

PROCESS FOR PRODUCING A VANADIUM PHOSPHORUS OXIDE CATALYST

THIS INVENTION relates to vanadium phosphorus oxide (VPO) catalysts. More particularly, the invention relates to a method of making a VPO catalyst suitable for the oxidation of C₄ and C₅ paraffins and olefins to maleic anhydride, phthalic anhydride and acetic acid, especially paraffins and olefins produced by Fischer-Tropsch processes, and to a VPO catalyst made in accordance with the method.

According to the invention there is provided a method of making a vanadium phosphorus oxide (VPO) catalyst, the method comprising the steps of:

- precipitating, from a solution comprising dissolved V⁴⁺ ions and V⁵⁺ ions at a total concentration of 45 - 65 g/l, a vanadium-containing and phosphorus-containing precipitate comprising a complex in accordance with the formula VOHPO₄ • ½H₂O; and
- calcining the precipitate under an inert atmosphere, to produce a VPO catalyst having an active phase in accordance with the formula (VO)₂P₂O₉,
- the solution from which the precipitate is precipitated comprising dissolved cations of at least two dopant metals selected from the group consisting of Bi, Zr, Cr, Ce, Co, Mn, Mg and Mo, said dissolved dopant metal cations being present in the solution in proportions such that the precipitate comprises 1 - 25% by mass of dopant metal cations in total, the balance being the VOHPO₄ • ½H₂O complex, each dopant metal forming 0.1 - 20% by mass of the precipitate.

Preferably, the proportion of dissolved V⁴⁺ ions relative to the proportion of dissolved V⁵⁺ ions is as high as practically feasible. Furthermore, the ratio of dissolved V⁴⁺ ions:V⁵⁺ ions in the solution may be such that the molar proportion of each of the V⁴⁺ ions and the V⁵⁺ ions in the VPO catalyst, after calcining, is 0.1 - 10 mole %, typically 0.5 - 5%.

Preferably the total concentration of dissolved V⁴⁺ ions and V⁵⁺ ions in the solution is 50 - 60 g/l, the dissolved dopant metal cations being present in the solution in proportions such that the precipitate comprises 2 - 20% by mass of the dopant metals in total, each dopant metal forming 0.5 - 15% by mass of the

precipitate, the ratio of dissolved V^{4+} ions: V^{5+} ions in the solution being such that the molar proportion of V^{5+} ions in the VPO catalyst is 0.1 - 10 mole %, typically 0.5 - 5 mole %.

The solution from which the precipitate is precipitated may comprise 5 dissolved cations of 2 - 3 dopant metals selected from said group consisting of Bi, Zr, Cr, Ce, Co, Mn, Mg and Mo.

One of the dopant metals may be Bi, Bi cations being present in the solution from which the precipitate is precipitated in a proportion such that Bi forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to the Bi 10 cations, cations of 1 - 2 other dopant metals selected from:

Zr;

Mn and Ce;

Co;

Ce;

15

Zr and Ce; and

Zr and Co.

Instead, one of the dopant metals may be Zr, Zr cations being present in the solution from which the precipitate is precipitated in a proportion such that Zr forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to 20 the Zr cations, cations of 1 - 2 other dopant metals, selected from:

Bi;

Cr;

Ce and Cr;

Ce;

25

Co;

Bi and Ce; and

Bi and Co.

Instead, one of the dopant metals may be Cr, Cr cations being present in the solution from which the precipitate is precipitated in a proportion such that Cr

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forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to the Cr cations, cations of 1 - 2 other dopant metals, selected from:

Zr; and
Ce and Zr.

5 Instead, one of the dopant metals may be Ce, Ce cations being present in the solution from which the precipitate is precipitated in a proportion such that Ce forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to the Ce cations, cations of 1 - 2 other dopant metals, selected from:

10 Zr and Cr;
Zr;
Bi and Mn;
Bi;
Bi and Zr; and
Mn and Mg.

15 Instead, one of the dopant metals may be Co, Co cations being present in the solution from which the precipitate is precipitated in a proportion such that Co forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to the Co cations, cations of 1 - 2 other dopant metals, selected from:

20 Zr;
Bi; and
Bi and Zr.

Instead, one of the dopant metals may be Mn, Mn cations being present in the solution from which the precipitate is precipitated in a proportion such that Mn forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to
25 the Mn cations, cations of 1 - 2 other dopant metals, selected from:

Bi and Ce;
Mg and Ce; and
Mo.

30 Instead, one of the dopant metals may be Mg, Mg cations being present in the solution from which the precipitate is precipitated in a proportion such that Mg forms 1 - 20% by mass of the precipitate, the solution comprising cations of Mn

and Ce dopant metals in addition to the Mg cations. Instead, one of the dopant metals may be Mo, Mo cations being present in the solution from which the precipitate is precipitated in a proportion such that Mo forms 1 - 20% by mass of the precipitate, the solution comprising cations of Mn dopant metal in addition to
5 the Mo cations.

The solution may comprise a solvent selected from alcohols and mixtures of two or more alcohols. When the solvent is a mixture of two alcohols, the alcohols may be present in a mass ratio of 1:2 - 2:1. In particular, the solvent may be anhydrous, the alcohol being selected from:

- 10 isobutanol;
- benzyl alcohol;
- ethanol;
- octanol;
- 2-butanol;
- 15 isopropanol; and
- mixtures of any two or more thereof.

More particularly, the solvent may be a mixture of two said alcohols.

The method may include the preliminary step of obtaining the solution of the V^{4+} ions and V^{5+} ions in the solution by dissolving V^{5+} ions in the solvent and
20 reducing a portion of the V^{5+} ions to V^{4+} ions. Reducing the V^{5+} cations to the V^{4+} cations may be by using a suitable reducing agent.

Dissolving the V^{5+} ions in the solvent may be by admixing vanadium pentoxide (V_2O_5) with the solvent. When the solvent is an alcohol and is anhydrous, the reducing agent may be selected from benzyl alcohol, isobutanol or
25 isopropanol, eg so that the solvent and reducing agent are the same alcohol. The reducing may be by refluxing the solution (conveniently at atmospheric pressure), optionally followed by stirring, at a suitable temperature, followed by the precipitation. In particular, the reducing of the V^{5+} ions to V^{4+} ions may be by means of a reducing agent, the method including refluxing the solvent containing

the V^{5+} ions dissolved therein with the reducing agent, the solvent and reducing agent optionally being the same alcohol.

The precipitation may be effected by adding phosphate ions to the solution, eg by adding phosphoric acid to the solution.

5 For the purpose of the reducing, routine experimentation can be employed to determine a suitable reducing agent and to determine a suitable proportion thereof to be used, to determine suitable periods respectively for refluxing and stirring, to determine a suitable stirring temperature, and to determine a suitable refluxing pressure and temperature if refluxing is at a pressure other than
10 atmospheric pressure. After the refluxing has been carried out for a desired period, eg 3 - 20 hours, preferably 6 - 15 hours, and the stirring has been carried out for a desired period, eg 12 - 36 hours, preferably 18 - 30 hours, to take the reduction to a desired degree of completion, the solution may be cooled to room or ambient temperature, the precipitated complex then being collected and washed
15 and dried, prior to calcining thereof.

Preferably, the calcining is carried out under an inert atmosphere for example under argon, eg in an oven flushed by argon, according to a suitable heating regime. Thus, heating rates, cooling rates, maximum temperature and the temperatures and durations of any temperature holds or plateaus may be
20 determined by routine experimentation, a maximum temperature of 400 - 500°C, preferably 420-480°C, eg 450°C being suitable. Thus the calcining may include heating the precipitate under an inert atmosphere to a maximum temperature of 400 - 500°C.

The dopant metal cations may be dissolved in the solvent by dissolving a
25 suitable dopant compound (also known as a promoter compound, the dopant cations also being known as promoter cations) in the solvent. Suitable dopant compounds are as follows:

For Bi cations, $(BiO)_2 \cdot CO_3$, can be used;

- For Zr cations, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, ZrOCl_2 , can be used;
For Cr cations, CrO_3 , can be used;
For Ce cations, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, can be used;
For Co cations, $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, can be used;
5 For Mn cations, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, can be used;
For Mg cations, MgO , can be used; and
For Mo cations, MoO_3 , can be used.

The invention extends to a VPO catalyst, whenever made in accordance with the method described above.

- 10 The invention will now be described, by way of non-limiting illustrative example, with reference to the following Examples. In the Examples, unless otherwise specified, refluxing, stirring and calcining were carried out at atmospheric pressure ; and room (ambient) temperature was 20 - 25°C.

EXAMPLE 1

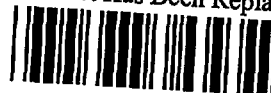
- 15 $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (97.5% by mass) + 1% Bi promoter + 1.5% Zr promoters:

- A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V_2O_5 , 0.14g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 0.211g of $(\text{BiO})_2\text{CO}_3$. The solution so formed was refluxed for 7 hours at
20 atmospheric pressure after which it was stirred for 16 hours at room temperature. 26g of 98% by mass H_3PO_4 was added to the solution and the mixture was stirred under reflux for 3 hours. The solution was cooled to room temperature and a precipitate which had formed in response to the H_3PO_4 addition was recovered by filtration. The
25 precipitate was washed thoroughly with water (about 5 l). A blue solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

The catalyst precursor was calcined in an inert atmosphere in a reaction vessel in the form of an oven. Argon was used as the inert atmosphere, a flow rate of argon of approximately 6 ml/min being used to flush the vessel. The temperature was steadily increased from room temperature to 300 °C over a 3-hour period, ie at a rate of roughly 100 °C/hour. The temperature was maintained at 300 °C for 2 hours. The temperature was then steadily increased to 450 °C over a further 3 hours at a rate of about 50 °C/hour. The temperature was maintained at 450 °C for 6 hours. The temperature was then steadily reduced to room temperature over a period of 3 hours at a rate of about 150 °C/hour, to form a novel VPO catalyst.

A micro-reactor was loaded with the novel VPO catalyst so formed. Butane, at a concentration of 1.3% by volume in air, was fed over the catalyst in the micro-reactor at a gas hourly space velocity of 1500 - 3000 h⁻¹, preferably 2000 - 2700 h⁻¹. The temperature for maximum maleic anhydride yield was found to be between 300 and 450 °C, preferably between 390 °C and 410 °C. It was surprising to note that, when the catalyst was used to catalyze butane conversion to maleic anhydride, after one day the butane conversion was 67% and the selectivity to produce maleic anhydride was 36%. It was found that the VPO catalyst out-performed a control (standard) VPO catalyst by a considerable margin as set forth in Table 1 hereunder.

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TABLE 1: Comparison of Standard and Novel VPO Catalysts at Equilibration

	Standard VPO	Novel VPO
% butane conversion	31%	80%
% selectivity to produce maleic anhydride	54%	70%
% selectivity to produce carbon oxides	46%	30%
% yield	16.7%	56%

TABLE 2: Comparison of Novel VPO Catalysts at Equilibration

These novel catalysts were tested regarding their ability to catalyze the conversion of butene to maleic anhydride, pentane to maleic anhydride and phthalic anhydride, and pentene to maleic anhydride and phthalic anhydride as set forth in Table 2 hereunder.

TABLE 2

	Butene	Pentane	Pentene
Gas hourly space velocity (h^{-1})	1500 - 3000, preferably 2000 - 2600	750 - 2000, preferably 800 - 1500	750 - 2000, preferably 1500 - 1800
Temperature for maximum yield ($^{\circ}\text{C}$)	350 - 450, preferably 380 - 410	320 - 380, preferably 330 - 350	300 - 380, preferably 310 - 340
% Conversion	80	82	90
% Maleic anhydride selectivity	65	30	32
% Phthalic anhydride selectivity	-	8	10

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EXAMPLE 2

$\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (97% by mass) + 1.5% Zr promoter + 1.5% Cr promoter:

5 A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V_2O_5 , 0.124g of CrO_3 and 0.4g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. The solution so formed was refluxed for 7 hours and was then stirred for 16 hours at room temperature. 24g of 98% H_3PO_4 was added to the solution, followed by stirring under reflux for 3 hours. The solution was then cooled to room temperature and
10 a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5l). A blue solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 3

15 $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (88.5% by mass) + 8.5% Ce promoter + 1.5 % Zr promoter + 1.5 % Cr promoter:

A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V_2O_5 , 0.4g of ZrOCl_2 , 0.124g of CrO_3 and 3.04g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The solution so formed was refluxed for
20 7 hours and was then stirred for 16 hours at room temperature. 24g of 98% H_3PO_4 was added to the solution followed by stirring under reflux for 3 hours. The solution was cooled to room temperature and a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5l). A blue
25 solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 4

VOHPO₄·½H₂O 90% by mass) + 1.5% Zr promoter + 8.5% Ce promoter:

5 A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅, 0.4g of ZrOCl₂·8H₂O and 3.04g of Ce(NO₃)₃·6H₂O. The solution so formed was refluxed for 7 hours and then stirred for 16 hours at room temperature. 26g of 98% H₃PO₄ was added to the solution followed by stirring under reflux for 3 hours. The solution was then cooled to room temperature and a
10 precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5ℓ). A blue solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 5

15 VOHPO₄·½H₂O (92% by mass) + 1.5% Zr promoter + 1.5% Cr promoter + 5% Ce promoter:

A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was added to 15g of V₂O₅, 1.79g of Ce(NO₃)₃·6H₂O, 0.4g of ZrOCl₂·8H₂O and 0.124g of CrO₃. The solution so formed was
20 refluxed for 7 hours and was then stirred for 16 hours at room temperature. 23g of 98% H₃PO₄ was added to the solution. The solution was cooled to room temperature and a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5ℓ). A blue solid was obtained which
25 was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 6

VOHPO₄·½H₂O (90% by mass) + 1.5% Zr promoter + 8.5% Co promoter:

5 A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅ and 0.4g of ZrOCl₂·8H₂O. The solution so formed was refluxed for 7 hours and was then stirred for 16 hours at room temperature. 26g of 98% H₃PO₄ was added to the solution followed by the addition of 1.2g of Co₃(PO₄)₂·8H₂O after which the solution was stirred under reflux for 3 hours. The solution
10 was then cooled to room temperature and a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5 l). A blue solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 7

15 VOHPO₄·½H₂O (89% by mass) + 1% Bi promoter + 5% Mn promoter + 5% Ce promoter:

A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅, 0.82g of MnCl₂·4H₂O, 1.79g of Ce(NO₃)₃·6H₂O and 0.211g of (BiO)₂CO₃. The solution so formed
20 was refluxed for 7 hours and was then stirred for 16 hours at room temperature. 24g of 98% H₃PO₄ was then added to the solution followed by stirring under reflux for 3 hours. The solution was then cooled to room temperature and a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with
25 water (about 5 l). A blue solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 8

VOHPO₄·½H₂O (90.5% by mass) + 1% Bi promoter + 8.5% Co promoter:

5 A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅ and 0.211g of (BiO)₂CO₃. The solution so formed was refluxed for 7 hours and then stirred for 16 hours at room temperature. 26g of 98% H₃PO₄ was added to the solution followed by the addition of 1.2g of Co₃(PO₄)₂·8H₂O, followed in turn by stirring under reflux for 3 hours. The solution was
10 then cooled to room temperature and a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5ℓ). A blue solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 9

15 VOHPO₄·½H₂O (90.5% by mass) + 1% Bi promoter + 8.5% Ce promoter:

A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅, 3.04g of Ce(NO₃)₃·6H₂O and 0.211g of (BiO)₂CO₃. The solvent so formed was refluxed for 7 hours after
20 which it was stirred for 16 hours at room temperature. 26g of 98% H₃PO₄ was added to the solution followed by stirring under reflux for 3 hours. The solution was cooled to room temperature and a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5ℓ). A blue
25 solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 10

VOHPO₄·½H₂O (89% by mass) + 1% Bi promoter + 1.5% Zr promoter + 8.5% Ce promoter:

5 A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅, 0.4g of ZrOCl₂·8H₂O, 3.04g of Ce(NO₃)₃·6H₂O and 0.211g of (BiO)₂CO₃. The solution so formed was refluxed for 7 hours and then stirred for 16 hours at room temperature. 28g of 98% H₃PO₄ was added to the solution followed by stirring under reflux for 3 hours. The solution was cooled to room
10 temperature and a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5ℓ). A blue solid was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 11

15 VOHPO₄·½H₂O (89%) + 1% Bi promoter + 1.5%Zr promoter + 8.5% Co promoter:

A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅, 0.4g of ZrOCl₂·8H₂O and 0.211g of (BiO)₂CO₃. The solution so formed was refluxed for 7 hours and then stirred for 16
20 hours at room temperature. 27g of 98% H₃PO₄ was added to the solution followed by the addition of 1.2g of Co₃(PO₄)₂·8H₂O followed in turn by stirring under reflux for 3 hours. The solution was cooled to room temperature and a precipitate which had formed was recovered by filtration. The precipitate was washed thoroughly with water (about 5ℓ). A blue solid
25 was obtained which was oven-dried for 12 hours at 150°C to form a catalyst precursor.

EXAMPLE 12

VOHPO₄·½H₂O (85% by mass) + 5% Mn promoter + 5% Mg promoter + 5% Ce promoter:

5 A solvent comprising 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅, 0.167g of MgO, 1.79g of Ce(NO₃)₃·6H₂O and 0.82g of MnCl₂·4H₂O. The solution so formed was refluxed for 7 hours after which it was stirred for 16 hours at room temperature. 27g of 98% H₃PO₄ was added followed by the addition of 1.2g of Co₃(PO₄)₂·8H₂O, followed in turn by stirring
10 under reflux for 3 hours. The solution was cooled to room temperature and a precipitate was obtained which was recovered by filtration. The precipitate was washed thoroughly with water (about 5 l). A blue solid was oven dried for 12 hours at 150°C to form a catalyst precursor.

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EXAMPLE 13

VOHPO₄·½H₂O (10% by mass) + 5% Mo promoter + 5% Mn promoter:

A solvent comprising of 90ml benzyl alcohol and 60ml isobutanol was used to dissolve 15g of V₂O₅, 0.82g of MnCl₂·4H₂O and 0.6g of MoO₃. The
20 solution so formed was refluxed for 7 hours and then stirred for 16 hours at room temperature. 27g of 98% H₃PO₄ was added, followed by the addition of 1.2g of Co₃(PO₄)₂·8H₂O, followed in turn by stirring under reflux for 3 hours. The solution was cooled to room temperature and a precipitate was obtained which was removed by filtration. The precipitate was washed
25 thoroughly with water (about 5 l). A blue solid was oven-dried for 12 hours at 150°C to obtain a catalyst precursor.

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With regard to Examples 1 - 13 it should be noted that the benzyl alcohol and isobutanol were fully miscible and formed a solvent to which the V_2O_5 was added to produce V^{5+} ions. The benzyl alcohol in turn acted as a reductant under refluxing to reduce the mixture of V^{4+} cations and V^{5+} cations to V^{4+} cations.

- 5 The various dopant or promoter compounds, containing the various dopant or promoter metals, were added, after the V_2O_5 was added, to the solvent from which the catalyst precursor was eventually precipitated upon cooling to room temperature after the stirring and refluxing were completed.

- In the case of Examples 2 - 13 the oven-dried blue precursor was in each case calcined according to the procedure and heating regime described in Example 1 to obtain various novel VPO catalysts. These novel catalysts were tested regarding their ability to catalyze conversion of butane to maleic anhydride, butene to maleic anhydride, pentane to maleic anhydride, phthalic anhydride and acetic acid, and pentene to maleic anhydride, phthalic anhydride and acetic acid, and in each case the novel catalysts were found to out-perform the standard or control catalyst with which they were compared, with regard to one or more of percentage butane conversion, percentage selectivity to produce maleic anhydride or percentage yield.

- It has also been found that by varying either the temperature or gas hourly space velocity or both, the selectivity to maleic anhydride and phthalic anhydride can be varied, as set forth in Table 3 hereunder.

TABLE 3: Comparison of Novel VPO Catalysts at Equilibration

	Butane	Butene	Pentane	Pentene
Gas hourly space velocity (h^{-1})	1500 - 3000, preferably 2000 - 2600	1500 - 3000, preferably 2000 - 2600	750 - 2000, preferably 800 - 1500	750 - 2000, preferably 800 - 1500
5 Temperature ($^{\circ}\text{C}$)	350 - 450, preferably 380 - 410	350 - 450, preferably 380 - 410	320 - 380, preferably 330 - 350	350 - 450, preferably 380 - 410
% Conversion	70 - 80	75 - 90	70 - 88	70 - 95
% Maleic anhydride selectivity	60 - 76	60 - 70	30 - 50	30 - 60
10 % Phthalic anhydride selectivity	-	-	5 - 15	10 - 20

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CLAIMS:

1. A method of making a vanadium phosphorus oxide (VPO) catalyst, the method comprising the steps of:
- precipitating, from a solution comprising dissolved V^{4+} ions and V^{5+} ions
5 at a total concentration of 45 - 65 g/l, a vanadium-containing and phosphorus-containing precipitate comprising a complex in accordance with the formula $VOHPO_4 \cdot \frac{1}{2}H_2O$; and
- calcining the precipitate under an inert atmosphere, to produce a VPO catalyst having an active phase in accordance with the formula $(VO)_2P_2O_9$.
- 10 the solution from which the precipitate is precipitated comprising dissolved cations of at least two dopant metals selected from the group consisting of Bi, Zr, Cr, Ce, Co, Mn, Mg and Mo, said dissolved dopant metal cations being present in the solution in proportions such that the precipitate comprises 1 - 25% by mass of dopant metal cations in total, the balance being the $VOHPO_4 \cdot \frac{1}{2}H_2O$ complex,
15 each dopant metal forming 0.1 - 20% by mass of the precipitate.
2. A method as claimed in claim 1, in which the total concentration of dissolved V^{4+} ions and V^{5+} ions in the solution is 50 - 60 g/l, the dissolved dopant metal cations being present in the solution in proportions such that the precipitate comprises 2- 20 % by mass of the dopant metals in total, each dopant metal
20 forming 0.5 - 15% by mass of the precipitate, the ratio of dissolved V^{4+} ions: V^{5+} ions in the solution being such that the molar proportion of the V^{5+} ions in the VPO catalyst is 0.1 - 10 mole %.
3. A method as claimed in claim 2, in which the solution from which the precipitate is precipitated comprises dissolved cations of 2 - 3 dopant metals
25 selected from said group consisting of Bi, Zr, Cr, Ce, Co, Mr, Mg and Mo.



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4. A method as claimed in claim 3, in which one of the dopant metals is Bi, Bi cations being present in the solution from which the precipitate is precipitated in a proportion such that Bi forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to the Bi cations, cations of 1 - 2 other dopant metals
5 selected from:

Zr;
Mn and Ce;
Co;
Ce;
10 Zr and Ce; and
Zr and Co.

5. A method as claimed in claim 3, in which one of the dopant metals is Zr, Zr cations being present in the solution from which the precipitate is precipitated in a proportion such that Zr forms 1 - 15% by mass of the precipitate, the solution
15 comprising, in addition to the Zr cations, cations of 1 - 2 other dopant metals, selected from:

Bi;
Cr;
Ce and Cr;
20 Ce;
Co;
Bi and Ce; and
Bi and Co.

6. A method as claimed in claim 3, in which one of the dopant metals is Cr, Cr
25 cations being present in the solution from which the precipitate is precipitated in a proportion such that Cr forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to the Cr cations, cations of 1 - 2 other dopant metals, selected from:

Zr; and
30 Ce and Zr.



7. A method as claimed in claim 3, in which one of the dopant metals is Ce, Ce cations being present in the solution from which the precipitate is precipitated in a proportion such that Ce forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to the Ce cations, cations of 1 - 2 other dopant metals,
5 selected from:

Zr and Cr;

Zr;

Bi and Mn;

Bi;

- 10 Bi and Zr; and
Mn and Mg.

8. A method as claimed in claim 3, in which one of the dopant metals is Co, Co cations being present in the solution from which the precipitate is precipitated in a proportion such that Co forms 1 - 15% by mass of the precipitate, the solution
15 comprising, in addition to the Co cations, cations of 1 - 2 other dopant metals, selected from:

Zr;

Bi; and

Bi and Zr.

- 20 9. A method as claimed in claim 3, in which one of the dopant metals is Mn, Mn cations being present in the solution from which the precipitate is precipitated in a proportion such that Mn forms 1 - 15% by mass of the precipitate, the solution comprising, in addition to the Mn cations, cations of 1 - 2 other dopant metals, selected from:

- 25 Bi and Ce;
Mg and Ce; and
Mo.

10. A method as claimed in claim 3, in which one of the dopant metals is Mg, Mg cations being present in the solution from which the precipitate is precipitated



in a proportion such that Mg forms 1 - 20% by mass of the precipitate, the solution comprising cations of Mn and Ce dopant metals in addition to the Mg cations.

11. A method as claimed in claim 3, in which one of the dopant metals is Mo, Mo cations being present in the solution from which the precipitate is precipitated
5 in a proportion such that Mo forms 1 - 20% by mass of the precipitate, the solution comprising cations of Mn dopant metal in addition to the Mo cations.

12. A method as claimed in any one of the preceding claims, in which the solution comprises a solvent selected from alcohols and mixtures of two or more alcohols.

10 13. A method as claimed in claim 12, in which the solvent is a mixture of two alcohols, the alcohols being present in a mass ratio of 1:2 - 2:1.

14. A method as claimed in claim 12 or claim 13, in which the solvent is anhydrous, each alcohol being selected from:

isobutanol;
15 benzyl alcohol;
ethanol;
octanol;
2-butanol;
isopropanol; and
20 mixtures of any two or more thereof.

15. A method as claimed in claim 14, in which the solvent is a mixture of two said alcohols.

16. A method as claimed in any one of the preceding claims, which includes the preliminary step of obtaining the solution of the V^{4+} ions and V^{5+} ions in the
25 solution by dissolving V^{5+} ions in the solvent and reducing a portion of the V^{5+} ions to V^{4+} ions.



17. A method as claimed in claim 16, in which the reducing of the V^{5+} ions to V^{4+} ions is by means of a reducing agent, the method including refluxing the solvent containing the V^{5+} ions dissolved therein with the reducing agent.

18. A method as claimed in claim 1, substantially as described herein with reference to the Examples.

19. A VPO catalyst, whenever made in accordance with the method of any one of the preceding claims.

