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International Office
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International patent classification ⁶ : B01J 23/22, 23/18, C07C 253/24	A1	(11) International publication number: WO 97/23287 (43) International publication date: 3 July 1997 (03.07.97)
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As printed

(54) Title: METHOD FOR PREPARING AMMOXIDATION CATALYSTS FOR A FLUIDISED-BED OR MOVING-BED REACTOR

(54) Titre: PROCEDE DE PREPARATION DE CATALYSEURS D'AMMOXYDATION POUR REACTEUR A LIT FLUIDISE OU A LIT TRANSPORTE

(57) Abstract

A method for preparing catalysts including mixed oxides based on vanadium, antimony and optionally tin and/or titanium and/or iron and/or other metals, and deposited on a carrier, as well as the use thereof for the ammoxidation of alkanes, are disclosed. Said method includes impregnating a solid oxide carrier with a solution of respective vanadium, antimony or optionally tin and/or titanium and/or iron and/or other metal compounds in at least one saturated alcohol, contacting the resulting impregnated solid carrier with an aqueous buffer solution having a pH of 6 to 8, separating and drying the solid, and calcining the solid in two stages, firstly at 300-350 °C, and then at 400-800 °C. Such catalysts are suitable for use in a fluidised or moving bed.

(57) Abrégé

La présente invention concerne un procédé de préparation de catalyseurs comprenant des oxydes mixtes à base de vanadium, d'antimoine et éventuellement d'étain et/ou de titane et/ou de fer et/ou d'autres métaux, déposés sur un support ainsi que leur utilisation pour l'ammoxydation des alcanes. Le procédé de préparation d'un catalyseur défini précédemment, est caractérisé en ce qu'il comprend: l'impregnation d'un support solide de type oxyde à l'aide d'une solution dans au moins un alcool saturé de composés respectifs de vanadium, d'antimoine, éventuellement d'étain et/ou de titane et/ou de fer et/ou d'autres métaux; la mise en contact du support solide imprégné obtenu, avec une solution aqueuse tampon à pH compris entre 6 et 8; la séparation du solide et son séchage; la calcination du solide en deux étapes, tout d'abord à une température de 300 °C à 350 °C, puis à une température de 400 °C à 800 °C. Ces catalyseurs sont adaptés à une mise en oeuvre en lit fluidisé ou en lit transporté.

PROCESS FOR THE PREPARATION OF AMMOXIDATION CATALYSTS
FOR A FLUIDIZED BED OR MOVING BED REACTOR

The present invention relates to a process for the preparation of mixed oxides based on vanadium, on antimony and optionally on tin and/or on titanium and/or on iron and/or on other metals deposited on a support and to their use as catalysts for the ammoxidation of alkanes.

Certain mixed oxides of vanadium and of antimony or of vanadium, of antimony and of other metals are known compounds which have been described, among many other mixed oxides, in Patent FR-A-2 072 334.

A description is given in Patent US 5 008 427 of a process for the ammoxidation of propane or butane in the presence of a catalyst which can in particular comprise oxides of vanadium, of antimony and of iron or of titanium or of chromium or of gallium or of tin and optionally of other metals. These catalysts have the essential characteristic of having been calcined at a temperature equal to or greater than 780°C.

Likewise, a description has been given in Patent EP-A-0 558 424 of a process for the ammoxidation of alkanes which is catalysed by mixed oxides of vanadium, of antimony, of iron and/or of gallium and/or of indium. These mixed oxides are prepared by mixing aqueous suspensions of compounds of the various metals,

heating with stirring and then evaporating the water, drying and calcination.

These patents give no specific indication regarding the reactor technology associated with the catalysts for the ammoxidation of alkanes which they describe.

However, for the type of reaction represented by the ammoxidation of alkanes, it turns out that the use of a fluidized bed or moving bed reactor is more advantageous. Due to the high exothermicity of the reactions involved in the ammoxidation of alkanes, the possibility of using one or a number of stationary bed reactors (multitubular reactors) on an industrial scale does not appear very realistic, indeed appears ruled out, in particular if it is desired to achieve high productivities. In fact, it would be necessary, in order to remove the heat given off, to use a multitubular reactor of very large size or a whole battery of multitubular reactors, which is ruled out from an investment viewpoint.

In comparison with the stationary bed reactor, fluidized or moving bed reactors have a greater ability to discharge the heat given off and appear, for this reason, better suited to the ammoxidation reaction of alkanes. This better ability to transfer the heat makes it possible to envisage an increase in productivity by increasing the alkane content in the feed mixture. Such an operation cannot

be envisaged in the case of a stationary bed reactor because the limitations with respect to heat transfer (which reveal themselves by the existence of a hot spot in the reactor) dictate the use of relatively low
 5 alkane contents, so as to avoid any problem of explosiveness or flammability of the gas mixture.

The present invention relates to a process for the preparation of a catalyst for a fluidized bed or moving bed reactor comprising an active phase of
 10 general empirical formula (I):



in which:

- E represents an element which can give an oxide of rutile structure or an element
 15 which, in combination with V, Sb, Sn, Ti, Fe and/or with another element E, can give a phase of rutile or trirutile structure or a solid solution of rutile structure
- a represents a whole or fractional number
 20 equal to or greater than 0.5
- b, c, d and e represent, independently of one another, a whole or fractional number from 0 to 100
- x represents a whole or fractional number
 25 determined by the oxidation number of the other elements,

and a solid support of oxide type,
the said process being characterized in that it
comprises:

- 5 - the impregnation of the solid support by a
 solution in at least one saturated alcohol of
 respective compounds of vanadium, of antimony
 and optionally of tin and/or of titanium
 and/or of iron and/or of element E,
- 10 - bringing the impregnated solid support
 obtained into contact with an aqueous buffer
 solution at a pH of between 6 and 8,
- the separation of the solid and the drying
 thereof,
- 15 - the calcination of the solid in two stages,
 first of all at a temperature of 300°C to
 350°C and then at a temperature of 400°C to
 800°C.

The elements E are in particular chosen from
germanium, manganese, ruthenium, niobium, tantalum,
20 gallium, chromium, rhodium, nickel, molybdenum,
aluminium, thorium, calcium, tungsten and magnesium.
There may be a number of elements E in the formula (I)
and, in the present text, the expression element E
covers one or a number of elements E.

25 The compounds of vanadium, of antimony, of
tin, of titanium, of iron and of the element E used in
the process must be soluble in a saturated alcohol or a
mixture of saturated alcohols.

In the present text, a compound is regarded as soluble when its solubility, measured at 25°C, is at least 5 grams per litre of saturated alcohol or of water. These compounds can be introduced together; 5 they can also be first of all dissolved separately in an alcohol, the different alcoholic solutions thus obtained then being mixed with one another. Generally, but non-limitingly, an alcoholic solution is prepared by dissolving the different compounds of vanadium, of 10 antimony and, if appropriate, of tin, of titanium, of iron and of element E, without the intermediate preparation of solutions of each of the compounds.

Mention may be made, as examples of soluble vanadium compounds, of vanadyl acetylacetonate, vanadyl 15 trichloride, vanadium trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium tribromide, vanadium dichloride, vanadium trichloride, vanadium tetrachloride or vanadium triiodide.

Mention may be made, as examples of soluble 20 antimony compounds, of antimony pentachloride, antimony trichloride, antimony tribromide, antimony trifluoride, antimony triiodide, antimony trioxide or stibine.

Mention may be made, as examples of soluble tin compounds, of stannic chloride, stannous chloride 25 or stannous bromide.

Mention may be made, as examples of soluble titanium compounds, of titanium dichloride, titanium tetrachloride, titanium trichloride, titanium

tribromide, titanium tetrabromide, titanium tetrafluoride or titanium diiodide.

Mention may be made, as examples of soluble iron compounds, of iron dichloride, iron trichloride, iron dibromide, iron tribromide, iron diiodide, ferrous nitrate, ferrous sulphate, ferric sulphate, ferrous thiosulphate, ferric formate, ferric acetate, ferric acetylacetonate, ferric benzoate, ferric oleate, ferrous lactate or ferric lactate.

The saturated alcohols used in the process of the invention are more particularly alkanols and cycloalkanols. Use will preferably be made of alkanols and cycloalkanols in which the boiling point is not excessively high, in order to facilitate the operations of separation or of recycling by distillation or evaporation. Thus, alkanols having from 1 to 6 carbon atoms, such as methanol, ethanol, n-propanol, 2-propanol, n-butanol, 2-butanol, tert-butanol, pentanols and hexanols, and cyclohexanol, are preferred.

The solid support is an oxide, such as an alumina, a silica, a silica/alumina, a zirconia, a cerite, a mixed oxide of cerium and of zirconium, a magnesia, a titanium oxide, a niobium oxide or a lanthanum oxide.

The size of the particles of the solid support is generally from 10 μm to 1,000 μm and preferably from 20 μm to 300 μm .

Another important characteristic of the solid support is its ability to be impregnated by a solution of the compounds of the metals of the active phase. Thus, use will be made of supports having a total pore volume of at least 0.1 cm³/g and preferably of at least 0.15 cm³/g.

The quality of the fluidization of the catalytic bed can also depend on other parameters such as in particular the relative density of the support, the void content of the support or the gas flow rate. The desired fluidization of the catalyst of the invention, in particular for application in the ammoxidation of alkanes, will be carried out under optimum conditions by the person skilled in the art, by taking into account these various parameters.

It is preferable, among solid supports exhibiting the characteristics indicated above, to use silicas in the process according to the invention.

The impregnation of the solid support by the alcoholic solution of the compounds of the metals forming part of the composition of the active phase of formula (I) is carried out by using a volume of alcoholic solution which is less than or equal to the total pore volume of the support. When the volume of the alcoholic solution is less than the total pore volume of the support, it will represent at least 50% of the said total pore volume. The duration of the impregnation step is not critical. It can merely vary

in practice according to the method of mixing the support and the solution which is chosen.

The impregnated solid support is then brought into contact with an aqueous buffer solution having a
5 pH of between 6 and 8 and preferably of between 6.5 and 7.5, the said buffer solution preferably being an aqueous solution of an ammonium salt, optionally containing aqueous ammonia. The ammonium salt used is more preferentially an ammonium carboxylate (for
10 example acetate, citrate or tartrate), ammonium oxalate, ammonium carbonate or ammonium hydrogenphosphate, which makes it possible to have a pH in the region of 7, optionally in the presence of aqueous ammonia. Thus, ammonium acetate/aqueous
15 ammonia buffer solutions are particularly well suited.

The volume of the buffer solution brought into contact with the impregnated support is equal to or greater than the total pore volume of the support and is preferably greater than the total pore volume of
20 the support.

The solid obtained is separated from the liquid by the means commonly used for this operation, for example by filtration or by centrifuging.

It is then dried at a temperature which makes
25 it possible to remove the water and which depends on the pressure under which the operation is carried out. If the operation is carried out at atmospheric pressure, the drying temperature will advantageously be

from 100°C to 200°C, preferably from 110°C to 180°C.

If the operation is carried out under a pressure lower than atmospheric pressure, the drying temperature can be lower, generally equal to or greater than 50°C.

5 The duration of the drying can vary widely according to the temperature chosen. It will generally be determined so as to remove most of the impregnation water. It is most often between a few minutes and a few tens of hours.

10 The solid thus dried is calcined in an oven at a temperature of 300°C to 350°C and then at a temperature of 400°C to 800°C, and more preferentially between 500°C and 750°C, for the second stage and for periods of time varying, by way of information, from a
15 few minutes to several hours, most generally from 30 minutes to 20 hours.

 The ratio by weight, in the final catalyst, of the active phase of formula (I) to the whole of the said catalyst is generally from 5 to 50%.

20 Preference is given, among the mixed oxides of the active phase of formula (I) which are defined above, to those for which:

- E represents one or a number of elements chosen from nickel, gallium, aluminium or
25 niobium
- a represents a whole or fractional number equal to or less than 100 and preferably of between 0.5 and 50

- b, c, d and e represent, independently of one another, a whole or fractional number from 0 to 50, at least one of these symbols being greater than 0 and preferably equal to or greater than 0.5
- x represents a whole or fractional number determined by the oxidation number of the other elements.

Another subject of the present invention is a process for the vapour-phase ammoxidation of alkanes in a fluidized bed or moving bed reactor, in the presence of a catalyst comprising an active phase of generally empirical formula (I):



in which:

- E represents an element which can give an oxide of rutile structure or an element which, in combination with V, Sb, Sn, Ti, Fe and/or with another element E, can give a phase of rutile or trirutile structure or a solid solution of rutile structure
- a represents a whole or fractional number equal to or greater than 0.5
- b, c, d and e represent, independently of one another, a whole or fractional number from 0 to 100

- x represents a whole or fractional number determined by the oxidation number of the other elements,

and a solid support of oxide type,

5 the said catalyst process being prepared by the process described above which comprises:

- the impregnation of the solid support by a solution in at least one saturated alcohol of respective compounds of vanadium, of antimony and optionally of tin and/or of titanium and/or of iron and/or of element E,
- bringing the impregnated solid support obtained into contact with an aqueous buffer solution at a pH of between 6 and 8,
- 15 - the separation of the solid and the drying thereof,
- the calcination of the solid in two stages, first of all at a temperature of 300°C to 350°C and then at a temperature of 400°C to 800°C.

20 According to the present invention, alkanes having from 3 to 12 carbon atoms per molecule are reacted in the vapour-phase with ammonia and oxygen in the presence of a catalyst, the composition and the preparation of which catalyst are indicated in the preceding description.

25 Of course, in the context of the present process, it is possible to use diluent gases which are

inert under the reaction conditions, such as helium, nitrogen and argon. Likewise, steam can be added to the gaseous reaction mixture within wide limits. Thus, the reactive gas (alkane, ammonia, oxygen) can be
5 diluted by an inert diluent and/or by steam. In this combination, the steam content by volume can vary within wide limits, in particular from 0 to 50% and preferably between 3 and 30%. For good implementation of the process according to the invention, the reactive
10 gas content will be at least 3% and preferably at least 20%.

The respective alkane, ammonia and oxygen contents by volume in the reactive gas can vary within wide limits.

15 The alkane content in the reactive gas is preferably between 5 and 70%. That of ammonia is preferably between 3 and 50% and that of oxygen is preferably between 3 and 45%.

Starting with propane, a mixture will be
20 obtained which contains essentially acrylonitrile. Acrylonitrile is an intermediate which is produced industrially on a large scale.

Starting with isobutane, methacrylonitrile will essentially be obtained.

25 The process according to the invention is more particularly suited to the ammoxidation of propane.

While the alkane used can be of technical

quality, it will not contain significant amounts of compounds with ethylenic unsaturation. Thus, the propane used will generally only contain minor amounts of propylene, for example less than 10%.

5 As indicated above, the process according to the invention is implemented in the form of a vapour-phase reaction in a fluidized bed or moving bed reactor. The process can be carried out continuously or non-continuously.

10 The reaction temperature is in general between 300°C and 550°C and preferably between 400°C and 500°C.

 The total pressure of the reaction mixture can be greater than or equal to atmospheric pressure.
15 It is generally between 1 and 6 bar and preferably between 1 and 4 bar.

 The hourly volume rate is generally between 100 and 36,000 h⁻¹. It depends on the gas flow rate but also on other parameters of the reaction. The hourly
20 volume rate is preferably between 200 and 20,000 h⁻¹.

 The hourly volume rate is defined as the total gas volume/volume of the catalyst/hour ratio.

 Of course, the person skilled in the art will be able to find a compromise between the temperature,
25 the gas flow rate, the precise nature of the catalyst used and the various other parameters of the reaction, taking into account his production objectives.

 The products of the reaction can be recovered

from the effluent gases by any suitable means. For example, the effluent gases can pass into a condenser containing dilute sulphuric acid in order to neutralize the unreacted ammonia. The gases can then pass through
5 a refrigerated absorbing column to condense the acrylonitrile, acetonitrile and hydrocyanic acid, the uncondensed vapours containing mainly unreacted propane, propylene, light hydrocarbons and, if appropriate, CO₂. The acrylonitrile and hydrocyanic
10 acid can then be separated from the acetonitrile by distillation and the recovered acrylonitrile/hydrocyanic acid mixture can then be distilled in its turn to separate the acrylonitrile from the hydrocyanic acid.

15 The examples below illustrate the present invention.

EXAMPLES OF THE PREPARATION OF MIXED OXIDES.

EXAMPLE 1 - Preparation of catalyst (A) according to the invention comprising a mixed oxide of empirical formula: VSb₅Sn₅O_x and a silica support
20

The dry impregnation is carried out (that is to say with a volume of solution which is less than or equal to the pore volume of the support) of 13 g of
25 silica, having particle sizes of 30 to 100 μ m, a BET specific surface of 320 m²/g, a pore volume of 1.2 cm³/g and a relative density of 0.36, with 15.6 cm³ of an

ethanolic solution containing 2.15 g of SnCl_4 , 0.437 g of vanadyl acetylacetonate and 2.46 g of SbCl_5 .

The impregnated solid is poured in 150 cm^3 of an aqueous solution containing of an ammonium acetate/aqueous ammonia (65/15 g/l) buffer and with a pH of 7.0.

The solid is then separated by centrifuging and dried at 120°C for 24 hours.

It is then calcined for 1 h at 350°C and then for 3 h at 700°C .

The catalyst thus obtained comprises 17% by weight of $\text{VSb}_5\text{Sn}_5\text{O}_x$ mixed oxide and 83% by weight of silica support and has a specific surface of $280 \text{ m}^2/\text{g}$ and a relative density of 0.43.

EXAMPLE 2 - Preparation of catalyst (B) according to the invention comprising a mixed oxide of empirical formula: $\text{VSb}_5\text{Sn}_5\text{O}_x$ and an alumina support

The dry impregnation is carried out (that is to say with a volume of solution which is less than or equal to the pore volume of the support) of 39 g of alumina, having particle sizes of 20 to 90 μm , a BET specific surface of $180 \text{ m}^2/\text{g}$, a pore volume of $0.4 \text{ cm}^3/\text{g}$ and a relative density of 0.74, with 15.6 cm^3 of an ethanolic solution containing 2.15 g of SnCl_4 , 0.437 g of vanadyl acetylacetonate and 2.46 g of SbCl_5 .

The impregnated solid is poured in 150 cm^3 of

an aqueous solution containing of an ammonium acetate/aqueous ammonia (65/15 g/l) buffer and with a pH of 7.0.

The solid is then separated by centrifuging and dried at 120°C for 24 hours.

It is then calcined for 1 h at 350°C and then for 3 h at 700°C.

The catalyst thus obtained comprises 6.5% by weight of $\text{VSb}_2\text{Sn}_2\text{O}_x$ mixed oxide and 93.5% by weight of alumina support and has a specific surface of 150 m^2/g and a relative density of 0.87.

EXAMPLES 3 TO 5 - Preparation of catalysts (C), (D) and (E) according to the invention comprising mixed oxides of empirical formulae:
 $\text{VSb}_2.5\text{Sn}_2.5\text{O}_x$
 $\text{VSb}_5\text{Sn}_5\text{O}_x$
 $\text{VSb}_2.5\text{Sn}_2.5\text{O}_x$
and a silica support

By using the procedure and the reactants described in Example 1 and by adapting, if appropriate, the amounts of the said reactants, the following catalysts are prepared:

- Catalyst (C) comprising 17% by weight of $\text{VSb}_{2.5}\text{Sn}_{2.5}\text{O}_x$ mixed oxide and 83% by weight of silica support and having a specific surface of 195 m^2/g ;
- Catalyst (D) comprising 23% by weight of

VSb₅Sn₅O_x mixed oxide and 77% by weight of silica support and having a specific surface of 235 m²/g;

- Catalyst (E) comprising 23% by weight of VSb_{2.5}Sn_{2.5}O_x mixed oxide and 77% by weight of silica support and having a specific surface of 250 m²/g.

GENERAL PROCEDURE FOR THE AMMOXIDATION TESTS

The catalytic performances of the catalysts (A) and (B) were evaluated in a glass fluidized bed reactor, with an internal diameter of 1.8 cm and with a height of 20 cm, equipped with an axial thermocouple, so as to be able to measure the temperature along the catalytic bed. Approximately 15 cm³ of catalyst are employed for each ammoxidation test; due to the difference in relative density between silica and alumina, this volume corresponds, for example, to 6.4 g for the catalyst (A) and to 13.0 g for the catalyst (B).

The reaction mixture used in the series of tests carried out on fluidized bed reactor has the following composition by volume: C₃H₈/NH₃/O₂/He = 25/10/20/45.

The total pressure of the reaction mixture is 1.3 bar for each example.

The total gas flow rate is adjusted so as to obtain different contact times; the contact time is calculated by taking the volume of the catalytic bed before fluidization (15 cm³) and the gas flow rate under

standard conditions of temperature and pressure. The contact times involved are as follows: 5 s (total flow rate: 180 cm³/min), 10 s (total flow rate: 90 cm³/min) and 15 s (total flow rate: 60 cm³/min). The corresponding linear velocities of the gas (velocities in an empty chamber), calculated for standard conditions of temperature and pressure and taking into account the presence of the axial thermocouple in the reactor, are 105 cm/min, 52 cm/min and 35 cm/min.

The principle of the ammoxidation test for propane is as follows:

- The catalyst is brought to a temperature T_1 , for example 310°C, and, after stabilizing for 30 min at the temperature T_1 , the composition of the mixture at the reactor outlet is determined by gas-phase chromatography.
- The conversion percentages and the selectivities obtained with respect to the catalyst examined at the inlet temperature T_1 are calculated using relationships of the type:

$$\text{conversion of propane (in mol \%)} = \frac{\text{converted propane}}{\text{introduced propane}}$$

$$\text{selectivity towards acrylonitrile (in mol \%)} = \frac{\text{propane converted to acrylonitrile}}{\text{converted propane}}.$$
- The catalyst is then brought from 310 to 550°C in increments of 20°C and the

conversion percentages and the selectivities are determined every 40 min.

In the ammoxidation examples below, the following conventions are used:

5 Temp = temperature of the reaction

DC C_3H_8 = conversion of propane

SACN = selectivity towards acrylonitrile

SACN+ C_3H_6 = selectivity towards acrylonitrile and propylene

10 SAMMox = selectivity towards acetonitrile, hydrocyanic acid and other ammoxidation by-products

ct(s) = contact time in seconds.

The remainder to 100% of the selectivities
15 corresponds to the formation of CO and CO_2 and optionally methane, ethane and ethylene.

EXAMPLES OF THE AMMOXIDATION OF PROPANE

EXAMPLES 6 TO 10

Ammoxidation of propane is carried out, as
20 described above, by using the catalysts A, B, C, D and E according to the invention.

It may be specified, by way of indication for the catalyst A, that the minimum fluidization flow rate is 9-10 cm^3/min (velocity in an empty chamber of
25 6 cm/min).

The expansion of the fluidized bed is linear as far as 60-70 cm^3/min (35-40 cm/min). The height of

the catalytic bed changes from 10.8 cm (dense bed which is not fluidized for flow rates of less than the minimum fluidization flow rate) to 16.5 cm. For flow rates greater than 70 cm³/min, the height of the

5 catalytic bed no longer varies.

The temperature conditions and the results obtained are collated in Table 1 below.

5

Examples	Catalys t used	ct (s)	Temp (°C)	DC C3H8 (in %)	SACN (in %)	SACN + C3H6 (in %)	SAMmox (in %)
Example 6	A	5	445 480	3.5 5	34 41	36 42	32 25
		10	455	8	50	51	26
		15	450 470	8 11	41 32	42 33	20 14
Example 7	B	5	455 490	18 27	5 7	25 28	16 12
		10	455 485	22 22	3 6	17 25	11 15
Example 8	C	5	470	9	55	55	14
		10	450 470	9 15	43 45	43 45	20 15
		15	450 470	15 20	45 42	45 42	26 18
Example 9	D	5	470	11	46	46	25
		10	450 470	12 13	41 41	41 41	26 21
		15	430 450 470 490	14 16 23 17	37 39 38 23	37 39 38 23	23 18 14 14
Example 10	E	15	390 410 430 450	8 17 24 22	29 26 30 31	29 26 30 31	35 22 16 14

10

Table 1

CLAIMS

1. Process for the preparation of a catalyst for a fluidized bed or moving bed reactor comprising an active phase of general empirical formula (I):



in which:

- E represents an element which can give an oxide of rutile structure or an element which, in combination with V, Sb, Sn, Ti, Fe and/or with another element E, can give a phase of rutile or trirutile structure or a solid solution of rutile structure
- a represents a whole or fractional number equal to or greater than 0.5
- 15 - b, c, d and e represent, independently of one another, a whole or fractional number from 0 to 100
- x represents a whole or fractional number determined by the oxidation number of the other elements,
- 20

and a solid support of oxide type,

the said process being characterized in that it comprises:

- the impregnation of the solid support by a solution in at least one saturated alcohol of respective compounds of vanadium, of antimony
- 25



and optionally of tin and/or of titanium
and/or of iron and/or of element E,

- bringing the impregnated solid support
obtained into contact with an aqueous buffer
5 solution at a pH of between 6 and 8,
- the separation of the solid and the drying
thereof,
- the calcination of the solid in two stages,
first of all at a temperature of 300°C to
10 350°C and then at a temperature of 400°C to
800°C.

2. Process according to Claim 1,
characterized in that the solid support is an oxide,
such as an alumina, a silica, a silica/alumina, a
15 zirconia, a cerite, a mixed oxide of cerium and of
zirconium, a magnesia, a titanium oxide, a niobium
oxide or a lanthanum oxide.

3. Process according to either of Claims 1
or 2, characterized in that the solid support has a
20 particle size from 10 μm to 1,000 μm and preferably
from 20 μm to 300 μm .

4. Process according to one of Claims 1 to
3, characterized in that the solid support exhibits a
pore volume of at least 0.1 cm^3/g and preferably of at
25 least 0.15 cm^3/g .

5. Process according to one of Claims 1 to
4, characterized in that the ratio by weight in the
final catalyst of the active phase of formula (I) to



the whole of the said catalyst is from 5 to 50%.

6. Process according to one of Claims 1 to 5, characterized in that the soluble vanadium compound is chosen from vanadyl acetylacetonate, vanadyl trichloride, vanadium trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium tribromide, vanadium dichloride, vanadium trichloride, vanadium tetrachloride or vanadium triiodide.

7. Process according to one of Claims 1 to 6, characterized in that the soluble antimony compound is chosen from antimony pentachloride, antimony trichloride, antimony tribromide, antimony trifluoride, antimony triiodide, antimony trioxide or stibine.

8. Process according to one of Claims 1 to 7, characterized in that the soluble tin compound is chosen from stannic chloride, stannous chloride or stannous bromide.

9. Process according to one of Claims 1 to 8, characterized in that the soluble titanium compound is chosen from titanium dichloride, titanium tetrachloride, titanium trichloride, titanium tribromide, titanium tetrabromide, titanium tetrafluoride or titanium diiodide.

10. Process according to one of Claims 1 to 9, characterized in that the soluble iron compound is chosen from iron dichloride, iron trichloride, iron dibromide, iron tribromide, iron diiodide, ferrous nitrate, ferrous sulphate, ferric sulphate, ferrous



thiosulphate, ferric formate, ferric acetate, ferric acetylacetonate, ferric benzoate, ferric oleate, ferrous lactate or ferric lactate.

11. Process according to one of Claims 1 to 10, characterized in that the saturated alcohol used is chosen from alkanols and cycloalkanols and preferably alkanols having from 1 to 6 carbon atoms, such as methanol, ethanol, n-propanol, 2-propanol, n-butanol, 2-butanol, tert-butanol, pentanols and hexanols, and cyclohexanol.

12. Process according to one of Claims 1 to 11, characterized in that the impregnation of the solid support by the alcoholic solution of the compounds of the metals which form part of the composition of the active phase of formula (I) is carried out by using a volume of alcoholic solution which is less than or equal to the total pore volume of the support, the said volume of the alcoholic solution preferably representing at least 50% of the said total pore volume.

13. Process according to one of Claims 1 to 12, characterized in that the impregnated solid support is brought into contact with an aqueous buffer solution of an ammonium salt, optionally containing aqueous ammonia, the ammonium salt used preferentially being an ammonium carboxylate, ammonium carbonate or ammonium hydrogenphosphate.

14. Process according to one of Claims 1 to



13, characterized in that the volume of the buffer solution brought into contact with the impregnated support is equal to or greater than the total pore volume of the support and is preferably greater than
5 the total pore volume of the support.

15. Process according to one of Claims 1 to 14, characterized in that the active phase corresponds to the formula (I) in which:

- E represents one or a number of elements
10 chosen from nickel, gallium, aluminium or niobium
- a represents a whole or fractional number equal to or less than 100 and preferably of between 0.5 and 50
- 15 - b, c, d and e represent, independently of one another, a whole or fractional number from 0 to 50, at least one of these symbols being greater than 0 and preferably equal to or greater than 0.5
- 20 - x represents a whole or fractional number determined by the oxidation number of the other elements.

16. Process for the vapour-phase ammoxidation of alkanes in a fluidized bed or moving
25 bed reactor in the presence of a solid catalyst, characterized in that the said catalyst is obtained by the process according to one of Claims 1 to 15.

17. Process according to Claim 16,



characterized in that alkanes having from 3 to 12 carbon atoms per molecule, preferably chosen from propane and isobutane, are reacted in the vapour phase with ammonia and oxygen.

5 18. Process according to either of Claims 16 or 17, characterized in that, within the reactive gas consisting of the alkane, ammonia and oxygen, the alkane content by volume is preferably between 5 and 70%, the ammonia content by volume is preferably
10 between 3 and 50% and the oxygen content by volume is preferably between 3 and 45%.

 19. Process according to one of Claims 16 to 18, characterized in that the reaction temperature is between 300°C and 550°C and preferably between 400°C
15 and 500°C.