is the possible interaction between VPO and phosphorus in $AlPO_4$. VPO catalysts are known to deactivate in long-term use due to the sublimation of phosphorus oxide (32). While $AlPO_4$ is thermally stable, its interaction with VPO, if it exists, could be long lasting.

In this paper, we report the results of our study on $AlPO_4$ as a support for VPO catalysts. Silica-supported and unsupported VPO were also studied for comparison. Selective oxidation of 1-butene to maleic anhydride was chosen as the test reaction.

EXPERIMENTAL

Synthesis of $AlPO_4$

$AlPO_4$ was made by the coprecipitation method. $Al(NO_3)_3 \cdot 9H_2O$ (Merck, 98.5%) was dissolved into doubly distilled water to form a 0.5 M solution and then mixed with 85% $H_3PO_{4(aq)}$ (Merck, GR) in a suitable amount. The solution was then added drop by drop to a 14.5% $NH_4OH_{(aq)}$ (Merck, GR) solution with vigorous stirring to form the precipitate. The pH value was maintained

at 9.0 throughout the precipitation process by adding concentrated $NH_4OH_{(aq)}$. The precipitate was filtered and dried at 120°C for 12 hr, and then ground and sieved. After calcination in air at 500 and 900°C for 16 hr each, the material was sieved once more. Only those with sizes in the range 100–200 mesh were used as the support materials.

By varying the P/Al ratio of the mother solution, one can obtain precipitates with different P/Al ratios. In this paper, however, $AlPO_4$ with P/Al ratio 1.0 is our greatest concern.

Preparation of VPO Catalysts

VPO catalysts were made following the method of Nakamura et al. (3). Specifically, 0.9 g of NH_4VO_3 (Merck, 99%) and 2.5 g d-tartaric acid (Shimakyu, 99.7%) as the reducing agent were dissolved into 10 ml water in a round flask by a 110°C reflux for 2 hr. A suitable amount of 85% H_3PO_4 (Merck, GR) was then added and refluxed for another 6 hr. The resulting solution was dark green and ready for impregnation. The impregnation was performed on $AlPO_4$ and silica simultaneously with the same solution under conditions of incipient wetness. Silica was obtained from Alfa U.S.A., with specifications similar to those of Davison 952. Only 100–200 mesh powder was used for the impregnation. After impregnation, the catalysts were dried at 120°C for 12 hr and calcined in air at 600°C for 4 hr.

If the refluxed solution was allowed to dry naturally at room temperature, the unsupported VPO catalyst was obtained. The catalyst was further dried at 120°C for 12 hr, ground and sieved into 100–200 mesh, and calcined in air at 600°C for 4 hr.

For the preparation of supported vanadium oxide (VO_x) catalysts, the same procedure was followed except that no H_3PO_4 was added.

Physical Characterizations and Composition Analysis

All supports and catalysts prepared in this study were characterized by X-ray dif-

fraction to investigate their crystallographic properties. A Shimadzu XD-5 diffractometer with a Cu target was used for this purpose. The specific surface areas of supports were measured by the traditional BET method with volumetric nitrogen adsorption. The pore size distributions of support materials were measured by the mercury penetration method on an Autopore II 9220. Powder was first pressed into a disk in a die and then crushed into granules for penetration measurement. The cation compositions of aluminophosphates and of supported VPO catalysts were measured by ICP-AES on a Kontron S-35. Materials were first dissolved by aqua regia and then diluted to a concentration of about 100 ppm for measurement. In this way, aluminophosphates and $VPO/AlPO_4$ were completely dissolved, while VPO/SiO_2 never reached complete dissolution. Some white silica powder remained undissolved even after a long period of time.

Catalytic Characterizations

VPO catalysts on different supports were catalytically characterized in a flow reactor under steady-state reaction conditions. The catalyst was loaded on a sintered glass disk in a Pyrex U-tube reactor, with reaction fluid flowing upward. The sintered disk served as a distributor as well as a good preheater. The catalyst usually formed a bed of less then 5 mm in thickness. Before reaction, the flow rates of 1-butene, oxygen, and helium were carefully set by adjusting fine needle valves with the reactor bypassed. Some experiments were done by using mass flow controllers instead of needle valves. Typical flow rates were 5, 20, and 100 ml/min for 1-butene, oxygen, and helium, respectively. For good mixing, the flow passed a glass bead column before passing through the reactor. After a steady flow was obtained, it was conducted through the reactor and the reactor temperature was carefully raised to the desired level in a few minutes. Because of the strong exothermic nature of the reaction,

reactor temperature can be overshot easily. Careful and skillful control of temperature is needed.

The reaction products were on-line analyzed by gas chromatography. The GC system was constructed following the original design by Muller and Baerns (33). Specifically, two 1-ml pulses of products were injected into the GC system simultaneously by using a 10-way valve. One pulse was carried by nitrogen flowing through a 3 ft × ¼ in. stainless-steel column packed with 22.5% di(2-ethylhexyl)sebacate- and 2.5% sebacic acid-coated Chromosorb W AW (80–100 mesh) and then to a flame ionization detector. This column and the injection valve were kept at 100°C in an isothermal oven with forced convection. Product line after the reactor was also well heated to avoid condensation of high boiling point products. Molecules analyzed by this column included furan, isobutylaldehyde, α-methylacrylaldehyde, butanone, acetic acid, propionic acid, acrylic acid, and maleic anhydride. The second pulse was carried by a flow of helium through a precolumn packed with Chromosorb at 0°C before reaching one of two separation columns. If CO_2 and C_4 hydrocarbons (butene isomers and butadiene) were to be analyzed, a 4 ft × ¼ in. copper column packed with 20% dimethylsulfolane-coated Chromosorb W AW (60–80 mesh) at 0°C was used. If CO was to be analyzed, a 2 ft × ¼ in. copper column packed with 60–80 mesh molecular sieve 13X at room temperature was used. Usually the two columns were switched alternately for the analysis of both CO and CO_2. A thermal conductivity detector kept at room temperature served for the detection.

In addition to GC analysis, high boiling point products including maleic anhydride, acetic acid, and propionic acid were collected in a condensed phase and further confirmed by mass spectrometry. Blank tests on the empty reactor and support alone showed little butene oxidation activity between 400 and 500°C.

If catalyst activation was to be per-
formed, the reactor temperature was first
raised to 550°C for 2 hr and then lowered to
the desired reaction temperature. The prod-
uct analysis was first made about $\frac{1}{2}$ hr after
reaction temperature was reached and then
continued once every $\frac{1}{2}$ hr. At each reaction
temperature, steady state was usually
reached within 2 hr. After that, the reactor
temperature was further lowered to another
reaction temperature and the product anal-
ysis repeated. If catalyst activation was not
performed, the reactor temperature was
first raised to 400°C for steady-state analy-
sis and then further raised stepwise.

RESULTS AND DISCUSSION

The Support Material AlPO₄

Precipitation of aluminophosphate was
studied with the P/Al ratio of mother solu-
tion varied from 1 to 6. The rate of precipi-
tation was decreased as the P/Al ratio in-
creased. Eventually, as the P/Al ratio
reached 4 and higher, no stable precipitate
was obtained. Listed in Table 1 are some
properties of the precipitates after high-
temperature calcination. Silica is also
added for comparison. As can be seen in
Table 1, precipitation from a mother solu-
tion of P/Al ratio 1.0 resulted in a precipi-
tate with P/Al ratio 0.8 and is denoted as
$AlP_{0.8}O_x$. From mother solutions of P/Al ra-
tios 1.5 and 3.0, AlPO₄'s having the same
P/Al ratio 1.0 were formed, but with very
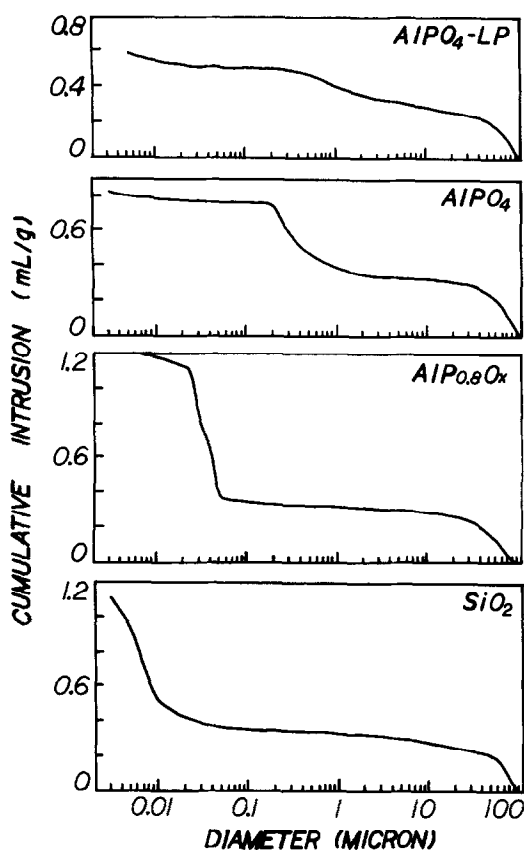different properties. The one made from

FIG. 1. Pore size distributions of several support
materials.

mother solution of P/Al ratio 1.5 is denoted
as AlPO₄, and that of P/Al ratio 3.0 is de-
noted as AlPO₄-LP for its larger pores.
Results of pore size distribution measure-
ments are given in Fig. 1. Initial intrusions
at about 100 μm in all samples were the
intrusions into interstices formed in the
pressing of powder. With this neglected,
reasonably narrow pore size distributions
were observed on all samples except
AlPO₄-LP. Figure 1 shows clearly that by
an increase in the P/Al ratio of mother solu-
tion, the pore size of the precipitate was
increased and the pore volume decreased
accordingly. Parallel shrinkage in the BET
surface area was also observed, as can be
seen in Table 1. Note that in both AlPO₄

TABLE 1

Physical Properties of Several Support Materials

Support material	P/Al ratio of mother solution	P/Al ratio of the precipitate	BET surface area (m²/g)	Pore volume[a] (ml/g)
AlPO₄-LP	3.0	1.0	6	0.25
AlPO₄	1.5	1.0	60	0.6
AlP₀.₈Oₓ	1.0	0.8	90	0.9
SiO₂	—	—	300	0.8

[a] Based on mercury penetration measurement, from pore
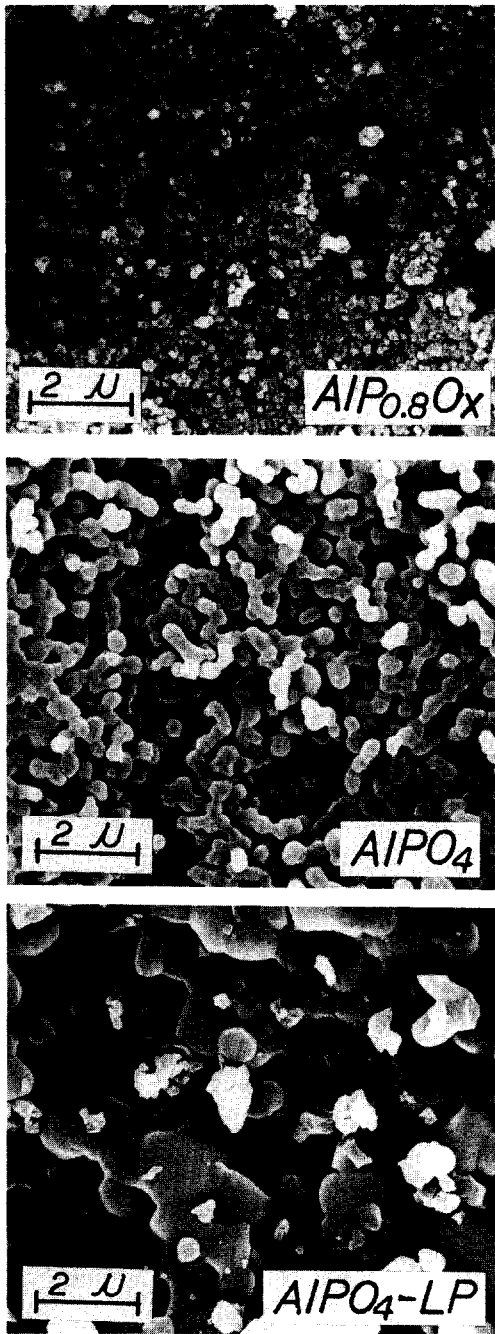diameter 10 to 0.005 μm.

FIG. 2. Scanning electron micrograph of AlP$_{0.8}$O$_x$, AlPO$_4$, and AlPO$_4$-LP.

and AlPO$_4$-LP, the volume of pores smaller than 0.1 μm in diameter was negligibly small (less than 0.05 ml/g). This is quite unique and different from others' results. AlPO$_4$ prepared by Cheung et al. (30) from Al(NO$_3$)$_3$ showed a pore volume of about 1.2 ml/g in the corresponding range of pore diameter. Starting from AlCl$_3$, AlPO$_4$ prepared by Campelo et al. (31) also resulted in a pore volume of about 0.5 ml/g within the same range of pore size. This difference in pore size distribution must be related to the differences in precipitation conditions. For our samples, the difference in pore size distribution is believed to result from the difference in the precipitation rate. As the P/Al ratio increased, the precipitation rate was decreased, resulting in a fewer number, a slower growth, and a larger size of the precipitation particles. This can be clearly seen in the scanning electron micrograph given in Fig. 2. Note that the material consisted of particles rather uniform in size and shape, and the pores were basically the interstices of the particles. The materials were all amorphous when just precipitated, and remained amorphous after 500°C calcination in air. Further calcination to 900°C resulted in the development of some crystallinity. The X-ray diffraction patterns are in good agreement with those reported in the literature (30, 31).

The VPO Catalysts

Supported VPO catalysts were prepared by incipient wetness impregnation. The optimum range of P/V ratio reported by Nakamura et al. (3) on their VPO/α-Al$_2$O$_3$ was between 1.5 and 1.8. In this study, two P/V ratios, 1.6 and 1.1, were selected and the P/V ratios of the resulting VPO catalysts were confirmed by ICP-AES as shown in Table 2. VPO catalysts with P/V ratio 1.6 are denoted as VP$_{1.6}$O$_x$ and those with P/V ratio 1.1 are denoted as VP$_{1.1}$O$_x$. Also given in Table 2 are the colors and the loadings of the VPO catalysts assuming that they were in the most oxidized form of V$_2$O$_5$-P$_2$O$_5$. The dispersions of the catalysts, however, are not known. The only information we have about the dispersion was obtained from X-ray diffraction. While the unsup-

TABLE 2

List of Catalysts and the P/V Ratios

Catalyst denotation	P/V ratio of impregnation solution	P/V ratio of calcined catalyst[a]	Color
Unsupported $VP_{1.6}O_x$	1.6	1.65	Dark green
14% $VP_{1.6}O_x$/AlPO$_4$	1.6	1.55	Grayish green
21% $VP_{1.6}O_x$/SiO$_2$	1.6	1.65	Green
12% $VP_{1.1}O_x$/AlPO$_4$	1.1	1.08	Yellow
18% $VP_{1.1}O_x$/SiO$_2$	1.1	1.13	Brown
7% VO_x/AlPO$_4$	0	0	Yellow
11% VO_x/SiO$_2$	0	0	Orange

[a] For AlPO$_4$ supported catalysts, P in AlPO$_4$ has been appropriately substracted.

ported VPO catalysts showed clear crystallinity, VPO on both AlPO$_4$ and SiO$_2$, before and after reaction, gave no diffraction peaks. This indicated that the supported VPO particles were too small to give detectable diffraction. A reasonably good dispersion can therefore be expected. Nevertheless, since no quantitative measurement of the dispersion is available, no attempt is made to quantitatively compare the activities of different catalysts in this study. Comparison will be focused mainly on the selectivity under comparable degrees of conversion.

The Effect of Catalyst Activation

The effect of activation on the performance of VPO catalysts has been studied and reported by many authors (4–6). Activation of catalysts in reaction fluid at elevated temperatures usually results in a significant increase in both activity and selectivity, probably due to the reduction of VPO to a partially reduced state. The activation effect has been tested and confirmed on 14% $VP_{1.6}O_x$/AlPO$_4$ and 21% $VP_{1.6}O_x$/SiO$_2$ in this study. Catalysts after 550°C activation showed significantly higher activities and maleic anhydride selectivities than those without activation. Also, the conversion increase due to activation was accompanied by a decrease in the extent of overoxidation, indicating that the overoxidation activity of the catalyst was suppressed.

Therefore, the 550°C activation in reaction fluid was performed as a standard pretreatment for all other experiments.

The Effect of O_2/C_4 Ratio

Performance of VPO catalyst depends on the O_2/C_4 ratio in the reaction stream. By fixing the 1-butene flow rate at 4 ml/min and the total flow rate at 120 ml/min, we changed the O_2/C_4 ratio from 4 to 8 to study the effect of the O_2/C_4 ratio. On both 14% $VP_{1.6}O_x$/AlPO$_4$ and 21% $VP_{1.6}O_x$/SiO$_2$, the results indicated an increase in conversion with increase in the O_2/C_4 ratio. The maleic anhydride selectivity was only slightly changed from O_2/C_4 ratio 4 to 6, but largely suppressed when the O_2/C_4 ratio was further raised to 8, along with a significant increase in total oxidation to carbon oxides. This result is in agreement with that of Nakamura et al. (3), who found an optimal O_2/C$_4$ ratio of 4 on their VPO/α-Al$_2$O$_3$. On the basis of this test, the O_2/C_4 ratio was kept between 4 and 6 for the rest of this study.

The Dependency of Selectivity on Conversion

The dependency of selectivity on conversion was studied by varying the catalyst amount under fixed reaction conditions. Our studies on both 14% $VP_{1.6}O_x$/AlPO$_4$ and 21% $VP_{1.6}O_x$/SiO$_2$ showed a strong dependency of selectivity on conversion, especially in the low-temperature region. In general, the maleic anhydride selectivity was increased with the increase in conversion, until the conversion approached 100%. Further doubling the amount of catalyst resulted in a larger production of carbon oxides, but the maleic anhydride selectivity was only slightly affected. The fact that maleic anhydride selectivity increased along with the conversion increase suggests that maleic anhydride is formed after multistep reactions. Increasing the conversion helped to convert more reaction intermediates into maleic anhydride. The extent of overoxidation was of course increased as well. Since the maleic anhydride selectivity
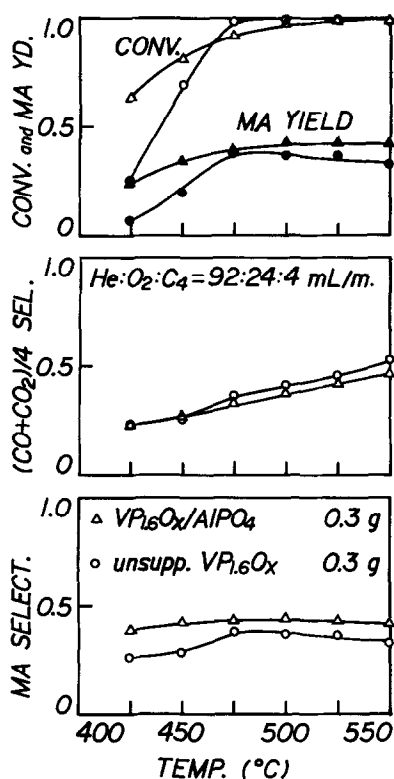
FIG. 3. Comparison between 14% VP$_{1.6}$O$_x$/AlPO$_4$ and unsupported VP$_{1.6}$O$_x$.

approached maximum when conversion approached 100%, most comparisons of different catalysts in this study were made at high conversions.

Comparison between VP$_{1.6}$O$_x$/AlPO$_4$ and Unsupported VP$_{1.6}$O$_x$

Figure 3 compares the performance of 14% VP$_{1.6}$O$_x$/AlPO$_4$ to that of unsupported VP$_{1.6}$O$_x$ under comparable extents of conversion. The performance of catalyst is presented by four important parameters: the conversion, the maleic anhydride selectivity, the degree of overoxidation to CO and CO$_2$, and the yield of maleic anhydride. All calculations were made on a molar basis, and all products were normalized to C$_4$ equivalent quantities. Selectivities to other products are not given in this paper, but are available elsewhere (34). As can be seen in

the figure, the two catalysts showed different dependencies on reaction temperature. While the conversion of VP$_{1.6}$O$_x$/AlPO$_4$ decreased slowly and smoothy with a decrease in reaction temperature, that of unsupported VP$_{1.6}$O$_x$ dropped sharply. The product distributions from the two catalysts followed, however, a similar pattern. The carbon oxide production increased monotonically with increasing temperature, while the selectivity to maleic anhydride increased to a maximum at a certain temperature and then started to drop at further higher temperatures.

The strong dependency of conversion on reaction temperature is rather unique on unsupported VPO catalysts. In the temperature range 400–550°C, no similar behavior was observed in this study on any supported VPO catalysts.

Comparison between VPO/AlPO$_4$ and VPO/SiO$_2$

Figure 4 compares the performance of 14% VP$_{1.6}$O$_x$/AlPO$_4$ with that of 21% VP$_{1.6}$O$_x$/SiO$_2$. At comparable degrees of conversion close to 100%, VP$_{1.6}$O$_x$/AlPO$_4$ showed a lower extent of overoxidation and a higher selectivity to maleic anhydride. Another important feature that makes 14% VP$_{1.6}$O$_x$/AlPO$_4$ superior than 21% VP$_{1.6}$O$_x$/SiO$_2$ is the steady maleic anhydride selectivity over a wide range of reaction temperatures. On 21% VP$_{1.6}$O$_x$/SiO$_2$, the optimum maleic anhydride production was achieved around 450°C. Either an increase or a decrease in reaction temperature resulted in a drop in maleic anhydride yield. On 14% VP$_{1.6}$O$_x$/AlPO$_4$, however, the selectivity and the yield of maleic anhydride were practically unchanged from 400 to 500°C, although a slight increase in overoxidation with increasing temperature was observed. The temperature insensitivity of VP$_{1.6}$O$_x$/AlPO$_4$ on maleic anhydride selectivity is particularly advantageous for this highly exothermic reaction. A better stability in reactor operation can be expected.

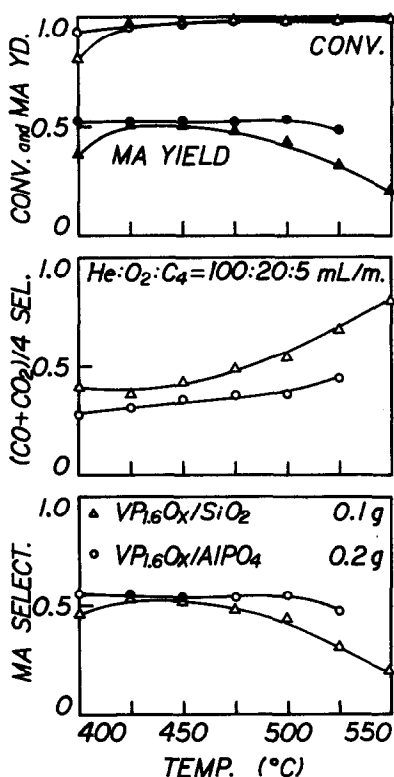A possible reason for the better perfor-

FIG. 4. Comparison between 14% $VP_{1.6}O_x/AlPO_4$ and 21% $VP_{1.6}O_x/SiO_2$.

reaction conditions. Without phosphorus, vanadium oxide on silica showed mainly overoxidation activity and practically no activity for maleic anhydride production, as can be seen in Fig. 5. The 7% $VO_x/AlPO_4$, however, produced a significant amount of maleic anhydride. This result has thus confirmed the existence of interaction between phosphorus in $AlPO_4$ and the supported vanadium oxide. The interaction could result from either direct contact of vanadium oxide with $AlPO_4$ at the interface or bulk phase reaction between the two materials.

To further confirm that the better performance of $VP_{1.6}O_x/AlPO_4$ over $VP_{1.6}O_x/SiO_2$ that we observed was not a special case specific to VPO with P/V ratio 1.6, we made a similar comparison on catalysts with P/V ratio 1.1. Although phosphorus was deficient and overoxidation activity
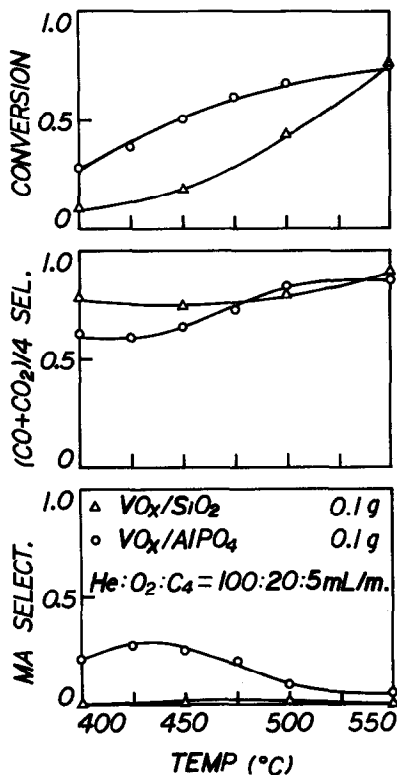
mance of $VP_{1.6}O_x/AlPO_4$ is its large pore diameter, making the pore diffusion easier and therefore reducing the degree of overoxidation. Another possible reason is the effect of phosphorus in $AlPO_4$. Although $AlPO_4$ is thermally stable, phosphorus on the surface of $AlPO_4$ can still be in direct contact with the supported VPO particles. Interaction between P in $AlPO_4$ and V in VPO particles is therefore anticipated. As was discussed in the literature (2, 3, 7), phosphorus helps stabilize vanadium to a partially reduced state, thus making the catalyst more selective to maleic anhydride production. Extra phosphorus, however, decreases the catalyst activity.

To further study the possible interaction between P in $AlPO_4$ and V in VPO, we compared the performance of 7% $VO_x/AlPO_4$ and that of 11% VO_x/SiO_2 under the same

FIG. 5. Comparison between 7% $VO_x/AlPO_4$ and 11% VO_x/SiO_2.

was strong, the superior performance of 12% VP$_{1.1}$O$_x$/AlPO$_4$ over 18% VP$_{1.1}$O$_x$/SiO$_2$ was clearly observed. At about 90% conversion, maleic anhydride selectivity on VP$_{1.1}$O$_x$/AlPO$_4$ was about 30% higher than that on VP$_{1.1}$O$_x$/SiO$_2$.

After reaction, VP$_{1.6}$O$_x$/SiO$_2$ turned black. The color change was believed to be due to the reduction of VPO but not to coking. By calcination in flowing oxygen at 500°C, VP$_{1.6}$O$_x$/SiO$_2$ resumed its original color with little CO$_2$ produced. A similar color change for VP$_{1.6}$O$_x$/AlPO$_4$ was also observed, but to a lesser extent. Also observed was a certain degree of agglomeration on VP$_{1.6}$O$_x$/SiO$_2$, but not on VP$_{1.6}$O$_x$/AlPO$_4$. This is probably due to the weak thermal stability of silica and possible chemical attack at high temperatures by phosphorus oxide on silica in the presence of water vapor.

Effect of P/Al Ratio of the Aluminophosphate Support

Catalytic performances of VP$_{1.6}$O$_x$/AlP$_{0.8}$O$_x$ and VP$_{1.6}$O$_x$/AlPO$_4$-LP were also studied in the temperature range 400–550°C for a comparison with VP$_{1.6}$O$_x$/AlPO$_4$. At almost identical conversion, the production of carbon oxides on VP$_{1.6}$O$_x$/AlPO$_4$-LP was about 15% less than that on VP$_{1.6}$O$_x$/AlPO$_4$, while the maleic anhydride selectivities were practically the same. This lower carbon oxide production on VP$_{1.6}$O$_x$/AlPO$_4$-LP can be attributed to its larger pores which allow a faster diffusion of product molecules, and thus a lower extent of overoxidation. With smaller pores, VP$_{1.6}$O$_x$/AlP$_{0.8}$O$_x$ showed a much stronger overoxidation activity and a lower selectivity to maleic anhydride than VP$_{1.6}$O$_x$/AlPO$_4$, forming a consistent correlation of overoxidation activity to pore size.

However, AlP$_{0.8}$O$_x$ has a P/Al ratio of 0.8 and is deficient in phosphorus. Possible chemical reaction between VPO and AlP$_{0.8}$O$_x$ could occur to redistribute phosphorus. The P/V ratio of the VPO would then decrease and result in an increase in overoxidation activity. Taken as a limiting case, VP$_{1.6}$O$_x$/γ-Al$_2$O$_3$ was similarly prepared and its catalytic performance studied. At about 50% conversion, the selectivity to maleic anhydride was less than 10% and that to carbon oxides over 80%. This observation is in agreement with our expectation and provides an additional explanation for the poor performance of VP$_{1.6}$O$_x$/AlP$_{0.8}$O$_x$.

Nakamura et al. (3) studied VPO/α-Al$_2$O$_3$ catalysts. α-Al$_2$O$_3$ is thermally stable and large in pore diameter. Although the reaction conditions were not exactly the same, comparison of the performance between VP$_{1.6}$O$_x$/AlPO$_4$ and VPO/α-Al$_2$O$_3$ can still be made under similar conditions. With conversion close to 100%, Table 3 compares the maleic anhydride yields from VP$_{1.5}$O$_x$/α-Al$_2$O$_3$, VP$_{1.6}$O$_x$/SiO$_2$, and VP$_{1.6}$O$_x$/AlPO$_4$ at varying temperatures. Although the differences are not very large, the performance of VP$_{1.5}$O$_x$/α-Al$_2$O$_3$ fell in a pattern different from that of VP$_{1.6}$O$_x$/AlPO$_4$, but similar to that of VP$_{1.6}$O$_x$/SiO$_2$, with an optimum obtained at 450°C.

Although the above discussion is based on the results of 1-butene oxidation, the superiority of AlPO$_4$ over silica is also anticipated in butane oxidation. An even more pronounced effect is expected since a higher reaction temperature is usually needed for butane oxidation. On the method of catalyst preparation, VPO catalysts prepared in organic solvents have

TABLE 3

Comparison of the Catalytic Performances of α-Al$_2$O$_3$, SiO$_2$, and AlPO$_4$ Supported VPO Catalysts[a]

Catalyst	P/V ratio	Maleic anhydride yield (mol%)		
		400°C	450°C	500°C
VP$_{1.5}$O$_x$/α-Al$_2$O$_3$	1.50	43	50	44
21% VP$_{1.6}$O$_x$/SiO$_2$	1.65	47[b]	51	45
14% VP$_{1.6}$O$_x$/AlPO$_4$	1.55	52	53	54

[a] O$_2$/C$_4$ = 4, conversion maintained above 96% for all experiments except [b].
[b] At 81% conversion.

been shown recently to be more active and selective than those from aqueous solution (2). Although it has not been verified experimentally, AlPO$_4$ is believed suitable for organic preparation of VPO catalysts as well.

CONCLUSION

In this study we have demonstrated that AlPO$_4$ can be used as a good support material for VPO catalysts. The advantages of using AlPO$_4$ as the support include (i) strong thermal stability suitable for highly exothermic reactions with possible local heating within catalyst particles, (ii) large pore diameter to minimize pore diffusion resistance and therefore the degree of overoxidation, and (iii) positive interaction between VPO and AlPO$_4$ to make the supported VPO more selective to maleic anhydride production.

When compared to VP$_{1.6}$O$_x$/SiO$_2$, VP$_{1.6}$O$_x$/AlPO$_4$ showed a much wider temperature range for stable operation. Increasing the reaction temperature from 400 to 500°C caused little selectivity loss on VP$_{1.6}$O$_x$/AlPO$_4$. While on VP$_{1.6}$O$_x$/SiO$_2$, a temperature increase over 450°C resulted in significant overoxidation and the loss of maleic anhydride selectivity. Phosphates of metals other than AlPO$_4$, especially FePO$_4$ and CrPO$_4$, are of interest as well. We shall report the results of our studies on other phosphates in the near future.

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