ELSEVIER

Catalysis Today 49 (1999) 161–169

CATALYSIS TODAY

Selective oxidation of light hydrocarbons over promoted vanadyl pyrophosphate

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Abstract

The catalytic behaviour of vanadyl pyrophosphate in the conversion of either *n*-butane, 1-butene, *n*-pentane or 1-pentene is reported. The results obtained indicate that the product selectivity and hydrocarbon conversion can be changed by varying the temperature and GHSV. The choice of doping elements has a significant effect on hydrocarbon conversion and product yield, much more than surface area. The maleic anhydride yield increases strongly with an increase in catalyst acidity when *n*-butane and *n*-pentane are feed materials. With the corresponding olefins the effect due to acidity is insignificant.

Keywords: Selective oxidation; Light hydrocarbons; Vanadyl pyrophosphate

1. Introduction

Bergman and Frisch [1] demonstrated in the mid 1960s that butane could be oxidised to maleic anhydride using vanadium phosphorus mixed oxides as the catalyst system. Initially, in the late 1960s, this process did not attract much attention because the benzene to maleic anhydride route was well established and more cost effective. However, the following factors contributed to *n*-butane gradually replacing benzene as the preferred feedstock for the production of maleic anhydride:

- decreasing cost of *n*-butane;
- increasing cost of benzene;
- increasing environmental concerns over benzene emissions.

The vanadium phosphorus oxide (VPO) catalyst system is the only system that has been found to be economically viable for the heterogeneous oxidation of *n*-butane to maleic anhydride. The annual worldwide production of maleic anhydride amounts to about 750 000 t and demand for maleic anhydride will continue to grow at approximately 5% per annum [2,3]. However, two new outlets could have a major influence on the economics of maleic anhydride, firstly the use in sequestering additives and secondly the conversion of maleic anhydride to important C_4 intermediates, viz. 1,4 butanediol, tetrahydrofuran and gamma butyrolactone.

Another attractive option would be to investigate the oxidation of C_5 hydrocarbons to maleic and phthalic anhydride. Phthalic anhydride is currently produced using *ortho*-xylene as feedstock, and an economic incentive could be obtained if C_5 hydrocarbons could be used as the feed material, also there

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PII: S0920-5861(98)00420-9

may be environmental concerns regarding the use of xylene.

Currently in most commercial plants the maleic anhydride yield is approximately 50%, it is obvious that improvements in the conversion of butane and maleic anhydride selectivity are desired [3]. One way of achieving these aims is by developing a better catalyst for *n*-butane oxidation to maleic anhydride.

As part of our on going studies that are directed towards VPO catalyst development for oxidation of hydrocarbons, a series of modified VPO catalysts were prepared. The promoter combinations were selected to yield catalysts with differing degrees of acidity, surface area and redox capabilities. The results for five of these catalysts are reported.

2. Experimental

2.1. Catalyst preparation

The catalysts are prepared in an organic medium, a solution of benzyl alcohol and isobutanol is added to V_2O_5 and the different metal promoters (M^{n+}=Ce, Zr, Bi, Mn, Mo, Cr) added as either the nitrate or the chloride (see Table 1). The mixture is refluxed with stirring for 7 h, cooled to room temperature and stirred overnight. Ninety-eight percent H_3PO_4 is added and stirred under reflux for 3 h. The mixture is cooled and the precipitate is removed by filtration. The precipitate is washed thoroughly with water (approx. 5l) and the blue solid oven dried for 12 h.

2.2. Calcination of catalyst

Twenty-five g of the catalyst precursor $VOHPO_4 \cdot \frac{1}{2}H_2O$ is calcined at a time. An inert gas like argon or nitrogen is used and the flow rate set at approximately 6 ml min^{-1}. The temperature is increased from room temperature to 300°C over a period of 3 h, it is maintained at 300°C for 2 h, then increased from 300°C to 450°C over a period of 3 h and maintained at 450°C for 6 h. Finally it is then reduced to room temperature. XRD studies are used to verify that $VOHPO_4 \cdot \frac{1}{2}H_2O$ is converted to $(VO)_2P_2O_7$.

Table 1
Molar percentage composition of metal promoters

Catalyst	Ce	Zr	Bi	Mn	Mo	Cr
VPS1	5	1				1
VPS2	5		1	5		
VPS3	5	1.25				1.25
VPS4	5			5	5	

2.3. Catalytic testing

Catalytic tests are carried out in a fixed bed microreactor at atmospheric pressure. The microreactor is loaded with 1.5 g of calcined VPO catalyst. The different feed mixtures to the reactor consist of 1.3% (v/v) *n*-butane in air, 1.2% 1-butene in air, 0.9% *n*-pentane in air and 0.9% 1-pentene in air. The concentration of hydrocarbon in air lies below the explosion limit for each hydrocarbon. Percentage selectivity and yield have been calculated on a molar basis.

After loading the catalyst, an air-flow is introduced into the microreactor, the initial GHSV was 1000 h^{-1} and the temperature was slowly increased from 25°C to 250°C. The butane–air mixture is introduced into the system at 250°C at a GHSV of 1000 h^{-1}; the temperature is increased to 350°C at 2°C min^{-1}. At 350°C, the GHSV of the butane–air mixture is increased to 2500 h^{-1}. The reactor temperature is increased by 10°C h^{-1} until a temperature of 400°C is attained. Studies with butene and the C_5 hydrocarbons are carried out on catalysts that were already equilibrated with *n*-butane.

2.4. Catalyst characterisation

The total acidity was determined using NH_3 TPD, and results reported in mmol NH_3 adsorbed per gram of catalyst. The calcined and uncalcined catalysts were also characterised using XRD, SEM, BET surface area and ICP elemental analysis.

3. Results and discussion

It is widely accepted that $(VO)_2P_2O_7$ is the active catalyst for that selective oxidation of *n*-butane to maleic anhydride. The reaction mechanism involves a series of H-abstraction and O-insertion steps and may be outlined as follows [4]:

$$n\text{-butane} \rightarrow \text{butenes} \rightarrow \text{butadiene} \rightarrow \text{tetrahydrofuran} \rightarrow \text{furan} \rightarrow \text{maleicanhydride}$$

The reaction mechanism for C_5 oxidation to maleic and phthalic anhydride is possibly similar to that of the synthesis of maleic anhydride from *n*-butane, but probably involves the additional step of C–C bond formation [5].

Initial studies were carried out on two catalysts to investigate the effect of changes in temperature and GHSV on conversion and product selectivity. The two catalysts (VPS1 and VPS2) differ with respect to the promoters added, surface area and total acidity.

3.1. Butane oxidation

The experimental runs for butane oxidation were carried out at three different temperatures, 380°C, 400°C and 420°C; at each temperature the GHSV was varied between 1000 and 2500 h^{-1}.

As expected, increasing the temperature results in a steady increase in conversion while an increase in GHSV results in a decrease in conversion over both catalysts. Increasing the temperature or GHSV has an effect on the selectivity to the different products (see Tables 2 and 3). When VPS1 is used as the catalyst, the maximum maleic anhydride selectivity is obtained at 380°C with a GHSV of 1750 h^{-1}, and increasing the temperature results in a small decrease in maleic anhydride selectivity. Increasing the GHSV results in an increase in maleic anhydride and acetic acid selectivity.

The results obtained with the two catalysts are significantly different at similar conditions. These differences in conversion and selectivity are probably due to the differences in the total acidity and surface area between the catalysts.

3.2. Butene oxidation

When butene was used as the feed gas, the runs were carried out at 400°C while the GHSV was varied between 1000 and 2500 h^{-1}, and a single run at 420°C with a GHSV of 2500 h^{-1}. The results obtained with VPS1 are listed in Table 4 while the results obtained with VPS2 are listed in Table 5.

When VPS1 is used as the catalyst at 400°C, the butene conversion and selectivity to acetic acid decrease as the GHSV is increased. However, the selectivity to maleic anhydride increases as the space velocity is increased. Increasing the temperature results in an increase in butene conversion and a reduction in maleic anhydride selectivity; this reduction in maleic anhydride selectivity is accompanied by an increase in carbon oxide selectivity.

When VPS2 is used as catalyst, the butene conversion and selectivity to acetic acid decrease as the GHSV is increased at 400°C. However, the selectivity to carbon oxides increases as the space velocity is increased. Increasing the temperature results in an increase in butene conversion and carbon oxide selectivity, this is accompanied by a reduction in maleic anhydride selectivity.

Higher butene conversion and maleic anhydride yields are obtained when VPS1 is used as catalyst.

Table 2
n-Butane oxidation over VPS1

Temperature (°C)	GHSV (h^{-1})	Conversion (%)	Maleic anhydride selectivity (%)	Acetic acid selectivity (%)	Butyric acid selectivity (%)
380	1000	85	22	0.5	6
	1750	75	37	2	0.6
	2500	70	35	2	0.5
400	1000	96	25	0.4	4
	1750	87	28	1	6
	2500	76	31	1	5
420	1000	90	22	0.5	0.4
	1750	86	25	0.5	0.2
	2500	81	30	0.4	0.6

Table 3
n-Butane oxidation over VPS2

Temperature (°C)	GHSV (h^{-1})	Conversion (%)	Maleic anhydride selectivity (%)	Acetic acid selectivity (%)	Butyric acid selectivity (%)
380	1000	67	33	1.13	3.23
	1750	66	40	2	3
	2500	60	43	7	2
400	1000	78	27	4	0.5
	1750	67	33	1	3
	2500	65	42	3	0.5
420	1000	74	35	0.6	0.4
	1750	80	44	0.7	1.8
	2500	72	32	0.6	0.4

Table 4
Butene oxidation over VPS1

Temperature (°C)	GHSV (h^{-1})	Conversion (%)	Maleic anhydride selectivity (%)	Acetic acid selectivity (%)
400	1000	90	41	6
	2500	67	71	2
420	2500	94	23	1

Table 5
Butene oxidation over VPS2

Temperature (°C)	GHSV (h^{-1})	Conversion (%)	Maleic anhydride selectivity (%)	Acetic acid selectivity (%)
400	1000	78	31	13
	2500	61	69	6
420	2500	84	13	4

Higher acetic acid yields are obtained over VPS2. One of the positive aspects was that these catalysts did not show any deactivation over the nine-week period that they were tested.

3.3. *Pentane oxidation*

The experiments were carried out at 325°C, 340°C, 360°C and 380°C, while the GHSV was varied between 750 and 1500 h^{-1} at each temperature. The objective was to try and maximise the total anhydride yield; a secondary objective was to try and produce maleic anhydride only by varying the operating conditions.

When VPS1 is used as the catalyst, the pentane conversion increases as the temperature is increased. A closer examination on the effect of temperature on selectivity to the anhydrides indicates that as the temperature is increased above 340°C, the total anhydride selectivity decreases. The GHSV also affects the selectivity to the anhydrides and acids (see Table 6).

In all the experiments carried out, increasing temperature and decreasing GHSV results in an increase

Table 6
Pentane oxidation over VPS1

Temperature (°C)	GHSV (h^{-1})	Conversion (%)	Maleic anhydride selectivity (%)	Phthalic anhydride selectivity (%)	Acetic acid selectivity
325	750	71	30	10	10
	1000	66	31	12	6
	1500	59	29	1	29
340	750	83	43	8	2
	1000	81	55	23	1
	1500	79	50	23	7
360	750	88	21	13	7
	1000	83	43	1	9
	1500	81	42	0	40
380	1000	92	19	3	22
	1500	88	36	1	14

in conversion. At 325°C there is no noticeable difference in selectivity to maleic anhydride, while the selectivity to phthalic anhydride decreases (after an initial increase) and the selectivity to acetic acid increases as the GHSV is increased. Increasing the temperature to 340°C results in maleic and phthalic anhydride selectivity reaching a maximum when the GHSV lies between 1000 and 1500 h^{-1}.

At 360°C, as the GHSV increases the selectivity to maleic anhydride increases. The selectivity to phthalic anhydride and acetic acid initially increase to a maximum and then decrease as the GHSV is increased above 1000 h^{-1}. The phthalic anhydride selectivity is lower than the acetic acid selectivity.

The maximum anhydride yield is obtained at a temperature of 340°C and GHSV of 1000 h^{-1}; the maleic anhydride yield is 45%, the phthalic anhydride yield is 19% and the acetic acid yield is 1%. Increasing the temperature to 380°C results in a higher conversion but also a large increase in selectivity to the carbon oxides and hence lower anhydride selectivities.

When VPS2 is used as the catalyst, the pentane conversion increases as the temperature is increased and the GHSV is decreased (see Table 7). At 325°C,

Table 7
Pentane oxidation over VPS2

Temperature (°C)	GHSV (h^{-1})	Conversion (%)	Maleic anhydride selectivity (%)	Phthalic anhydride selectivity (%)	Acetic acid selectivity (%)
325	750	60	24	9	26
	1000	52	34	15	29
	1500	42	23	1	15
340	750	67	37	27	16
	1000	60	48	14	28
	1500	52	52	10	17
360	750	78	28	0	20
	1000	74	32	4	30
	1500	71	46	1	23
380	1000	81	24	9	26
	1500	72	37	1	13

the acetic acid and the maleic and phthalic anhydride selectivities initially increase with increasing GHSV but decrease once the GHSV is increased above 1000 h^{-1}. It is also interesting to observe that the acetic acid selectivity is greater than the phthalic anhydride selectivity. At 340°C, as the GHSV is increased the maleic anhydride selectivity increases. The acetic acid selectivity reaches a maximum at GHSV=1000 h^{-1} and then decreases as GHSV increases. The phthalic anhydride selectivity decreases with increasing GHSV; at lower GHSV the phthalic anhydride selectivity is higher than acetic acid selectivity while as the GHSV is increased the acetic acid selectivity is greater.

At 360°C, as the GHSV increases, the selectivity to maleic anhydride increases. The selectivity to phthalic anhydride and acetic acid initially increases to a maximum and then decreases as the GHSV is increased above 1000 h^{-1}. The phthalic anhydride selectivity is lower than the acetic acid selectivity at all GHSV conditions tested.

The maximum anhydride yield is obtained at a GHSV of 750 h^{-1} and temperature of 340°C; the maleic anhydride yield is 25%, the phthalic anhydride yield is 18% and the acetic acid yield is 11%. The maximum maleic anhydride yield (33%) is obtained at a temperature of 360°C and a GHSV of 1500 h^{-1}. Increasing the temperature to 380°C results in a higher conversion but also a large increase in selectivity to the carbon oxides and hence lower anhydride selectivities.

It is evident from the results obtained that VPS1 is a better catalyst for the oxidation of pentane to maleic and phthalic anhydrides. Another difference is that the amount of acetic acid produced over VPS1 is not very large. The differences in pentane conversion and product selectivity are probably due to the fact that different promoters have been used in different catalysts. The difference in surface areas and total acidity could also play a role.

3.4. Pentene oxidation

The runs were carried out at 340°C and 360°C while the GHSV was varied between 750, 1000 and 1500 h^{-1} at each temperature. These temperatures were chosen because the best results were obtained for *n*-pentane oxidation at 340°C and 360°C.

When either VPS1 or VPS2 are used as catalysts the conversion of pentene increases as the GHSV is decreased or the temperature is decreased. In addition, with either catalyst maleic anhydride selectivity increases as the GHSV is increased while acetic acid selectivity decreases as GHSV increases. The selectivity to phthalic anhydride increases gradually as well, however the amount of phthalic anhydride formed is relatively small. Fig. 1 illustrates a typical example of the trends observed for conversion and product selectivity. The only difference in the results obtained for either catalyst lies in the fact that the conversion for VPS1 is higher than that obtained for VPS2.

A comparison with the oxidation of *n*-pentane shows that the per cent C_5 conversion for both pentane and pentene is similar. However, the amount of phthalic anhydride formed is less when pentene is the feed gas than when pentane is used. Another difference is that the amount of acetic acid that is formed at lower GHSV is higher when pentene is used as the feed gas, and acetic acid selectivity decreases as GHSV is increased when pentane is the feedstock.

Increasing the temperature results in an increase in conversion (for both catalysts); however, this is accompanied with a decrease in anhydride selectivity and hence an increase in selectivity to carbon oxides. It is apparent now that the oxidation of pentene occurs at lower temperatures and higher space velocities than the oxidation of pentane.

3.5. Effect of surface area

The experiments to determine the effect of surface area on hydrocarbon oxidation were carried out at 340°C for C_5 oxidation and 400°C for C_4 oxidation. The results in Table 8 indicate the influence of surface area on conversion. It is difficult to notice any particular trend for hydrocarbon conversion. It does not appear that an in increase in surface area results in an initial increase in conversion; however, after a certain maximum surface area has been attained, there does not seem to be any improvement in conversion. In general, the butene and pentene conversions are higher than the butane and pentane conversions at the same operating conditions, but it is possible that the changes in catalyst composition mask the surface area effect.

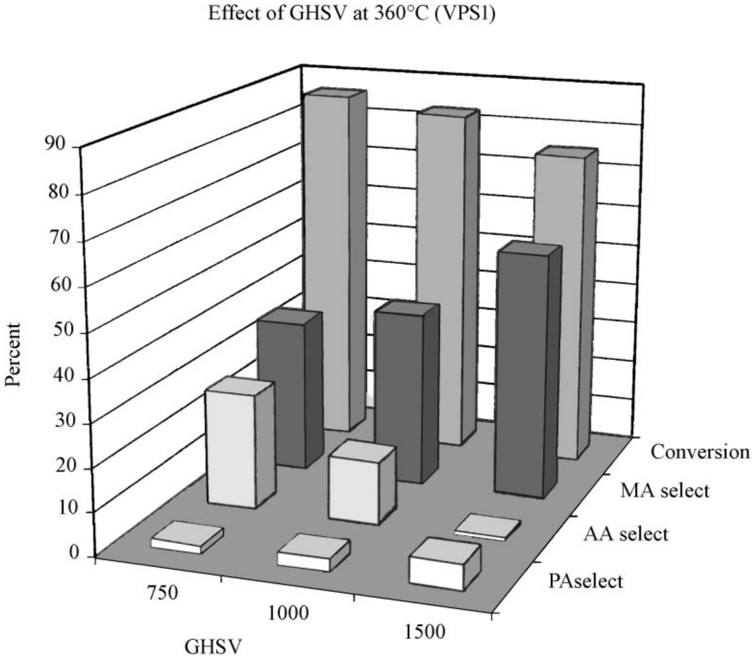

Fig. 1. The effect of GHSV on the oxidation of pentene over VPS1.

Table 8
Effect of surface area on hydrocarbon conversion

Catalyst	Surface area (m^2 g^{-1})	Butane conversion (%)	Butene coversion (%)	Pentane conversion (%)	Pentene conversion (%)
STD[a]	10	36	40	0	0
VPS1	11	87	90	85	85
VPS2	12.3	67	84	80	80
VPS3	19.3	55	84	62	85
VPS4	13	47	80	53	85

[a] Non-promoted VPO catalyst.

Figs. 2 and 3 illustrate the effect of surface area on selectivity to maletic and phthalic anhydride. It does not seem that increasing the surface area results in any significant difference in the maleic anhydride and phthalic anhydride yields.

3.6. *Effect of total acidity*

The effect of increasing total acidity on C_4 conversion is illustrated in Fig. 4. It is clear that an increase in the total acidity results in an increase in C_4 hydrocarbon conversion. A similar trend is observed for pentane conversion; however, changes in total acidity do not seem to affect the pentene conversion. It does appear that the effect of total acidity is more marked on the paraffins than the olefins. Total acidity strongly influences the yields of maleic anhydride in *n*-butane and *n*-pentane oxidation, higher yields are obtained with catalysts having higher acidity. This effect is insignificant in butene and pentene oxidation (see Table 9 and Fig. 4). These observations are consistent with the literature, where existence of catalyst acidity is imperative for the conversion of *n*-butane to maleic anhydride, but not for *n*-butane [6,7].

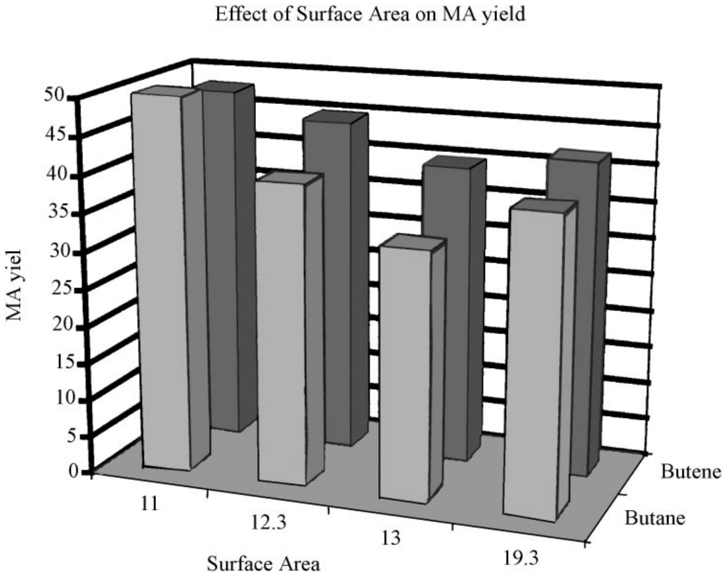

Fig. 2. The effect of surface area on product selectivity for C_4 hydrocarbon oxidation.

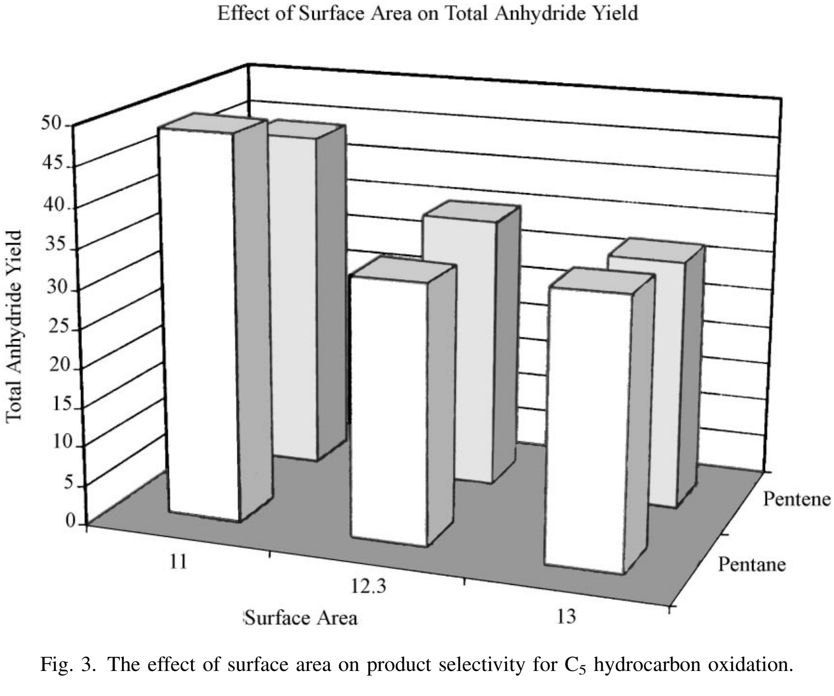

Fig. 3. The effect of surface area on product selectivity for C_5 hydrocarbon oxidation.

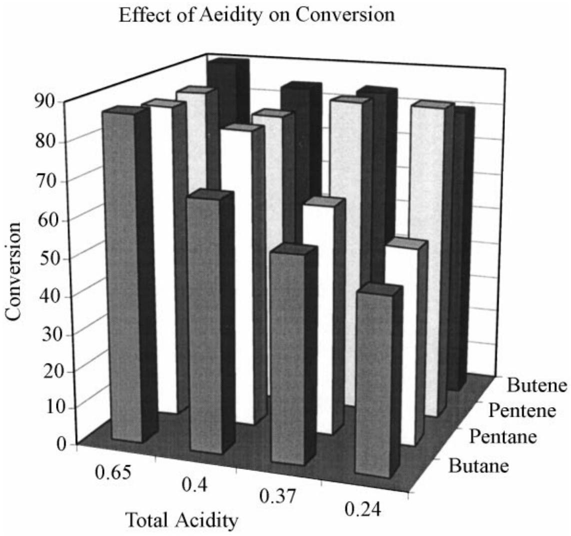

Fig. 4. The effect of total acidity on hydrocarbon conversion.

Table 9
Effect of total acidity on anhydride yield

Catalyst	Acidity	Maleic anhydride yield (%)		Total anhydride yield	
		Butane	Butene	Pentane	Pentene
VPS1	0.65	50	48	49	44
VPS3	0.4	40	45	33	35
VPS2	0.37	39	42	36	36
VPS4	0.24	33	40	34	32
STD	0.02	17	18	0	0

Total anhydride yield=maleic anhydride+phthalic anhydride yield.

4. Conclusions

These results lead one to hypothesise the following:

1. An increase in surface results in a small improvement in anhydride yields; however, there does appear to be a maximum surface area, above which improvements in anhydride yields are negligible.
2. The choice of doping elements has a greater effect on conversion and product yield than surface area.
3. Within the range measured, increasing acidity of the catalyst results in an increase in maleic anhydride yield when *n*-butane or *n*-pentane are the feed materials. This effect is not observed with the corresponding olefins as feed materials. The results are consistent with the literature.

Further studies on a wider range of modified catalysts are required to determine if these trends are general or limited to certain VPO catalysts.

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